Monday Morning, April 27, 2020

Plenary Lecture
Room Town & Country - Session PL-MoPL

Plenary Lecture
Moderator: Grzegorz (Greg) Greczynski, Linköping University, Sweden

8:00am **PL-MoPL1 Organic Bioelectronics – Nature Connected***, Magnus Berggren (magnus.berggren@liu.se),* Linköping University, Norrköping, Sweden **INVITED**

Organic electronic materials are unique as the signal translator across the biology-technology gap. These biocompatible materials are also easily complexed with polyanions, polycations and functional biomaterials and can then be included in various device architectures to form flexible, stretchable and even gelled devices. Such organic bioelectronics can then process electronic, ionic and charged biomolecules in combination. These combined features make organic electronic materials unique in many aspects as the recorder and actuator of various functions and physiology of biological systems. A brief review of some of the recent achievements from the Laboratory of Organic Electronics is here given. In the BioComLab technology platform various organic bioelectronic sensors and actuators are combined with communication technology to form a body area network for future healthcare applications. Various sensors are included within electronic skin patches, then connected to electronic drug delivery components via capacitive body-coupled communication. This system provides sensor-actuator feedback and improves its decision-making performance using deep-learning protocols provided from cloud connectivity. With the BioComLab platform we target an array of neuronal disorders and diseases, such as epilepsy, Parkinson's disease and chronical pain. The BioComLab technology is also explored to regulate functions and physiology of plants, in an effort termed e-Plants. Some of the recent results of using organic bioelectronics to sense and actuate plant physiology is here also presented.

Coatings for Use at High Temperatures
Room Pacific Salon 1 - Session A1-1-MoM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderators: Sebastien Dryepondt, Oak Ridge National Laboratory, USA, Shigenari Hayashi, Hokkaido University, Japan, Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK

10:00am **A1-1-MoM1 Oxidation Kinetics of γ-TiAl Based Coating Materials***, **Stefan Kagerer (stefan.kagerer@tuwien.ac.at)**, O. Hudak, H. Riedl, P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The reduction of carbon emissions as well as the improving of fuel efficiencies tied to modern aerospace and aviation have heavily invested in the development of lighter and more durable high temperatures materials. γ-TiAl bulk materials, with their low density and distinguished creep resistance, fulfill all these tasks till 780°C. Above 780°C, oxidation protection of γ-TiAl based alloys is a challenging task for the aero- and automotive industry. Here, especially thin films rise the possibility to protect these alloys while not affecting other material properties. Typically, ceramic like thin films are applied to defend the bulk materials against oxidation and corrosion attacks. Within this study, we applied a different approach utilizing metallic coating materials deposited by PVD.

Therefore, we grow Al-rich γ-TiAl based coatings onto well-established TNM bulk alloys using a semi-industrial scaled unbalanced magnetron sputtering system. To study the oxide scale formation and its kinetics, also on a long-term view, all coatings were oxidized at 850 °C up to 1000 h in ambient air. The scale formation and accompanying diffusion processes have been investigated methodically by various electron imaging techniques (SEM and HR-TEM) as well as structural and chemical analysis. The prevalent diffusion process was separated in two dominating effects: *(i)* oxygen inward diffusion and outermost scale formation as well as *(ii)* Al interdiffusion between the coating and bulk interface. The so obtained diffusion lengths were used to estimate diffusion coefficients by Ficks´s 1st and 2nd law. In a further step, the adhesion behavior of the formed oxide scale and an observed void formation in the unoxidized areas of the coating material was investigated in detail. The highly dense, thermally grown oxide (alumina based scale) reaches a thickness up to maximum of 4 µm depending on the coating thickness (> 10 µm) leading to superior protection of the bulk material. The void formation is localized in the thermally grown oxide near region. The chemical environment of these pores has been analyzed by HR-TEM to understand the formation process in more detail.

In summary, the application of γ-TiAl based coating materials to enhance the oxidation resistance of TNM bulk alloys is an interesting alternative to ceramic like coatings, also on a long-term perspective.

10:20am **A1-1-MoM2 Effects of Temperature and the KCl + K_2SO_4 Load on the Behavior of Several Aluminide Coatings on Ferritic Steels Tested under a Biomass Combustion Atmosphere***, **Alina Agüero (agueroba@inta.es)**, M. Gutiérrez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Energy from biomass corresponds to more than 60% of all renewable energy sources in Europe and is currently the most widely used worldwide. However, it has not reached yet the efficiency that can be obtained with fossil fuels, as temperatures cannot be increased due to severe corrosion taking place due to biomass combustion products. New materials and/or coatings are required, and screening laboratory testing is needed to evaluate the high temperature corrosion resistance of these new materials. However, there is no general agreement regarding the methodology to carry out biomass corrosion laboratory tests, which can allow realistic ranking of materials and coatings. In INTA, a laboratory test procedure based data obtained from a thistle-burning pilot plant employing oxy-combustion conditions, was established and the corresponding rig implemented. The present work studies the effect of temperature and the amount of deposits of KCl + K_2SO_4 under an atmosphere containing 60 CO_2, 30 H_2O, 8 O_2, 2 N_2 (v. %), 400 vppm HCl and 2 vppm SO_2.The behaviour of T22 and P92 and as well as of two slurry applied diffusion aluminide coatings with different Al contents was studied. Exposure was performed at 550ºC, 600ºC and 650ºC for more than 600 h and the samples were covered with 0.7 mg/cm^2 of a KCl + K_2SO_4 mixture prior to exposure. In addition, the same substrates and coatings were tested at 550º C employing a salt load of 2.1 mg/cm^2 in order to study the influence of the amount of salt.

Both uncoated substrates exhibited important mass gain/losses indicating a high degree of corrosion as well as of oxide spallation. P92 gained significant weight and there was evidence of spallation based on visual observation of the samples, whereas T22 lost weight after a short weight increase period and even from beginning of the test at 650º C. This indicates that the Cr content (9 wt.% in P92 and 2 in T22) plays a role in developing more protective and adhesive scales. For both alloys the corrosion rates increased with temperature and the higher salt load resulted in earlier and heavier spallation for both substrates.

On the other hand, the coatings exhibited much better behaviour under all conditions and very little variation for the different salt loads. However, at 650º C both coatings exhibited significant degradation but no substrate attack was observed. Microstructure analysis of the tested samples was carried out to study the coatings protection and degradation mechanisms.

10:40am **A1-1-MoM3 PGM based Diffusion Coatings for Ni-based Superalloys by a Paste Method***, **Hideyuki Murakami (MURAKAMI.Hideyuki@nims.go.jp)**, D.C. Tue, A. Ishira, L.C. Honglien,* National Institute for Materials Science (NIMS), Japan **INVITED**

In this study, the new route to develop oxidation resistant coatings on Ni-based single crystal superalloy is introduced. A paste, which contains Pt or Pt-xIr (x = 0-30 at%) alloy nano-powder was sprayed on some Ni-based single crystal superalloys. Then the annealing diffusion treatment at 1100 °C for 1 h in flowing Ar atmosphere was conducted to develop Pt and Pt-Ir coatings. Cyclic oxidation tests were carried out at 1150 °C in still air in order to investigate the thermal stability and oxidation behavior of the coatings and they were compared with electroplated diffusion coatings. It was found that Ir can retard the formation of voids in both the coating and substrate. In addition, by replacing the electroplating method to the paste coating method, the crack problem due to the brittle feature of electroplated Pt-Ir coatings could be solved. Therefore, the Pt-20Ir diffusion coating prepared by the paste-coating method is promising as the bond-coating material due to formation of less voids, no cracks and stable Al_2O_3 on the surface. To further evaluate the pasted Pt and Pt-Ir diffusion coatings, hot corrosion tests and fatigue tests were conducted. Both tests confirmed that Pt-Ir diffusion coatings, developed by the paste method performed promising characteristics.

The Pt-Ir paste diffusion coatings introduced above have several aditioinal advantages: they are easy to recoat, cause less damage to substrates, and offer comparable oxidation resistance. Thus the method can be applicable to the remanufacturing of blades, which may extend the life of components. The future aspect of the paste coating, effect of composite coatings, will also be discussed.

11:20am **A1-1-MoM5 High-Temperature Corrosion Resistance of TiCrAlSiN Thin Deposited by Cosputtering***, G. Yomayuza,* Universidad Nacional de Colombia, Colombia*; **Oscar Piamba (oepiambat@unal.edu.co)**,* Universidad Nacional e Colombia, Colombia*; J.J. Olaya,* Universidad Nacional de Colombia, Colombia

This study shows the high-temperature corrosion resistance of TiCrAlSiNthin films deposited by co sputtering technique. The corrosion test at high temperature were made with 100 cycles in air atmosphere at 600 °C, each cycle consisting 1 hour of heating and 1 hour of cooling. Mass loss was measured and corrosion products were characterized by x-ray diffraction (XRD), Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). The results showed a good corrosion resistance up to 60 thermal cycles where a noticeable degradation of the coating was observed. The corrosion mechanism produced on TiCrAlSiNthin films will be discuss in this work.

11:40am **A1-1-MoM6 Ti_2AlC MAX Phase Coating Deposited by Kerosene-fuelled High Velocity Oxy-fuel (HVOF) Spray***, **Jisheng Pan (js-pan@imre.a-star.edu.sg)**, Z. Zhang, S.H. Lim, D.M.Y. Lai,* Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), Singapore

A family of ternary carbides and/or nitrides, $M_{n+1}AX_n$ (n = 1, 2 or 3) or MAX phase materials, has attracted considerable interests since mid-1990s due to their uniqueness in possessing both metallic and ceramic properties. As a representative MAX phase material, Ti_2AlC has been explored for its application in the fields including high temperature protective coatings and radiation-tolerant cladding material for the nuclear power plants. In such applications, coatings thicker than 100 mm are usually required. Thermal spray can provide a feasible and low cost method to fabricate such thick coatings. In this work, kerosene-fueled high velocity oxy-fuel (HVOF) spray was employed to deposit commercial Ti_2AlC MAX phase powders onto Inconel 600 substrates. After optimization of the thermal spray process, a dense Ti_2AlC coating with a very low decomposition comparable with the optimum Ti_2AlC coatings sprayed by H_2-fueled HVOF and cold spray was obtained. This optimized Ti_2AlC coating was further analyzed by a variety of techniques to probe its surface chemistry, morphology, cross-sectional microstructure, mechanical properties and salt fog corrosion resistance. Isothermal oxidation of 100 µm Ti_2AlC coatings have been carried out and examined between 200 and 1000 °C for 5 h at 200 °C intervals.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-1-MoM

CVD Coatings and Technologies I

Moderators: Raphaël Boichot, Université Grenoble Alpes, CNRS, France, Kazunori Koga, Kyushu University, Japan

10:00am **B2-1-MoM1 Atomic Layer Deposition for Complex-Shape and Temperature Sensitive Objects: Towards New Functions and Products***, Frédéric Mercier (frederic.mercier@simap.grenoble-inp.fr),* Univ. Grenoble Alpes, CNRS, France **INVITED**

Atomic Layer Deposition (ALD) technique finds many applications today in the fields of microelectronic, batteries and catalysts. Indeed, the intrinsic advantages of ALD like conformality, uniformity and precise control of the thickness at the atomic scale can meet the requirements of the increasing complexity and the variety of objects to be coated. Besides the aforementioned fields, other emerging fields can benefit from the advantages of the ALD technique to provide objects with enhanced functionalities or new products. To illustrate the opportunities and challenges of depositing conformal layers on either complex-shape or temperature sensitive objects or both, the talk will focus on ALD coatings on additive manufactured metallic structures and on biopolymers like cellulose matrices. The talk will include a discussion on their potential applications in energy and packaging industry. Our recent results on enhanced functionalities provided by ALD like surface finishing (color, surface smoothing), high temperature oxidation resistance and gas diffusion barrier among others will be presented. The understanding and improvement of the chemical/thermal compatibility between the object to be coated and the coating will be discussed based on a comprehensive evaluation of the structure and composition.

10:40am **B2-1-MoM3 Ald-Pvd Multilayers: Deposition, Thermal Stability And Mechanical Properties***, Thomas Edwards (thomas.edwards@empa.ch), T. Xie, L. Petho, S. Büchel, X. Maeder, B. Putz, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

The extent of the embrittlement in ductile-brittle multilayers often depends on the modulation period ($t_{brittle}$ + $t_{ductile}$) as well as on the modulation ratio ($t_{brittle}/t_{ductile}$) [1]. In this work, ductile-brittle multilayers of Al / Al_2O_3 / Al… and Ti / TiO_2 / Ti… were produced on Si substrates by a unique combination of atomic layer (ALD, Al_2O_3, TiO_2) and physical vapor deposition (PVD, Al, Ti) within a single deposition system. Using this ALD/PVD combination, neighbouring layer thicknesses can easily differ by one order of magnitude or more. In particular, the ability to deposit continuous sub-nm layers with ALD opens up a wide range of otherwise unachievable modulation and thickness ratios. The thicknesses and structures of the ALD layers were verified by HR-TEM imaging of lift-outs. Further depositions on flexible substrates have also been performed with thinner Al layer thicknesses to minimize residual stresses. The Al_2O_3 or TiO_2 layer thickness is varied across the multilayer cross-section (0.1 nm – 10 nm) to study the effect on strength of the film as determined by microcompression, and on crack onset and propagation as a function of oxide layer thickness in tensile tested multilayer films. Single layered films (Al or Al_2O_3, etc.) are used as reference materials. Further the thermal stability of such multilayer films was studied up to 0.9 T/T_m, considering the stability and crystallinity of the ALD interlayers and the texture of the PVD layers. Grain growth of Al is limited by the Al_2O_3 layer, allowing for easy discrimination of individual Al layers necessary for locating onset of cracks, and for cross-sectional fragmentation analysis by focused ion beam (FIB) cross-sectioning under tension which avoids crack closure upon unloading. The multilayer structure has good adhesion between individual layers as well as to the polymer substrate and the oxide layers show increasing stretchability with decreasing film thickness, as a result of being extremely well defined and practically defect free. This study helps improve the understanding of deformation mechanisms in flexible thin film structures and can give useful guidelines for strong and damage tolerant thin film metallic systems.

[1] K. Wu, J.Y. Zhang, J. Li, Y.Q. Wang, G. Liu, J. Sun, Acta Mater. 100 (2015) 344–358.

11:00am **B2-1-MoM4 High Throughput Deposition of Hydrogenated Amorphous Carbon Films using High-Pressure Ar+CH_4 Plasmas***, Kazunori Koga (koga@ed.kyushu-u.ac.jp), S.H. Hwang, K. Kamataki, N. Itagaki, M. Shiratani,* Kyushu University, Japan

Plasma chemical vapor deposition (CVD) method has attracted much attention for fabricating hydrogenated amorphous carbon (a-C:H) films because it can realize to deposit large area films with a good uniformity [1]. In the conventional plasma CVD, the working gas pressure was the range between 0.05 Torr and 1 Torr. The lifetime of carbon-related radicals tends to be shorter for larger gas pressure resulting in a low deposition rate. Here we found a high rate deposition of a-C:H films with high-pressure Ar+CH_4 plasmas.

The experiments were carried out using a capacitively coupled plasma reactor [2, 3]. Ar diluted CH_4 gas was introduced to the chamber. The total gas flow rate and CH_4 concentration were at 98.8 sccm and 3.8 %, respectively. A 1cm x 1cm Si substrate was placed on a substrate holder. 28 MHz voltage of 170 V was applied to the powered electrode. The substrate temperature was room one. To analyze the deposition rate and the mass density, a scanning electron microscopy (JEOL JIB-4600F) and microbalance (Mettler Toledo) were used.

We have examined dependence of substrate position from the powered electrode on deposition rate as a parameter of the gas pressure. For the pressure below 2 Torr, the deposition rate monotonically decreases with increasing the distance *d* between the powered electrode and the substrate from 20 nm/min to 10 nm/min. In contrast, for the pressure above 5 Torr, the deposition rate decreases from around 60 nm/min for *d*= 15 mm to about 30 nm/min for *d*= 30 mm. Photos of the plasmas suggest that the radical generation tends to be localized near the powered electrode and the rate increases with the gas pressure in the region. Therefore, the high deposition rate realizes for *d*= 15 mm for 5 and 7 Torr. The mass density for 7 Torr and *d*=15 mm is 1.41 g/cm^3. To further improve the film characteristics, we studied the effects of dc pulse bias on the substrates. A dc pulse bias voltage Vdc with 1 µs in the pulse duration and 25 kHz in the reputation frequency was applied to the substrates. We found high mass density film of 1.67 g/cm^3 is deposited at 66.7 nm/min for V_{dc}= -202 V. This indicates that the impinging ions can modify the newly deposited films and generate the dangling bonds at the surface, leading to the determination of the mass density and deposition rate [4].

[1] K.J Clay et al, J. Diam. Relat. Mater, 7,1100 (1998).

[2] X. Dong et al, J. Phys: Conf. Ser., 518, 012010 (2014).

[3] K. Koga et al, Jpn. J. Appl. Phys, 55, 01AA11 (2016).

[4] M. Shiratani et al, J. Surf. Coat. Technol, 228, 15 (2013).

11:20am **B2-1-MoM5 CVD Alumina-based Nanocomposite Coatings***, Zhenyu Liu (Zhenyu.Liu@kennametal.com),* Kennametal Inc., USA

Nanocomposite is a multiphase solid material where one of the phases has the size of less than 100 nanometers (nm) in at least one dimension, or structures having nano-scale repeat distances between the different phases that make up the material. Nanocomposite coating represent a new generation of materials exhibiting completely new properties with respect to the conventional used materials. The superior mechanical properties of nanocomposites originate from their peculiar nanostructures (size effects) and high density of interfaces. The unique structure and exceptional properties make nanocomposite materials a possible alternative to traditional polycrystalline materials, which have met their limits in many recent engineering applications.

Inspired by nanolayer coatings of PVD and multilayer CVD coatings development, we demonstrate a couple of potential Al_2O_3-based nanosomposite systems deposited by CVD process directly using multilayer concepts with well-controlled deposition conditions to maintain the deposited “thin film” at early stage, nucleation regime. As a consequence, the “thin film” would maintain at the island forms or particles/nanoparticles states with the size smaller than 100 nm at least in one dimension, whilst the alumina matrix would keep depositing to form a continuous matrix. Ultimately, a nanocomposite coating can be formed with improved wear resistance and metal-cutting performance. The ability to process nanocomposite by direct nucleation and growth of ceramic materials via CVD technique should provide new technical opportunity on the advanced materials and application development.

Keywords: CVD, Al_2O_3-based nanocomposite, thin films, nucleation, crystal growth

11:40am **B2-1-MoM6 The Challenge and Strategy of a-Si CVD Coating on Aluminum Alloys***, Min Yuan (min.yuan@silcotek.com),* SilcoTek Corporation, USA

Aluminum alloys in general present a particular challenge in thermal CVD of amorphous silicon coating.

Aluminum is known to catalyze the crystallization of amorphous silicon and induce nanowire growth under thermal CVD conditions. The deposited thin film usually contains a mixture of amorphous and microcrystalline silicon, which not only manifest as undesirable cosmetic defects on finished products, but also compromise other coating properties such as coating adhesion, corrosion resistance and chemical inertness.

Here we present a modified thermal CVD process that is designed to prime the aluminum substrate at the beginning of CVD, so that subsequent a-Si deposition can proceed smoothly. The priming step acts to prevent aluminum from catalyzing the amorphous-to-crystalline transition and stop the undesirable silicon nanowire growth. The coated products from this process deliver more appealing cosmetic finish, as well as superior coating properties that will be discussed in the presentation.

The priming effect is achieved by exposing the aluminum substrate to a mixture gas at the initial stage of the CVD process. The synergistic reaction of the gas mixture deposits a thin barrier layer at the substrate/coating interface, which serves to cut off the negative influence of aluminum on the coating. The barrier layer itself has strong adhesion to both the aluminum substrate and the a-Si coating deposited on top of it, thus improving the overall adhesion properties.

This modification is easily incorporated as part of the CVD process and does not require separate wet chemistry or vacuum break. This makes it straightforward to implement and scale up in a manufacturing setting, as has been demonstrated in the facility at SilcoTek Corporation.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B6-1-MoM

Interplay Between Computational and Experimental Design of Coatings and Processes I

Moderators: Yin-Yu Chang, National Formosa University, Taiwan, Paul Heinz Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria

10:00am **B6-1-MoM1 Superlattice Design for Superior Thin Films***, Nikola Koutná (nikola.koutna@tuwien.ac.at)*[1]*, R. Hahn, J. Buchinger,* TU Wien, Institute of Materials Science and Technology, Austria*; D.G. Sangiovanni,* Linköping University, Sweden*; M. Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Superlattice architecture—comprising coherently grown nanolayers of two or more materials—provides a vast playground for tuning physical properties of thin films via altering different phases and their mutual orientation, the bilayer period, or the defect content and distribution close to interfaces. Changes in these parameters can induce remarkable effects, such as partial structural transformations, superhardening and/or supertoughening. Nevertheless, identifying the layer materials, optimising the film deposition setup and performing micromechanical testing requires delicate experimental work. This talk illustrates the necessary interplay between modelling and experimental techniques to understand and control bilayer-period-dependent trends coming hand in hand with microstructural changes in superlattices. The model superlattice systems are cubic-based MoN/TaN, TiN/WN, and TiN/TaN. In particular, we highlight the important role of vacancies triggering local changes in the electronic structure, stabilisation of (novel) metastable phases or compositional variations at different layer thicknesses, which directly influence mechanical properties. Furthermore, atomistic processes governing strength, plasticity, and fracture of superlattices subject to tensile and shear deformation are discussed in light of the experimental results as well as ab initio molecular dynamics simulations.

10:20am **B6-1-MoM2 Fracture Toughness Trends in Modulus-matched TiN/(Cr,Al)N Thin Film Superlattices***, Julian Buchinger (julian.buchinger@tuwien.ac.at), A. Wagner,* TU Wien, Austria*; L. Löfler,* Montanuniversität Leoben, Austria*; Z.L. Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; P.H. Mayrhofer,* TU Wien, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; M. Bartosik,* TU Wien, Austria

The superlattice (SL) architecture has proven a highly viable strategy to enhance the fracture toughness of transition metal nitride thin films, however its underlying mechanisms remain largely elusive. For our study, we therefore design TiN/(Cr,Al)N superlattices, in which the involved layers have effectively identical elastic moduli, but sizeably different lattice parameters. Thereby, we isolate the effect of the lattice mismatch between the SL layers, and virtually eliminate the influence of elastic disparities. To find the appropriate Al content, at which the elastic moduli of TiN and (Cr,Al)N overlap, we rely on density functional theory (DFT) calculations.

We synthesise – using DC reactive magnetron sputtering – a series of TiN/(Cr,Al)N SLs with various bilayer periods and the desirable composition identified by DFT. The coatings are analysed regarding their structural, morphological, and chemical properties using X-ray diffraction, and electron microscopy techniques. Insight into the mechanical, and fracture-related properties is provided by nanoindentation, and microcantilever bending tests, respectively.

Our results show a clear enhancement of the fracture toughness K_{IC} of the SLs (2.48 ± 0.03 MPa√m) compared to monolithic TiN (1.97 ± 0.06 MPa√m), and (Cr,Al)N (1.32 ± 0.08 MPa√m). Combining the experimental data with a model based on continuum mechanics, we analyse the observed bilayer period dependent trends – focusing on the influence of coherency strains, and the formation and distribution of misfit dislocations within the nanolayers of our TiN/(Cr,Al)N SLs.

10:40am **B6-1-MoM3 Weakest Links in Superlattices: Insights from Ab Initio Modelling***, David Holec (david.holec@unileoben.ac.at),* Montanuniversität Leoben, Austria*; N. Koutná,* TU Wien, Austria*; L. Löfler, L. Hantzenbichler,* Montanuniversität Leoben, Austria*; P. Řehák,* Central European Institute of Technology (CEITEC), Brno University of Technology, Czech Republic*; M. Bartosik,* TU Wien, Austria*; M. Friák,* Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic*; M. Černý,* Central European Institute of Technology (CEITEC), Brno University of Technology, Czech Republic*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

Superlattice design has been shown effective to improve Young's modulus, hardness and toughness of many nitride systems beyond the performance of individual building blocks, especially when the bi-layer period is very small, in nm range. Such developments are crucial in order to reach the ever-increasing demands on the coatings (often based on nitrides, carbides or oxides) protecting various working tools. While a structural heterogeneity---as interfaces---serves as an obstacle for dislocation motion, it could also act as a sink for impurities or other point defects with a possibly detrimental effect on interface strength. And even if one thinks about an ideal interface, chemical inhomogeneity certainly influences local electronic structure and hence bonding, which could lead to weakened bonding.

This contribution deals with a principal question whether interfaces are the weakest link in the superlattices. We will present examples of calculated tensile strength of various cubic nitride systems (TiN/CrN, TiN/AlN, AlN/VN, MoN/TaN...) and discuss the local strength together with details of the local atomic structure. A large set of systems (with different lattice mismatch, stability, magnetic state, etc.) we have treated in the past will serve as a basis for drawing general conclusions (e.g., can strength be locally enhanced by modifying interatomic distances?). In addition, we will compare these trends with those predicted for a purely metallic Ti/Ta superlattices as well as cubic/wurtzite TiN/AlN multilayers.

11:20am **B6-1-MoM5 Fracture Toughness of Superlattice Thin Films: A Multiscale Modeling Approach***, Antonia Wagner (antonia.wagner@tuwien.ac.at),* TU Wien, Institute of Materials Science and Technology, Austria*; L. Löfler,* Montanuniversität Leoben, Austria*; M. Todt,* TU Wien, Institute of Lightweight Design and Structural Biomechanics, Austria*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; M. Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria

Micromechanical experiments of sputtered thin films have revealed that multilayer systems with a periodicity length in the range of a few

[1] **Student Award Nominee**

nanometers exhibit superior fracture properties compared to their monolithic building blocks.

We present an approach linking results obtained from ab-initio calculations with continuum mechanics. Using density functional theory we gain information about the cleavage behavior of both the constituents of the multilayer as well as the interfaces between them. Further we estimate the residual stress state after the deposition process due to lattice misfit by applying an analytical model based on an energy balance considering strain and dislocation energy. Combining these results within finite element simulations of the experimental set-up we predict the crack growth behavior of transition metal nitride superlattices. Doing so, we can not only show a good qualitative agreement with experimental findings but also study the governing mechanisms of the fracture toughness enhancement.

11:40am **B6-1-MoM6 Tribological and Mechanical Properties of CrNbTiVZr(N) High Entropy Alloy Nitride Coatings**, *Y.Y. Chang, **Cheng-Hsi Chung (40471255@gm.nfu.edu.tw)***, National Formosa University, Taiwan

PVD coatings are now frequently used to improve the tribological performance of cutting tools, forming tools and machine components. Multi-element material systems have received many attentions for improving the mechanical performance in industry. However, they are still focused on ternary systems and seldom beyond quaternary ones. High Entropy Alloy (HEA) are systems that each comprised of five or more principal metal elements in equal- or nonequal-mole proportions. Previous studies found that some high-entropy alloys have much better strength than traditional alloys. In this study, CrNbTiVZr high entropy alloy and nitrogen contained CrNbTiVZr(N) nitride coatings were synthesized by cathodic-arc deposition . A chromium-vanadium alloy target, a titanium-niobium alloy target and a pure zirconium target were used for the deposition. During the coating process of CrNbTiVZr and CrNbTiVZr(N), CrV and TiNb were deposited as interlayers to enhance adhesion strength between the coatings and substrates. By controlling the different nitrogen contents and cathode currents, the CrNbTiVZr(N) coating with gradient or multilayered composition control possessed different microstructures and mechanical properties. In this study, the microstructure of the as-deposited coatings was characterized by field emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD) using Bragg-Brentano and glancing angle parallel beam geometries. Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention and Vickers microhardness tests . Ball-on-disc wear tests were conducted to evaluate the correlation between tribological properties and coating structures of the deposited coatings. The design of multilayered CrNbTiVZr(N) coatings is anticipated to be advantageous to enhance the lives of the mechanical tools and mechanical parts.

Coatings for Biomedical and Healthcare Applications
Room Royal Palm 1-3 - Session D1-1-MoM

Surface Coating and Surface Modification in Biological Environments I

Moderators: Mathew T. Mathew, University of Illinois at Chicago, Rockford, USA, Phaedra Silva-Bermudez, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

10:00am **D1-1-MoM1 Biomimetic Extracellular Matrix Coating for Titanium Implant Surfaces to Improve Osteointegration**, ***Sriram Ravindran (sravin1@uic.edu)***, *P. Gajendrareddy, J. Hassan, C.-C. Huang,* University of Illinois at Chicago, USA **INVITED**

Titanium implants are used widely in orthopedic and dental applications. Their primary function is to integrate with the surrounding bone and provide biomechanical support. Although, several surface modification technologies have been adopted to improve the osteointegration, it remains elusive in normal and more so in diseased individuals. Here, we propose a methodology to apply a biologically active natural extracellular matrix (ECM) coating to implants. Titanium implant surfaces were coated with a natural osteogenic ECM from human bone marrow derived mesenchymal stem cells (HMSCs) using a decellularization technique. The ECM coating was verified quantitatively and qualitatively by immunological characterization. The enhanced ability of coated surfaces to promote attachment, proliferation and osteogenic differentiation of HMSCs was evaluated *in vitro* quantitatively and qualitatively by means of proliferation assays, live cell imaging and qPCR analyses. Osteointegration was evaluated *in vivo* in a rat tibial model. Results indicated that the procedure resulted in an even coating of ECM on the implants. *In vitro* studies indicated that the coated implants promoted enhanced attachment, proliferation and osteogenic differentiation of HMSCs. *In vivo* experiments revealed enhanced bone formation around coated implants as observed by m CT analysis. Overall, these results indicate that coating titanium implant surfaces with a biomimetic ECM can enhance their functionality by generating a bioactive surface and promoting enhanced osteointegration.

10:40am **D1-1-MoM3 Physical Vapor Deposition for Growth of Large Area Molecular Sensor Arrays**, *N.R. Glavin, D.R. Austin, D.C. Moore, M.J. Motala,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; ***Christopher Muratore (cmuratore1@udayton.edu)***, University of Dayton, USA

Low temperature synthesis of high quality 2D materials directly on flexible substrates remains a fundamental limitation towards realization of robust, strainable electronics possessing the unique physical properties of atomically thin structures. Here, we describe room temperature synthesis of uniform, stoichiometric amorphous MoS_2, WSe_2, and other transition metal dichalcogenides and subsequent large area (>5 cm^2) photonic crystallization to enable direct fabrication of devices based on two-dimensional materials on large area flexible or rigid substrates. Fundamentals of crystallization kinetics for different monolithic and heterostructured TMDs are examined to apply this new synthesis approach for affordable, wearable devices. Example devices include photodetectors with photocurrent output and response times comparable to those fabricated via CVD and exfoliated materials on rigid substrates and the performance is unaffected by strains exceeding 5%. Flexible molecular sensors fabricated in this way detect diverse vapor phase substances with sub-ppm sensitivity. Functionalization of laser-written 2D TMD sensor transducers is also demonstrated for healthcare applications. Other devices and circuits directly written from photonically annealed monolithic TMDs thin films deposited on large area flexible substrates, with no photolithography or patterning, are also presented.

11:00am **D1-1-MoM4 Very Thin Gold Films Deposited on Collagen Fabric in Skin Cell Experiments**, ***Sheng Yang Huang (drugholic@vghtc.gov.tw)***, Feng Chia University, Taichung Veterans General Hospital, Taiwan; *P.-Y. Hsieh,* Institute of Plasma, Feng Chia University, Taiwan; *C.M. Chou,* Taichung Veterans General Hospital, National Yang-Ming University, Taiwan; *C.J. Chung,* Central Taiwan University of Science and Technology, Taiwan; *J.L. He,* Feng Chia University, Taiwan

The goal of this study is to test a novel biomedical material with very thin gold thin film deposited on collagen fabrics. Composition of such material is successfully processed by high-power impulse magnetron sputtering (HIPIMS). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) disclose signature wavy appearance of gold film on collagen fibers. Fourier transform infrared spectroscopy (FTIR) and Amide I FTIR absorbance curve fitting show the unchanged functional groups and secondary structure of collagen, respectively. In the previous studies, tunable gold thin film distribution and film thickness are established by different deposition time of HIPIMS. Fibroblasts and keratinocytes are used in cell experiments of this study in order to simulate the condition of skin wound healing process. Results of cell toxicity, attachment and proliferation are demonstrated.

Keywords: gold thin film; high-power impulse magnetron sputtering (HIPIMS); collagen fabrics; skin cells, fibroblasts, keratinocytes

11:20am **D1-1-MoM5 Biocompatible and Mechanical Properties of TiNbZr(N) Coatings Synthesized by Cathodic Arc Deposition**, ***Yu-Ju Yang***, *Y.Y. Chang (yinyu@nfu.edu.tw),* National Formosa University, Taiwan; *H.L. Huang,* China Medical University, Taiwan; *M.T. Tsai,* Hungkuang University, Taiwan

Ti6Al4V alloy has been widely used in biomedical implants with high strength to weight ratio, corrosion resistance and good biocompatibility. However, the alloy has insufficient surface wear properties and tends to deteriorate in sliding contact with similar or other metals. In addition, elevated levels of V and Al release may result in cytotoxicity. Further researches are necessary to improve the mechanical properties and biocompatibility of the Ti6Al4V alloy. In order to improve the biocompatible and mechanical performance of the Ti6Al4V alloy, in this study, the TiNbZr and nitrogen doped TiNbZr(N) coatings with different nitrogen content were deposited by cathodic arc deposition (CAD), followed by an annealing treatment to obtain surface oxidation of the coatings. The surface morphology, crystal structure, and bonding state of the films were identified by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention and Vickers microhardness.

To evaluate the biocompatibility of the coating, cell viability was analyzed by in vitro MTT. The effect of the TiNbZr(N) coatings on the cell attachment morphology of human skin fibroblasts (SKF) and human osteoblasts (MG-63) and biocompatibility were studied. To evaluate the antibacterial ability, Staphylococcus aureus (S. A., Gram-positive bacteria) and Actinobacillus actinomycetemcomitans (A. A., Gram-negative bacteria) were tested. It is expected that the prepared TiNbZr(N) series coatings possess better biocompatibility than the uncoated Ti6Al4V through an optimized coating design.

11:40am **D1-1-MoM6 Mesenchymal Stem Cells Response to Metal Oxide Thin Films***, **Phaedra Silva-Bermudez (phaedrasilva@yahoo.com)**,* Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico*; M. Fernández-Lizárraga,* Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, Mexico*; S.E. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, México*; J. Garcia-Lopez, R. Sanchez-Sanchez,* Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

Biomaterials with adequate surface properties to direct the biological response and appropriate bulk properties to meet the biomechanical requirements of bone regeneration applications are essential for orthopedic and dental implants. Mechanical and biodegradation properties are mainly determined by the bulk properties while the biological response is mainly directed by the surface properties. Thus, coatings are interesting options to tailor/functionalize the surface of mechanically adequate bulk materials, to direct the biological response towards enhanced osteoinduction and/or osteointegration. Biocompatible metal oxides such as ZrO_2, Nb_2O_5 and Ta_2O_5 are of great interest as coatings for orthopedic and dental implants. It has been shown that they decrease the biocorrosion of different materials, and they might induce adequate osteointegration and enhanced mesenchymal stem cells (MSC) differentiation towards the osteoblastic phenotype (osteoinduction), in the same way as it has been proved for TiO_2.

Thin films of TiO_2, ZrO_2, Ta_2O_5 and NO_2O_5 were deposited on Si(100) substrates as a model to study the potential of these oxide as biocompatible coatings capable of modulating the biological response. Thin films were deposited from pure metallic targets by reactive magnetron sputtering, under an Ar/O_2 (80:20) atmosphere and using RF-power. The roughness and topography of the coatings were characterized by profilometry and Scanning Electron Microscopy. The surface energy and water wettability were determined by contact angle measurements. To characterize the biological response of the oxide coatings, human MSC were independently plated on bare and oxide-coated Si(100) substrates and cultured at 37 °C, changing the culture media every three days. Cell viability and metabolic activity were assessed at different days of culture using the Calcein-AM/Ethidium homodimer fluorescent kit and the MTT-Formazan assay, respectively . To evaluate early-stage cell adhesion, cells seeded on the samples were harvested after 1 and 4 h of incubation and DNA was isolated and quantified. At 7 days of culture, cells on independent samples were fixed, dehydrated and evaluated by SEM. Potential cell differentiation to the osteoblastic phenotype was assessed at culture day 7 by immunofluorescence assays against characteristic markers of the osteoblastic phenotype such as, osteocalcin and RUNX2. Phosphatase alkaline assays in cells culture supernatants were also performed. Metal oxide coatings studied were biocompatible; however, r esults suggested that number of cells adhered on the substrate and cell differentiation were dependent on the coatings physicochemical properties.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific Salon 2 - Session G4-MoM
Pre-/Post-Treatment and Duplex Technology

Moderators: Heidrun Klostermann, Fraunhofer FEP, Germany, Hiroyuki Kousaka, Gifu University, Japan

10:00am **G4-MoM1 Electrolytic Plasma Polishing as Post-Treatment for Additively Manufactured Stainless Steel***, **Nicolas Laugel (nicolas.laugel@manchester.ac.uk)**,* *A. Matthews, A. Yerokhin,* The University of Manchester, UK

Electrolytic plasma polishing (EPPo) is a finishing method used for the polishing, cleaning, deburring, smoothing of metals and alloys. In contrast with techniques requiring careful control of directionality, such as mechanical polishing and laser or water jet based methods, EPPo effects the surface as a whole. Among geometry-independent approaches, such as electropolishing or chemical etching methods, EPPo stands out with benign water-based electrolytes, low material removal for a given target surface state, and treatment times in the minutes. With these characteristics, the method complements Additive Manufacture (AM) particularly well, with little-to-none constraints put on piece design and ease of application for industrial actors who do not necessarily have experience in hazardous chemical handling and waste management.

The work presented here focuses on two complementary approaches for in-depth characterization, of the process itself and of the resulting surfaces respectively, with the ultimate goal of streamlining the optimization of EPPo on an application-by-application basis. *In situ* process analysis could allow the user to fine-tune process parameters through direct feedback. To help realize this, comprehensive analysis in the frequency domain of the electrochemical cell current response, in particular, was conducted and shown to give real-time information on the balance between the different reactions and physico-chemical phenomena at play. Additionally, both the plasma light emission and gas evolution accompanying EPPo were anlyzed to further inform the interpretation of this electrical response and the role of different parameters.

In the second line of characterization effort, extensive analysis of the resulting surfaces was performed in terms of morphology and atomic and chemical composition. Very superficial (~10nm) dealloying could be demonstrated in the case of Ni-Cr steels which, along with the overall roughness decrease, is believed to drive moderate improvements in resistance to corrosion and microhardness. Surface profilometry over macroscopic areas was used to determine the strength of the smoothing effect as a function of the lateral size of features. This aspect is particularly pertinent to the EPPo of AM pieces, as they tend to display long range roughness, in the order of tens of micrometers. The development of a metric to assess which combination of parameters will best smoothen features of the most relevant length scale to a given application opens the way to novel options for EPPo optimization.

10:20am **G4-MoM2 Notable Difference between Rapid-Thermal and Microwave Annealing on Ge pMOSFETs***, **Yu-Hsuan Chien (teresa.chien888@gmail.com)**,* *K.-S. Chang-Liao, D.-B. Ruan, S.-H. Yi, F.-Y. Chu,* National Tsing Hua University, Taiwan

Effects of rapid-thermal-annealing (RTA) and microwave annealing (MWA) on GeOx interfacial layer (IL) and HfO2 gate dielectric in Ge pMOSFET are studied in this work. High gate leakage and low hole mobility may be induced by diffusion of GeOx during RTA thermal process. The electrical characteristics, such as high hole mobility of ~510 cm2/V-s, low EOT of ~0.7 nm, and very low gate leakage density (JG) of ~10-4 A/cm2 at VG=VFB+ 1 V in Ge pMOSFET, can be simultaneously achieved by the efficient annealing effects of MWA on hydrogen plasma (H*) treated GeOx IL, thanks to the suppression of GeOx out-diffusion. The notable different between RTA and MWA can be attributed to good annealing effect on gate stack with low thermal budget of MWA.

10:40am **G4-MoM3 Effect of Annealing Environment on Performance of InWZnO CBRAM***, **Chih-Chieh Hsu**,* *P.-T. Liu (ptliu@mail.nctu.edu.tw), K.-J. Gan, D.-B. Ruan, Y.-C. Chiu, S.M. Sze,* National Chiao Tung University, Taiwan

The influence of annealing on the microstructure and electrochemical properties of the InWZnO CBRAM was studied. Structural and chemical composition analysis are studied with TEM and XPS. The Cu/TiW/InWZnO/Pt device showed most endurance cycles (>10^3) and stable retention characteristics for over 10^4 s at 85°C. Furthermore, this result has given notable improvement of a TAOS based material by annealing treatment utilizing in CBRAM.

11:00am **G4-MoM4 Plasma Pretreatment of Small Parts in Bulk Vacuum Coating***, **Heidrun Klostermann (heidrun.klostermann@fep.fraunhofer.de)**,* *B.G. Kraetzschmar, F. Fietzke,* Fraunhofer FEP, Germany

Bulk coating seems to be an intriguing variant of vacuum coating for small mass parts. Compared to individual part coating, the handling effort is considerably reduced. This applies to indirect and direct labor such as the production and maintenance of adapted fixtures and the charging and de-charging of individual parts. Furthermore, the utilization of processing volume can be maximized, avoiding void space between the parts. This benefit turns into a drawback during plasma etching due to the competitive processes of sputter cleaning and re-deposition on the parts. However, plasma pretreatment of the surfaces is an indispensable step also in bulk vacuum coating. Otherwise, the permanent mechanical impact during agitation will entail delamination defects due to interface imperfections. Identification of appropriate plasma pretreatment regimes is as important as the coating step itself.

Fraunhofer FEP has developed a technology for aluminum based corrosion protection coating of rivets as bulk goods. The plasma pretreatment is an essential step of the technology that precedes the multilayer deposition, which is accomplished by alternating processes of high-rate plasma-activated evaporation and magnetron sputtering. In this contribution the focus will be laid on the plasma pretreatment. To establish such processes, many aspects have to be considered: 1. Generation of a sufficiently dense plasma close to the bulk of small parts to be treated, 2. Facility to apply a bias voltage to the substrates, 3. Identification of parameters for effective material removal, 4. Verification of a uniform treatment of all parts in the batch, 5. Qualification of etching efficiency, 6. Coating qualification including the indirect approval of the pretreatment step. The presentation will give insight into procedures and results along this sequence.

11:20am **G4-MoM5 Comprehensive Characterization of Surface Modification Mechanisms in Boron Nitride Films Prepared by a Reactive Plasma-assisted Coating Technique**, ***Koji Eriguchi (eriguchi.koji.8e@kyoto-u.ac.jp)***, Kyoto University, Japan; *M. Noma,* SHINKO SEIKI CO., LTD, Japan; *M. Yamashita,* Hyogo Prefectural Institute of Technology, Japan; *K. Urabe,* Kyoto University, Japan; *S. Hasegawa,* Osaka University, Japan **INVITED**

Boron nitride (BN) films are of great importance in a wide variety of engineering fields such as machinery, electronic devices, and space applications [1–4]. Various process technologies have been developed to form stable BN films. Recently, we proposed a reactive plasma-assisted coating (RePAC) system [5] to fabricate high-hardness (cubic) BN stack structures on a Si substrate and investigated the surface modification under various plasma exposures [6]. In this study, we performed comprehensive characterization of the BN films on crystalline Si substrates using various analysis techniques, *i.e.*, indentation and electrical tests in combination with a molecular dynamics (MD) simulation. The (µm-thick) BN films prepared by the RePAC system exhibited characteristic electron tunneling behaviors governed by the Frenkel–Poole effects [7][8] in response to process conditions (*e.g.* the energy of incident Ar ions). The relationship between the electrical dielectric constant determined by capacitance–voltage test and the Knoop hardness was clarified for various process conditions. An inductively-coupled Ar plasma reactor where the energy and flux of incident ions were controlled was used to investigate the surface modification mechanisms of the BN films. The formation of a surface plasma-damaged layer (a few nm thick) was identified by a nanoindentation technique [9]. The energy dependence of the sputtering yield of the BN films was compared with that of SiO_2 films, indicating that the BN film is one of the promising candidates for the usage in harsh environments such as a long-time plasma exposure. The MD simulations predicted the formation and reconstruction of the sp^3-bonded BN phase in the hexagonal background under the irradiation of ions, showing a good agreement with the experimental findings. The comprehensive characterization as performed in this study should be employed for future BN process designs.

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Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific Salon 6-7 - Session H1-1-MoM

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces I

Moderators: Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France, Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

10:00am **H1-1-MoM1 Cross-sectional Nanodiffraction and TEM Reveal In-situ Indentation Response of AlN-CrN Superlattice Multilayer**, ***Juraj Todt (juraj.todt@oeaw.ac.at)***, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; *C. Krywka,* Helmholtz-Zentrum Geesthacht, Germany; *Z.L. Zhang,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria; *J. Keckes,* Montanuniversität Leoben, Austria; *M. Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria

Indentation at small penetration depths is a relatively easy and fast method to probe the mechanical properties of surfaces that have been coated or treated otherwise. However, due to the actual complexity of the mechanical interaction between indenter tip and tested material, there is considerable interest in the mechanical, structural and morphological changes induced during loading of a sample. Until recently, most research in this area has focused on numerical studies and on ex-situ characterization using electron microscopies, as there is a distinct lack of experimental methods that are capable of accessing the relevant material volume during indentation. This is where cross-sectional scanning X-ray nanodiffraction (CSnXRD), coupled with a suitable in-situ indentation sample environment, can really help to gain more insight [1].

For this contribution, an epitaxially stabilized AlN-CrN superlattice multilayer coating with a total thickness of ~4.5µm was loaded with an indentation device available at the MiNaXS beamline P03 of the PETRA III synchrotron facility at DESY and CSnXRD was carried out in-situ at various loads imposed on the sample [2]. Using this method it was possible to map multi-axial stresses that evolve in response to the applied indentation loads and which are ultimately modified by the formation of cracks and a limited amount of plasticity. Since there is an inherently regular microstructure present in superlattice materials, it was also possible to track the small-angle X-ray scattering (SAXS) signal and thereby, to assess changes to the morphology of the sample. In order to support the findings, a complementary characterization was performed ex-situ using TEM.

The results indicate that (i) mostly compressive stresses, reaching up to 13GPa, are induced during indentation, but also (ii) significant tensile in-plane stress and characteristic shear stresses, which eventually result in the formation and growth of through-thickness cracks. Moreover, (iii) compression of the bi-layer period in the superlattice has been observed up to ~7%, which seems to be mostly elastic, but also (iv) the mean orientation of the layers is tilted in close vicinity to the indenter tip, by several degrees.

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10:20am **H1-1-MoM2 Nano-scale Residual Stress Profiling in Ultra-thin Si_3N_4/ZnO Multilayer Stacks using FIB-DIC Method**, ***Marco Sebastiani (seba@uniroma3.it)***, Roma TRE University, Italy

Silicon nitride (Si_3N_4) is commonly used in many optical applications because of its transparency over a wide spectral range from near-ultraviolet (UV) to the infrared (IR) region. One example is the low emissivity (Low-E) coatings, which are applied to large area architectural glazing to reduce heat losses from buildings. They combine high visible transparency with high reflectance in the far-infrared region. To achieve such combination of properties, Low-E coatings generally consist of dielectric/Ag/dielectric multi-layers stacks, where the thin (~ 10 nm) Ag layer reflects long wavelength IR back into the building while the dielectric layers both protect the Ag and act as an anti-reflective layer.

The architecture of the multi-layer stack influences its mechanical properties and it is strongly dependent on the residual stress distribution in the stack. Residual stress measurement by micro-ring core focused ion beam (FIB) milling at the surface offers lateral resolution better than 1 mm and provides information about the residual stress depth profiling with a resolution better than 50 nm. The method is suitable for both equi-biaxial and non-biaxial stress distribution and hence covers a large number of material systems. In this work, thin Si_3N_4/ZnO/Si_3N_4 stacks with varying thickness (100, 160 and 200 nm) were deposited by magnetron sputtering onto glass substrate and post deposition annealed at 650 °C for 12 minutes. Residual stress measurement by FIB-DIC revealed that the individual Si_3N_4 layers in the multi-layer stack are under different amount of compressive stresses. The magnitude of these stresses changes after the heat treatment cycle and provides useful insight into the multi-layer architecture. The results show that FIB-DIC is a reliable method for accurately probing the residual stresses with nanoscale resolution.

10:40am **H1-1-MoM3 EBSD and TKD Techniques for Stress, Defect and Nano-structural Analyses of Thin Films and Coatings***, Xavier Maeder* ***(xavier.maeder@empa.ch),*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; A. Sharma,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Thin film properties are directly influenced by their microstructure, such as texture, grain size, grain boundary distribution, as well as their residual stresses. For such analyses in nanostructured materials, X-rays diffraction (XRD), or transmission electron microscope (TEM) are generally considered as the tool of choice. Both techniques have however some limitations, such as the poor lateral resolution for XRD and the only very local analyses for TEM. With sub-100nm resolution, electron backscatter diffraction (EBSD) and related technique such as high-angular resolution EBSD (HR-EBSD) can be applied for such characterizations in large grain coatings. Spatial resolution of EBSD can be however increased by one order of magnitude down to the sub-10nm scale by reducing the interaction volume between the specimen and the electrons, such as in transmission kikuchi diffraction (TKD) where a thin section of the sample, typically between 300 and 50nm, is analyzed. We will show how we can apply TKD on directly deposited thin film on TEM grids, without sample preparation, for quick full microstructural analyses. We will also show the application of EBSD and TKD techniques for cross-sectional analyses of PVD and PVD-ALD multilayer coatings. Combined with EDS analyses, coating thermal resistance, diffusion processes and phase transformation can be investigated in details. HR-EBSD and TKD can be used to map the geometrically necessary dislocation distribution in the coatings and reveal the role of the microstructure and the multilayer architecture in their mechanical properties.

11:00am **H1-1-MoM4 Deformation Mechanisms in Nanocrystalline-Amorphous Cu/Ta Coatings***, Teodor Huminiuc* ***(T.Huminiuc@soton.ac.uk),*** University of Southampton, UK*; A. Bahrami,* Universidad Autónoma de Ciudad de México, Mexico, México*; S.E. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, México*; T. Polcar,* University of Southampton, UK

Amorphous-nanocrystalline composite metallic coatings have the unique ability to conform to a multitude of industrial requirements in terms of mechanical properties, morphology and corrosion resistance. The emerging properties are easily tuned by varying the ratio of the component metals. The amorphous-crystalline composites are in theory ideal systems where the dislocation-based plasticity should be contained by high-strength interstitial glassy regions while being able to retain ductility and avoid the characteristic low strain brittle failure. At the same time, the low density of crystal to crystal grain boundaries should minimise the accumulation of free energy and prevent grain growth within the coating when subjected to high temperatures thus maintaining the hardness values [1].

In this study, a prototype Cu-Ta binary alloy coating was deposited by means of sputtering and the Ta concentration was varied between 0 and 100%. The structural and mechanical properties of the thin films were analysed in the as-deposited and annealed state by means of x-ray diffraction, scanning, transmission electron microscopy, nanoindentation and scratch testing. A notable increase in the hardness and toughness of the coatings is observed (0,9 to 12 GPa) when increasing the ratio of Ta to Cu. Our study aims to discover the limitations of such metallic nanocomposites and highlight the prevalent deformation and failure mechanisms observed when subjecting the films to extreme mechanical stress. As the glassy and crystalline phases show different types of deformation and failure mechanisms, a suitable ratio between the two materials needs to be achieved in order for the coating to combine successfully the strengthening and stabilising characteristics under increased mechanical strain. A complete picture is presented and gathers the the grain size, shape and distribution within the film, phase separation and crystallinity, chemical mapping and response to increased mechanical strain with emphasis on the limits of the Cu-Ta composite.

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11:20am **H1-1-MoM5 Multimodal and *in situ* Electron Microscopy to Understand Local Deformation Mechanics***, Josh Kacher* ***(josh.kacher@mse.gatech.edu),*** Georgia Institute of Technology, USA **INVITED**

Understanding dislocation generation mechanisms and interactions with obstacles such as grain boundaries and other dislocations is central to understanding the mechanical behavior of metals and alloys, including thin films. This has motivated decades of research into the unit processes governing dislocation interactions by *in situ* transmission electron microscopy (TEM) mechanical testing, resulting in the establishment of basic rules that govern how these interactions occur. However, much of this research has been largely observation based with direct quantification of the interactions in terms of the local and global stress state limited. With the advent of high speed electron detectors and the continued improvement of quantitative *in situ* mechanical testing platforms, it is now possible to extract accurate information on the material stress state associated with dislocation generation and their interactions with surrounding microstructural features, spurring renewed interest into these fundamental dislocation interactions. These advances have also necessitated the increased integration of data analytics based analysis of results as data acquisition rates now exceed what can be manually processed and understood.

In this talk, I will discuss the development of advanced *in situ* TEM testing techniques, including local stress mapping and multimodal imaging via scanning nanobeam diffraction as well as quantification of the global sample stress state using MEMS-based mechanical testing platforms. I will discuss these advances in terms of two materials applications: understanding transgranular and intergranular dislocation mechanisms in ultrafine grained thin films and understanding the influence of the deformation-induced grain boundary state on dislocation/grain boundary interactions in coarse-grained thin films.

Topical Symposia
Room Pacific Salon 3 - Session TS5-1-MoM
Thin Films on Polymer Substrates: Flexible Electronics and Beyond I

Moderator: Barbara Putz, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

10:00am **TS5-1-MoM1 Flexible Printed Sensors for Biomechanical Measurements***, Tse Nga Ng* ***(tnn046@ucsd.edu),*** University of California San Diego, USA **INVITED**

Rapid, on-site assessment is highly desirable in the fields of both medical treatment and novel robotics. To achieve this goal, my group's research aims to develop low-cost, flexible, large-area sensor devices for different health and environmental applications. In this presentation, we discuss case studies using similar pressure sensors for two different point-of-use applications:

1) Motor skills characterization. There is no objective metric for evaluating motor skill training progress in autistic children, and current assessments rely on qualitative surveys. We have fabricated an instrumented glove with touch sensors on textile for finger tapping patterns characterization. This glove could find future use for characterizing motor skills of people suffering from autism, Parkinson's disease, epilepsy seizures, and other neurological motor disorders.

2) Robotic sensors for simultaneous pressure and chemical detection. There is an urgent need of sensor technologies to monitor hazardous materials for security and environmental applications. Rapid on-site detection of chemicals through remote robotic sampling is highly desired to avoid placing people at exposure risks. We have combined printed chemical and pressure sensors together on disposable gloves, and demonstrated successive simultaneous tactile sensing and pesticide detection in a point-of-use platform that is scalable and economical.

10:40am **TS5-1-MoM3 Atomic Layer Deposited Al_2O_3/ZnO Nanolaminate Thin Films on PET Substrates: Fracture Mechanics and Oxygen Gas Permeation Properties**, *V. Chawla, M. Ruoho, J.-P. Niemelä, B. Putz,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *M. Weber, A.A. Chaaya,* Institut Européen des Membranes, IEM, France; *A.A. Taylor,* University of California Santa Barbara, USA; *C. Charmette,* Institut Européen des Membranes, IEM, France; *P. Miele,* Institut Européen des Membranes, IE, France; *M. Bechelany,* Institut Européen des Membranes, IEM, France; *J. Michler,* ***Ivo Utke (Ivo.Utke@empa.ch),*** Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Gas-barrier coatings are increasingly needed e.g. for organic electronics and for food and drug packaging. Atomic layer deposition (ALD) is well suited for fabrication of such coatings as it allows for exceptional control over the thickness, uniformity and conformality of pinhole-free coatings [1]. While ALD-fabricated nanolaminates have been extensively studied for their moisture-barrier properties [2-4], reports on oxygen-barrier properties are scarce [1], and are rarely combined with the mechanical failure analysis of the coating-substrate systems.

Here we present on mechanical and oxygen-barrier properties of 200-nm thick Al_2O_3 and ZnO films, and Al_2O_3/ZnO nanolaminates deposited on polyethylene terephthalate (PET) substrates by ALD at 90 °C from $AlMe_3$, $ZnEt_2$ and H_2O precursors [5]. Electron microscopy studies indicated that $AlMe_3$ and H_2O diffused into the PET substrate during the first ALD cycles of Al_2O_3. This lead to substantial sub-surface growth of Al_2O_3 in the case of single-layer Al_2O_3 and the nanolaminates, an effect that was not seen for ALD of ZnO. Uniaxial tensile strain experiments indicated the single-layer ZnO to exhibit superior performance (vs. single-layer Al_2O_3 and the nanolaminates) in terms of crack-onset strain 0.77% (vs. 0.47-0.57%) and interfacial shear stress 59 MPa (vs. 15-24 MPa). The superior fracture and adhesive properties of ZnO were linked to the absence of the sub-surface growth. Interestingly, the sub-surface growth was not a factor for the oxygen barrier properties. Oxygen permeability values for the PET foils coated with the nanolaminate films were in the range of $9.4\text{-}14\times10^3$ $cm^3m^{-2}day^{-1}$, while the values for the single-layer coated foils and uncoated foils were higher by one and four orders of magnitude, respectively.

The superior barrier performance of the nanolaminates highlights nanolaminating as an effective approach for fabrication of gas barrier coatings, while lack of interdependency between the gas barrier and the mechanical properties provides us with means for independent tailoring of these properties for mechanically rigid and impermeable thin film coatings.

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11:00am **TS5-1-MoM4 Low-temperature Plasma enhanced Atomic Layer Deposition of Al_2O_3 Thin Films for Applications in Flexible Electronic Devices**, *J.R. Castillo,* ***David Mateos (david.mateos@uabc.edu.mx)****, B. Valdez, M. Curiel, O.M. Perez, N. Nedev,* Universidad Autónoma de Baja California, Mexico

Thin films of Aluminum oxide (Al_2O_3) were grown by plasma-enhanced atomic layer deposition (PE-ALD) using O_2 and H_2O plasma at 70 °C. An optimization of deposition parameters was performed to obtain an atomically saturated layer. The films were grown on substrates of quartz, p-type silicon and polyethylene terephthalate (PET). X-ray photoelectron spectroscopy (XPS) revealed a high purity of the obtained Al_2O_3 films. The optical constants and thicknesses of the grown layers were determined by spectroscopic ellipsometry, while the roughness was measured by atomic force microscopy, giving RMS values in the 0.25 - 0.37 nm range for films deposited under different conditions and having different thicknesses. High transmittance, above ~95 %, was measured by UV-Vis spectroscopy. Electrical characterization was carried out using Keythley 4200 Semiconductor Characterization System. The obtained excellent optical, morphological, compositional and electrical properties of the deposited films, comparable to that of thermally grown Al_2O_3 at 200 °C, make them a promising candidate for electronic and optoelectronic applications, which require low temperature processes.

Keywords: PE-ALD, Al_2O_3, low temperature, thin films, flexible electronic

11:20am **TS5-1-MoM5 Conversion of Aluminium Oxide Coated Films for Food Packaging Applications – From a Single Layer Material to the Finished Pouch**, *C. Struller,* Bobst Manchester Ltd., UK; ***Peter Kelly (peter.kelly@mmu.ac.uk),*** Manchester Metropolitan University, UK; *N. Copeland,* Bobst Manchester Ltd, UK

Transparent barrier films based on vacuum deposited aluminium oxide (AlO_x) layers are continuing to create large interest in the market with regards to their use as food and healthcare packaging materials. Nevertheless, their post-metalliser conversion to the final packaging material still presents challenges to current AlO_x producers and the wider converting industry. In this work, AlO_x coated PET films have been developed and then converted in long duration industrial-scale trials via topcoating, printing, lamination and finally pouch making. Throughout this process, each conversion step has been investigated for its effects on the barrier performance. It was found that the printing processes, especially, induce significant damage to the ceramic barrier layer. However, by the use of a protective topcoat prior to any conversion step, the barrier properties of the AlO_x coated film were preserved, or could even be significantly enhanced, depending on the topcoat material. Furthermore, for a barrier topcoat, remarkable stretch- and flex-durability properties were achieved in the final laminate.

11:40am **TS5-1-MoM6 Optically Transparent Bacterial Nanocellulose Composites and Fibroin Substrates for Flexible Organic Devices**, ***Marco Cremona (cremona@fis.puc-rio.br),*** Pontifícia Universidade Católica do Rio de Janeiro, Brazil; *H.S. Barud,* Universidade de Araraquara, Brazil; *R. dos S. Carvalho,* Pontifícia Universidade Católica do Rio de Janeiro, Brazil; *A.V.S. Cebrian,* UNESP, Brazil; *A.R.J. Barreto,* PUC-Rio, Brazil; *F.E. Maturi,* UNESP, Brazil; *R.R. Silva,* Chalmers University Technology, Sweden; *C. Legnani,* Universidade Federal de Juiz de Fora, Brazil; *S.J.L. Ribeiro,* UNESP, Brazil

Cellulose is the most abundant organic material on Earth and an important resource for eco sustainable platform for flexible electronics. Bacterial cellulose (BC) is a good biopolymer choice for applications in the medical field and already reported as substrates for organic devices as organic light emitting diodes (OLEDs). BC can be produced by some species of bacteria as *Gluconacetobacter xylinus* and have been demonstrating a quite promising material due to its high degree of polymerization and higher tensile strength (200-300MPa) and Young's modulus (up to 80GPa). BC substrates are in general semitransparent in the visible region due to the presence of air in the interstices between the cellulosic nanofibers. Efforts to solve this disadvantage have been reported in the literature, with the use of several polymers to fill BC interstices. However, such methods are not always economically feasible, scalable, simple, fast and with chemically green synthetic route. In this work, a polymer from recyclable source, Expanded Polystyrene (EPS), dissolved in a green solvent, d-limonene, was used as biocompatible and conformable substrates for highly efficient green OLEDs. Polystyrene is a polymer having a refractive index (h = 1.5916) close to that of the BC and can be used to fill the interstices between the cellulosic nanofibers increasing the optical transmission. Visible light transmission improves to up 88%, instead of 40% previously achieved by pristine BC. BC-PS substrates were produced by airbrush technique deposition of PS on BC pristine films. These multifunctional composite substrates were successively covered with silicon dioxide (SiO_2) and Indium Tin Oxide (ITO) thin films to be used as conductive substrates. Finally, transparent BC-PS was evaluated as conformable substrate for OLED application. The biocompatible and conformable green OLEDs produced presented current efficiency up to 5cd/A and power density around 2.8mW/cm^2, and are promising as light source for light therapy such as PDT and burning wound healing. Additionally, organic field emission transistors (OFETs) using polyurethane as dielectrics, P3HT as organic semiconductor and Au as contacts and Al as gate were fabricated onto transparent fibroin substrate. The devices retained their properties even under high curvature stresses, presenting maximum values for mobility of 1.8×10^{-2} cm^2/Vs, threshold voltages of -7.6V and low leakage current up to 50V.

Special Interest Talks
Room Town & Country - Session SIT1-MoSIT

Special Interest Session
Moderator: Grzegorz (Greg) Greczynski, Linköping University, Sweden

1:00pm **SIT1-MoSIT1 Plasma Aspects in the Deposition of Advanced Coatings***, **André Anders (andre.anders@iom-leipzig.de)**,* Leibniz Institute of Surface Engineering (IOM), Germany **INVITED**

Advanced thin films and coatings are based on the design and control of their chemical composition and microstructure, with the latter determined by the deposition technique, affecting optical, electrical, magnetic, mechanical and other properties. Over the last decades, it was demonstrated for a wide range of material systems that deposition with plasma assistance, or film synthesis from the plasma phase, can deliver microstructures (and thereby properties) not achievable by thermal means. Plasma offers ion and/or electron assistance, with both kinetic and potential energy having an effect. To parse and understand the effects is not always trivial. Several well-known systems can be used to illustrate the concepts such as transparent conducting oxides, diamond-like carbon, and transition metal compounds. While adding kinetic energy to the growth process has often shown to be beneficial in terms of the coating properties needed for applications, the approach “more is better” is generally not correct. Rather, working at a “sweet spot” with optimized (e.g. bias) conditions is desirable. A trending example of plasma assist is the use of bipolar biasing which, often in conjunction with pulsed plasmas, affects both the composition and microstructure. The presentation aims to elucidate the underlying physics concepts.

Coatings for Use at High Temperatures
Room Pacific Salon 1 - Session A1-2-MoA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II

Moderators: Sebastien Dryepondt, Oak Ridge National Laboratory, USA, Shigenari Hayashi, Hokkaido University, Japan, Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK

2:00pm **A1-2-MoA1 Advanced Coatings for Clearance Control in Turbine Components***, **Zhihong Tang (zhihong_tang@praxair.com)**, A. Athans, K. Garing, W. Jarosinski,* Praxair Surface Technologies Inc., USA

Improvement in gas turbine compressor and turbine blade tip clearance provides significant benefits of increased engine efficiency, reduced fuel consumption, and longer time-on-wing. Abradable & abrasive coatings have been used to allow the blade abrasive tip to cut a path into the shroud abradable coating to improve the seal between blade tip and casing. Thermal spray process is typically utilized to make an abradable coating, while composite electroplating is commonly used method to deposit abrasive coatings on blade tip.

This presentation reviews current coating systems for clearance control that have been used in compressor and turbine components, with focus on abrasive tip coatings. Next-generation abradable/abrasive coatings require higher-temperature capability with better resistance to oxidation, hot corrosion, and longer cutting performance. An update is presented with regards to new laboratory capabilities for evaluating current and next-generation coatings.

2:20pm **A1-2-MoA2 Intrinsic and Extrinsic Size Effects on the High Temperature Oxidation of APS and HVOF MCrAlY Coatings***, **Damien Texier (damien.texier@mines-albi.fr)**, M. Ecochard,* ICA, France*; T. Gheno,* ONERA, France*; M. Salem, P. Lours,* ICA, France

MCrAlY coatings are widely used in the manufacturing of high temperature structural components as a protective layer against intermediate and high temperature oxidation and corrosion. They are generally applied with line-of-sight deposition processes such as low-pressure plasma spray (LPPS), air plasma spray (APS), vacuum plasma spray (VPS) or high velocity oxygen fuel (HVOF). Projected coating microstructures typically comprise fine lamellas of melted and resolidified powder particles, un-melted powder particles, pores, and dispersed alumina. The defects present in these complex microstructures act as fast diffusion paths and cause oxide intrusion in the bulk of the coating [1]. In addition, the thickness of overlay coatings can range from tens of micrometers to nearly one hundred of micrometers depending on the application (aeronautical versus marine and versus power plant applications). Aluminum and chromium, which enable the formation of protective oxide scales, are present in limited amounts, and are consumed by both oxidation and interdiffusion with the substrate. Therefore, the coating thickness can be an important factor in the high temperature oxidation behavior of the system. In the present study, 800 µm-thick β-γ NiCoCrAlY coatings were deposited on sacrificial substrates by HVOF and APS. Free-standing NiCoCrAlY specimens were then prepared using a precision Jig and a lapping machine in order to ensure good control over the thickness and surface finish [2]. Freestanding NiCoCrAlY specimens with thicknesses ranging from 9 to 400 µm were oxidized in air at 1150°C for various holding times up to 500 h. Interestingly, the mass gain was found to decrease with decreasing specimen thickness, due to oxide intrusion in the bulk, especially for the HVOF coating. The specific surface is thus increased with the internal defects, as for materials with open porosity. In addition, very thin specimens were found to form different oxide layers as compared to thick specimens, due to complete Al consumption through the specimen thickness (reservoir effect). A progressive mass loss was noticed for high temperature exposures longer than the occurrence of this breakaway phenomenon. The breakaway occurred at longer oxidation time for thicker specimens.

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2:40pm **A1-2-MoA3 Active Corrosion Protection of PEO Coatings on Magnesium Alloys***, **Beatriz Mingo (beatriz.mingo@manchester.ac.uk)**, Y. Guo, R. Garcia-Leiva, B. Connolly, A. Matthews, A. Yerokhin,* The University of Manchester, UK

The increasing interest in magnesium for weight sensitive applications has led to the development of several surface protection methods to increase its poor corrosion performance. Plasma Electrolytic Oxidation (PEO) is an environmental friendly protection technique capable of producing highly corrosion and wear resistant coatings on light alloys. PEO is a high voltage electrolytic technique where plasma assisted micro-discharges are formed on the metallic substrate that facilitates the coating growth. PEO coatings usually present a layered and porous morphology, which is usually sealed in order to prevent corrosion damage. Most sealings enhance the barrier properties of the coatings by blocking the porosity and preventing the electrolyte access to the metallic substrate.

The aim of this work is to provide PEO coatings with active properties through a sealing treatment. For that, halloysite nanotubes are used as nano-containers to carry corrosion inhibitors, which are incorporated into the coatings by an immersion sealing post-treatment. The active functionalisation is based on the controlled release of the corrosion inhibitors triggered by pH changes arisen from the electrochemical activity.

The combination of magnesium protection and active functionalization opens a range of possibilities in the applicability of PEO coatings in other fields, such as in biomaterials. The same encapsulation approach might be used for the development of biodegradable metallic implants loaded with anti-inflammatory and antibiotic drugs.

3:00pm **A1-2-MoA4 Early Detection and in-situ Monitoring of the Oxidation of an MCrAlY Coating by Thermoreflectometry***, **Maxime Ecochard (maxime.ecochard@mines-albi.fr)**, B. Javaudin, R. Gilblas, D. Texier, T. Sentenac,* ICA, France

Change in oxide formation in thermal barrier coating (TBC) systems is of major interest since the formation of fast-growing oxides instead of the thermally gr own oxide (TGO) could ruin the integrity of TBC systems. Understanding the damage mechanisms associated with the microstructure of surface materials requires a local study of the thermal and oxidation mechanisms of the surface. These mechanochemical phenomena involve local changes in surface reactivity, which is observed in particular by changes in emissivity during a temperature test. An optical monitoring to assess defects in TBC components leading to local thermal variations or change in oxide formation accompanied with a change in emissivity is particularly suitable. Thermoreflectometry is an optical near-infrared (NIR) technique capable to measure both temperature and the emissivity fields of opaque materials (metals, several oxides). The principle is based on the indirect measurement of emissivity through reflectivity (active phase), coupled with a luminance temperature fields measurement (passive phase). The true temperature and emissivity field are calculated from the resolution of a system of equations written for two NIR wavelengths. This method thus allows non-contact measurement of true temperature and emissivity fields on most of the materials with centimetric dimensions subjected to dynamic processes with high thermal gradients [1].

The goal of the present investigation is to capture early local oxidation events that differ from TGO formation at high temperature, e.g. the formation of a Cr_2O_3, NiO, via *in-situ* evaluation of temperature and emissivity by thermoreflectometry.

The approach initially consists of an *ex-situ* and multi-scale analysis of the oxides formed in order to correlate the local optical signature of oxides with their chemical and morphological nature [2]. Such an investigation was possible by tracking change in oxide formation due to breakaway events on ultrathin specimens, leading to a limited content of reactive elements to form the TGO. Once these validations were conducted, an *in-situ* mesoscopic instrumentation approach is developed to monitor the local evolution of the first stages of degradation of oxidized surfaces (local formation of rapidly growing oxides).

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3:20pm **A1-2-MoA5 High-Temperature Tribology and Oxidation Behavior of Laser-Deposited High-Entropy Alloy Claddings***, **Pascal Lordat (pascal.lordat@research.deakin.edu.au)**, Q. Chao, J. Joseph, D. Fabijanic,* Deakin University, Australia

High entropy alloys (HEAs) containing 4-5 principal (5-35 at.%) alloying elements can form simple solid solutions instead of brittle intermetallic compounds, contrary to conventional phase rule prediction. Bulk samples of these alloys have demonstrated an attractive suite of properties, especially at elevated temperatures. Much less explored is the prospect of HEAs as protective high-temperature coatings.

In this work, $Al_xCoCrFeNi$ (x = 0.78, 1 and 1.25) and $AlCoCrFeNi_{2.1}$ HEA cladding systems were produced by coaxial Direct Laser Deposition (DLD, Optomec LENS MR-7) on an Inconel 718 substrate using pure elemental powders. These systems were selected to produce claddings with a wide range of phase compositions and phase distribution (from coarse dendritic to fine lamellar eutectic), all forming protective thermally grown oxide scales. Isothermal oxidation, thermal stability and wear mechanisms of carefully selected HEA claddings on Inconel 718 were investigated in ambient atmospheres at temperatures up to 1000°C for extensive period of times. The effect of secondary alloying elements such as Molybdenum on these properties was also investigated, due to the lubricant capabilities of its oxides.

The as-deposited, oxidized and post-wear claddings were extensively characterized for phase content (XRD), micro- and macro-chemical homogeneity (SEM-EDS line scans and mapping), crystallographic texture (SEM-EBSD), and micro-hardness profiles determined.

3:40pm **A1-2-MoA6 The Effect of Cr-addition on Hot Corrosion Resistance of Hot-dip Aluminized Low Carbon Steel under Static Load***, **Huan-Chang Liang (d10303013@mail.ntust.edu.tw)**, C.-J. Wang,* National Taiwan University of Science and Technology, Taiwan

In this study, the low carbon steel was immersed into molten aluminum with 2.5, 5, and 10 wt% Cr for 120s at 700 °C. The aluminized specimen was deposited with 2 mg/cm^2 of Na_2SO_4/NaCl salt mixture, with a portion of 50:50 wt% ratio. The static load testing was performed at 750 °C under 12.8 MPa. The failure behavior of aluminide with Cr addition was studied by using SEM and OM on the deformed specimen without rupture. The Fe_2Al_5 intermetallic layer with Cr addition presents similar trends in thickness. The addition of Cr forms spheroidal intermetallic phase, Al_7Cr, in topmost aluminide. The size and the distribution of Al/Cr precipitate depend on the amount of Cr. The results of static load testing show that the Cr-addition improves the adhesion of aluminide as well as decreases the total elongation of the specimen before rupture. The Al/Cr precipitate acts as the primary candidate of stress concertation ending in crack deflection, which retards the crack propagation toward the coating/substrate interface. In addition, the amount of Cr inside aluminide reduces the potential of intergranular corrosion induced by salt fluxing. The chromium-aluminide improves the lifetime of the aluminized specimens.

4:00pm **A1-2-MoA7 Hot Corrosion in Aero Gas Turbine Engines: Current Understanding and Future Research Directions***, E. Zaleski, **Mike Task (Michael.Task@pw.utc.com)**,* Pratt & Whitney, USA **INVITED**

Hot corrosion of turbine components is a significant lifecycle cost driver for modern aero gas turbine engines. The consequences of these degradation modes include increased scrap rates, unscheduled engine removals as a result of failed on-wing inspections, and in extreme cases, in-flight engine shutdowns. The financial penalties incurred by engine manufacturers for such disruptions to service can be staggering. Combating high temperature corrosion requires a multi-disciplinary approach, including input from designers, experts in thermal and structural analysis, manufacturing engineers, and materials engineers. In this presentation, the current state of understanding of high temperature corrosion processes in gas turbine engines will be reviewed, with a focus on corrosion of metallic components. It will be demonstrated that although relevant high temperature corrosion mechanisms have been studied for many years, the industry still faces significant challenges as components are continually pushed to extremes of temperature and stress. Examples of failed commercial engine hardware will be given, and component-specific mitigation strategies will be discussed.

4:40pm **A1-2-MoA9 Effect of Nickel Percentage on the Morphology, Wear and Corrosion Resistance of Zn-Ni Alloy Coating***, **Ameeq Farooq (ameeq.farooq@gmail.com)**, S. Ahmad,* University of the Punjab, Pakistan*; K.M. Deen,* University of British Columbia, Canada

The aim of this research work is to develop Zn-Ni alloy electroplating on mild steel substrate in acidic sulphate bath. Different concentration of nickel ions varies from 10gL^{-1}, 15gL^{-1},20gL^{-1} and 25gL^{-1} in the electroplating bath effect morphology, mechanical and electrochemical properties of the Zn–Ni alloy coatings. At constant current density of 1.5Adm^{-2} for one hour with sulphate containing bath having pH 3 at 35^{o}C with continuous agitation through air purging. The thickness of the coating was measured by microscopic method. Scanning electron microscope along with the Energy dispersive spectroscopy was used to find the surface morphology of the coating along with elemental mapping. Scratch adhesion testing was also conducted on the coated samples at different loads to find the adhesion and wear properties of the coating with the mild steel substrate. The electrochemical behaviour of different coatings was evaluated by using cyclic polarization and electrochemical impedance spectroscopy (EIS) in 3.5% NaCl solution. Salt spray test was also conducted for 96 hours to find the performance of alloy coating in moist saline environment. The results of alloy coating show that Ni content influences the thickness, phase structure, morphology and adhesion of coatings. The thickness decreases with the increase in the concentration of nickel from 38.2 ± 0.5 mm to 20.7± 0.5 mm. Stereomicroscope results shows after scratch test shows that the Zn-Ni alloy resist the propagation of the scratch at all loads independent of the concentration of nickel ions. The free corrosion potential shifted towards the more noble potential with the increase in the nickel ions concentration from -1083 mV $_{vs\ Ag/AgCl}$ to -1060 mV $_{vs\ Ag/AgCl}$. The electrochemical results showed that Zn-Ni coatings had better corrosion resistance compared to that of the zinc and nickel single layer coating. The Zn-Ni coatings are more pitting resistance in saline environment as compare to nickel coating.

5:00pm **A1-2-MoA10 Vacuum Annealing of ZrO_2-Coated Zircaloy-4 with ZrN Interlayer***, **I-Sheng Ting (gary820902@yahoo.com.tw)**,* National Tsing Hua University, Taiwan*; H.-M. Tung,* Institute of Nuclear Energy Research, Taiwan*; J.-H. Huang,* National Tsing Hua University, Taiwan

The purposes of this study were to investigate the effect of vacuum annealing on ZrO_2-coated Zircaloy-4 (Zry-4) with ZrN interlayer and evaluate the feasibility to use vacuum heat treatment on ZrN at different temperatures. Oxidation is a crucial problem for Zry-4 fuel claddings in light water nuclear reactor, and the naturally formed oxide layer is insufficient to protect the Zry-4 substrate. Owing to the excellent thermal stability and mechanical properties, transition metal nitrides or oxides can act as an effective diffusion barrier and prevent the substrate from further oxidation. Our previous study showed that the ZrN interlayer can act as an effective diffusion barrier and the weight gain of Y-ZrO_2-coated Zry-4 with ZrN interlayer could be significantly reduced about 51% under 700°C thermogravimetric analysis (TGA). However, several cracks were observed after the TGA oxidation test which might be ascribed to the residual stress and the stress distribution of the bilayer structure. Therefore, vacuum annealing was adopted to reduce the residual stress and enhance the crystallinity of the films. Yttria-stabilized zirconia thin film with ZrN interlayer was deposited on both sides of the Zry-4 plate by unbalanced magnetron sputtering. After deposition, vacuum heat treatment was conducted at 600°C for 1h. Additionally, vacuum heat treatment of ZrN-coated Zry-4 was also used to produce similar ZrO_2/ZrN structure at 1000°C for 1 h. The crystal structure and chemical composition was characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy, respectively. The uniformity of the films were examined using average X-ray strain method [1] with azimuthal $\cos^2\alpha\sin^2\Psi$ XRD technique [2]. The average residual stress of deposited Y-ZrO_2 and ZrN layer is -1.52±0.20 GPa and -2.63±0.08 GPa, respectively. The distribution of residual stress is not completely uniform, and the stress gradient gradually decreases from the ZrN layer to the Y-ZrO_2 layer, indicating that the stress state may not be able to impede the propagation of surface cracks. Through the vacuum annealing of the films, both crystallinity and stress distribution of the coatings would be improved, and the feasibility of vacuum annealing at different temperatures is evaluated in this study.

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5:20pm **A1-2-MoA11 Corrosion Behavior and Durability of Microstructure of Stainless Steel Rebars in Simulated Concrete Pore Solution Containing Chloride with Different PH***, **Dhruba Babu Subedi (dhrubacsubedi@gmail.com)**,* Chinese Academy of Sciences, China

Corrosion is a problem of science and technology. It cannot eliminate completely although the corrosion control is becoming more practical and achievable to decrease its rate. Nowadays, the corrosion control method of metals and alloys using various types of eco-friendly coating to save passive film on metal surface is becoming a fundamental academic and research concerns corrosion scientists.

All the experiments were conducted under static or dynamic flow conditions at room temperature. The corrosion rate evaluations were implemented by electrochemical measurements (open circuit potential, linear polarization, potentiodynamic polarization, and electrochemical impedance spectroscopy), while surface analytical techniques (SEM/EDS, XRD and XPS) were employed to examine and characterize the compositions, microstructure of alloys and the corrosion product films.

Fig1;Nyquist plot, 1-28day Austenitic Stainless Steel Fig1; Nyquist plot of three Stainless Steel

The corrosion resistance performance of the different stainless steel, 304ss, 410ss and 2304ss

Ware evaluated in different chloride condition at 9.3 pH comparing with microstructure and mechanism of passivation film formation. EIS results of both accelerated corrosion tests showed the corrosion resistance performanceof different alloys

Fig; Phase and Bode plot of Austenitic stainless steel for 1- 28day

The results of a study examining the Cl_ induced corrosion resistance of austenitic,duplex, and ferritic high-strength stainless steels in simulated alkaline and carbonated concretesolutions during exposed to carbonated solutions, corrosion resistancewas reduced and only duplex grades 2304SS exhibited high corrosion resistance.

Fig; surface srtructure of duplex stainless steel after 14 days

A strong correlation between microstructural defects and corrosion damage was observed by the help of morphology of SEM picture and optical observations. The pitting corrosion behavior of 304ss, 2304ss and 410ss in 3.5% NaCl solution has been investigated by electrochemical noise M-S Curve and the experimental data was analyzed based on stochastic theory. The change in the pit initiation site and the outstanding repassivation ability of 2304ss thin film determined that metastable pit events occurred more frequently and the probability of stable pits developing from metastable pits was lower than that of 304ss and 410ss, which improved the pit corrosion resistance of duplex thin film.he difference between growth mechanisms of stable pits on two materials led to different corrosion resistance, thus enhancing the pit corrosion resistance of duplex thin film compare to other two alloys.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-2-MoA

CVD Coatings and Technologies II

Moderators: Raphaël Boichot, Université Grenoble Alpes, CNRS, France, Kazunori Koga, Kyushu University, Japan

2:00pm **B2-2-MoA1 Silicon Carbide Coatings for High Temperature Receiver of Concentrated Solar Power Plants**, ***Michel Pons (michel.pons@grenoble-inp.fr)***, *D. Chen,* University of Grenoble Alpes, France*; J. Colas,* PROMES-CNRS, France*; F. Mercier,* University Grenoble-Alpes, France*; L. Charpentier, M. Balat-Michelin,* PROMES-CNRS, France

There is a growing interest in concentrating solar power plants as electricity generation systems. M irrors concentrate the sun's energy to drive traditional steam turbines or engines that create electricity. The thermal energy concentrated in a CSP plant can be stored and used to produce electricity when it is needed, day or night. One of the challenges is to build the solar receiver which can work at temperatures near or higher than 1000 °C for optimizing the yield. Current candidate materials are metallic alloys such as Inconel, or bulk ceramics like silicon carbide, but their operating temperatures may be limited due to oxidation or mechanical problems. Silicon carbide coatings, deposited by chemical vapor deposition technology at 1100 °C, are selected for their high thermal conductivity, low thermal expansion coefficient, high temperature stability and oxidation resistance. They forms stable and protective silica scales at temperatures higher than 1000°C. Oxide dispersion strengthened (ODS) FeCrAl alloys (Kanthal APMT), are alumina-forming alloys which can resist to high temperature oxidation. They are chosen as model substrates to study the potential of SiC coatings. Accelerated cyclic oxidation and high temperature emissivity measurements are performed in Promes solar furnace facilities (France), confirming the potential of silicon carbide coatings as materials for high temperature central receivers. The SiC based multilayered system exhibits low degradation after 1500 h of oxidation at 1000 °C in air. The modelling and simulation of stresses during thermal cycles taking into account the creep and growth of the oxide layer are used to show the limits of use of these materials.

2:20pm **B2-2-MoA2 *In-situ* Investigation of the Oxidation Behaviour of Chemical Vapour Deposited Zr(C,N) Hard Coatings Using Synchrotron X-ray Diffraction**, ***Florian Frank (florian.frank@unileoben.ac.at)***, *M. Tkadletz, C. Saringer,* Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Helmholtz-Zentrum Geesthacht, Germany*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

ZrN, ZrC and $ZrC_{0.4}N_{0.6}$ coatings were successfully deposited via chemical vapour deposition (CVD) in an industrial scale CVD plant on cemented carbide substrates and steel foils. The microstructure and the mechanical properties of the as-deposited coatings were investigated by scanning electron microscopy, X-ray diffraction (XRD) and nanoindentation tests. To gain insight into the high temperature oxidation behaviour, *in-situ* synchrotron XRD experiments were performed. Powdered samples were annealed in air between 100 °C and 1000 °C, while 2D XRD patterns were recorded. Subsequently, the 2D XRD patterns were azimuthally integrated and the resulting 1D diffractograms were evaluated by sequential and parametric Rietveld refinement. Applying these techniques, the phase evolution during oxidation could be determined. The results were then correlated with differential scanning calorimetry measurements, in order to further illuminate the oxidation mechanism of each coating system. It was shown that all Zr(C,N) samples form tetragonal, cubic and monoclinic ZrO_2 phases, whereas the onset temperature of the individual phases depends on the chemical composition. The investigated ZrCN coating exhibits the highest oxidation resistance, followed by ZrC and ZrN.

2:40pm **B2-2-MoA3 Plasma-assisted Deposition using Microdroplets**, ***Tsuyohito Ito (tsuyohito@k.u-tokyo.ac.jp)***, *K. Nitta, K. Terashima,* The University of Tokyo, Japan **INVITED**

With recent development of atmospheric-pressure technologies, various plasma applications with liquid have been extensively studied. In this presentations, we are demonstrating spherical particle deposition as well as pattern drawing via atmospheric-pressure non-equilibrium plasma using microdroplets. By using microdroplets, we can apply more various raw materials hopefully obtaining certain controllability, which are difficult only with gas phase processing.

The first part of the presentation will be demonstration of sub-micrometer spherical particles deposition [1]. Here, we apply microdroplets as semi-closed micro-reactors to control size distribution of synthesized particles. A mist atomizer was used to generate microdroplets with diameter of approximately 5 µm. Such microdroplets were carried by He gas to the plasma reactor. Zinc acetate ($Zn(Ac)_2$) solution was used as a raw material for ZnO particles synthesis and the concentration was regulated at 0.5, 1, and 2 mM (mol/L). The generated particles are deposited on a silicon substrate locating under the plasma generator. The size distributions of the generated particles agree well with the ones expected by the distribution of microdroplets and the concentrations of the raw materials; demonstrating that one particle is generated from one microdroplet in conditions tested here. Thus microdroplets could be used as semi-closed micro-reactors at least for controlling particle sizes.

The later part of the presentation will be about plasma-assisted inkjet printing (PIP), where a microdroplet is injected through plasma by an inkjet system. By using an inkjet system, the controllability of a microdroplet in time and space can be significantly improved, developing a new printing technique, PIP. So far, we have successfully demonstrated silver line drawing [2] as well as the simultaneous polymerization of 3,4-ethylenedioxythiophene (EDOT) monomer stock solution ink and printing of the resulting poly(3,4-ethylenedioxythiophene) (PEDOT) [3]. With silver line fabrications, compared with heat treatment, the line with lower electrical resistivity and a narrower width could be achieved with a much shorter treatment time. As for PEDOT line fabrications, it was demonstrated that plasma-assisted chemical reactions could be combined with inkjet printing method.

Details will be presented at the conference.

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3:20pm **B2-2-MoA5 Fundamental Study of (100) Oriented cubic AlTiN Coating with High Al content by Chemical Vapor Deposition**,
Takuya Ishigaki (ishigaki@mmc.co.jp), *K. Yanagisawa, H. Nakamura, H. Homma,* Mitsubishi Materials Corporation, Japan

In last decade, Aluminum Titanium Nitride (AlTiN) coatings deposited by thermal CVD have attracted attention as novel wear resistant coating having superior performance and surprising limit of Al ratio higher than 0.80 as fcc phase compared to the conventional PVD coatings. It is well known that cubic AlTiN shows various growth orientations such as (111), (100), (110) and random. Within this work, microstructure, mechanical properties and cutting performance of (100) oriented cubic AlTiN coating with high Al ratio were investigated. First, (100) oriented cubic $Al_xTi_{(1-x)}N$ coatings with x = 0.84 were prepared on cemented carbide substrate by CVD. Then, the microstructure of deposited coatings was observed by SEM and TEM. The crystallographic orientation of these coatings was examined by XRD and EBSD analysis. And, the hardness was measured by nano-indentation and crack resistance properties were evaluated by Vickers indentation. Finally, cutting performance of coatings was evaluated by cutting operations of AISI 4140 steel.

As the result of microstructural observation, unique microstructure like spiral structure was observed in coating surface, and many submicron pores were found along the grain boundaries in cross sectional observation. Moreover, nano-lamellae structure was observed in the grains, and the lamella structure has two types of compositional fluctuation related to the growth direction. One was normal to the growth direction as previous reports, another was parallel to the growth direction. Additionally, narrow hcp-AlN phases were confirmed along grain boundary. EBSD analysis revealed that misorientation in grains was higher than that of conventional CVD coatings. Then, the hardness of (100) oriented cubic AlTiN coating was 29GPa, which was lower than that of conventional coatings.

The coatings showed inferior cutting performance to conventional coatings in turning operation, but showed superior cutting performance to conventional coatings in milling operation in spite of relatively lower hardness.

As these results, machining application of (100) oriented cubic AlTiN coatings would be suitable for milling operation. In this case, the coating hardness isn't seems to be necessary, but outstanding mechanical impact toughness and thermal shock toughness are more important. We surmise that these features would be derived from these unique characteristics different from conventional films.

3:40pm **B2-2-MoA6 Chemical Quantifications of LPCVD Nanolamellae $Ti_{1-x}Al_xN_{1-y}$Coatings by Analytical Electron Microscopy and Atom Probe Tomography**,
Ren Qiu (renq@chalmers.se), *O. Bäcke, H. Aboulfadl,* Chalmers Tekniska Högskola, Sweden*; T. Manns, J. Kümmel, W. Janssen, D. Stiens,* Walter AG, Germany*; M. Thuvander, H.-O. Andrén,* Chalmers Tekniska Högskola, Sweden*; M. Halvarsson,* Chalmers tekniska högskola, Sweden

The $Ti_{1-x}Al_xN_{1-y}$cubic phase has been intensively used in hard wear-resistant coatings for cutting tool applications. A periodic Al-rich and Ti-rich coherent nanolamellae structure along the [100] direction without significant lattice mismatch has been reported in $Ti_{1-x}Al_xN_{1-y}$coatings synthesized by low pressure chemical vapour deposition (LPCVD) with rotational gaseous precursor supply [1][2][3]. Zalesak *et al*. reported that the coherent lattice matching was maintained by a noticeable N deficiency and excess in the Ti-rich and the Al-rich lamellae, respectively [1]. However, no such significant variation of the N content was found according to our electron energy loss spectroscopy (EELS) measurements [3]. In addition, coherent lattice matching of the (001) planes and lattice straining along the [001] direction were suggested to mainly accommodate the coherent lattice matching between the Ti-rich and Al-rich lamellae [3]. Therefore, to help understand the formation of the nanolamellae $Ti_{1-x}Al_xN_{1-y}$phase by CVD, it is necessary to accurately quantify the chemical compositions of the Ti-rich and Al-rich nanolamellae.

In this work, Al and Ti contents are quantified by X-ray energy dispersive spectroscopy (XEDS) in scanning transmission electron microscopy (STEM) mode. However, due to inferior energy resolution of XEDS and overlapping of N (392 eV) peak with Ti (452 eV) peak, it is difficult to quantify the N content by XEDS. STEM EELS is thus used to measure the Ti/N ratio, while STEM XEDS is used to determine the Ti/Al ratio. A TiN sample with known composition (48.1 at. % Ti and 51.9 at. % N) was used to calibrate the cross-section ratio of the Ti $L_{23}$and the $N_K$edges. Complimentary atom probe tomography (APT) experiments were also performed, and the measured composition was compared with that measured by the analytical STEM experiments.

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4:00pm **B2-2-MoA7 Hot Filament CVD Diamond Coatings for Hard-to-machine Materials**,
Michael Woda (michael.woda@cemecon.de), *W. Puetz, M. Frank, W. Koelker, C. Schiffers, O. Lemmer,* CemeCon AG, Germany

In the group of carbon-based coatings, polycrystalline CVD diamond thin films reveal some extraordinary material properties. Applying the very high hardness of up to 10000HV onto cutting tools enables economically feasable tool usage when machining very high abrasive materials. CVD diamond thin films are typically coated by either microwave or hot filament CVD techniques. On cutting tools with cemented carbide substrates and complex geometries hot filament CVD is well established on an industrial scale nowadays. The basics of hot filament CVD diamond coating technology are briefly introduced in the scope of this presentation. The films coated by this method can be utilized to address cutting of work piece materials including Carbon fiber reinforced plastics (CFRP), ceramics, graphite, Aluminum-Silicon alloys or even sintered carbide. This work presents results of case studies revealing the benefits of CVD diamond coatings upon cutting operations on these very demanding work piece materials.

4:20pm **B2-2-MoA8 Protective Amorphous CrC_x Coatings Grown at Very Low Temperature by Direct Liquid Injection MOCVD**,
Ionela Iliescu (ionela.iliescu@toulouse-inp.fr), *Y. Gazal,* CIRIMAT, CNRS - University of Toulouse, France*; A. Michau, F. Addou,* CEA Saclay, France*; T. Duguet,* CIRIMAT, CNRS - University of Toulouse, France*; E. Monsifrot,* DEPHIS, France*; F. Schuster,* CEA, Université Paris-Saclay, France*; F. Maury,* CIRIMAT, CNRS - University of Toulouse, France

It is well known that a major constraint of CVD processes is the high deposition temperature. For targeted applications, solutions have been found by activating the process for example by plasma, photons or hot filament, and as a result, CVD processes often become hybrids. The use of metalorganic precursors is another route to lower the deposition temperatures. Although carbides, nitrides, and other metallurgical coatings can be deposited by CVD the growth temperatures limit their application. Most of them can also be deposited by MOCVD with performance properties but the temperature lowering can be harmful.

As an example of lowering temperature, CrC_x coatings are produced at 1050°C by the halide CVD process (pack cementation) while similar crystalline coatings in composition, structure and growth rate can be elaborated at 550°C by MOCVD. This significant decrease in temperature is due to the greater reactivity of the vapor phase but the scaling of the process is more complicated, hindering its industrial development. In addition, in a wide range of temperatures, a diversity of composition, microstructure and properties can be obtained, and it is important to know them.

With the aim of developing a large-scale MOCVD process for the deposition of CrC_x coatings to protect various metal parts in extreme environments, a Direct Liquid Injection system delivering high vapor flow rates was connected to a horizontal, stainless steel hot-wall reactor 1 m long. The coatings obtained with this DLI-MOCVD process at 450°C have a composition close to Cr_7C_3 and a high nanohardness (23 GPa). Furthermore they exhibit a very good resistance to high temperature oxidation in air and steam. As a result, they were used as internal protective coating of fuel cladding tubes 1 m long and 8 mm in inner diameter. Both kinetics experimental studies and numerical modeling led to thick coatings with satisfactory thickness uniformity along these narrow tubes. For this geometry, very low temperatures are required to promote surface reactions.

This paper reports the influence of low deposition temperatures on the main features of these CrC_x coatings. They were characterized by SEM-FEG, XRD, TEM, EPMA, Raman and RBS. For growth temperatures higher than 525°C coatings are polycrystalline and two-phased (Cr_7C_3, Cr_3C_2). In the temperature range 525-350°C they are amorphous, glassy-like, *i.e.* without grain boundary. At 325°C they are amorphous but a self-organized multilayer structure was observed. The origin of the lamellar structure could be due to temporal variations of the growth temperature, which would cause rapid changes in the deposition mechanism and therefore of composition.

4:40pm **B2-2-MoA9 High Rate SiO2 by Microwave Induced PECVD for Transparent Wear Resistant Coatings**, ***Tobias Radny (radny.tobias@robeko.de)***, *K.-D. Nauenburg, R. Schäfer,* robeko GmbH & Co.KG, Germany

Microwave induced plasma has many benefits, low ion energies with high plasma densities among others, but distributing the microwave emission uniformly for large area coatings (LAC) can be problematic. This talk demonstrates a source concept that uses an array of independent microwave emitters to build a scalable linear plasma source. Among other benefits the independent control of every emitter allows to achieve high uniformity and even locally compensate for non-uniform gas distribution by adjusting the emission power of every single emitter in the array. The design of those microwave emitters allows easy cleaning and operation in the same pressure range as typical magnetron sputter processes, allowing operation in hybrid process systems.

Using Precursors like HMDSO or TMDSO it is possible to produce high quality SiO2 with good optical properties and scratch resistance on plastics.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B6-2-MoA

Interplay Between Computational and Experimental Design of Coatings and Processes II

Moderators: Yin-Yu Chang, National Formosa University, Taiwan, Paul Heinz Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria

2:00pm **B6-2-MoA1 Controlling Phase and Microstructure of Ti-Cr-Al-N System Deposited by Arc Ion Plating**, ***Kenji Yamamoto (Yamamoto.kenji1@kobelco.com)***, Kobe Steel Ltd., Japan **INVITED**

Since the discovery of metastable cubic TiAlN [1], which had superior mechanical and chemical property compared to TiN[2,3], experimental effort in searching of composition for improved property has been continued mainly in compositional frame of Ti, Cr and Al such as AlCrN [4-6] and TiCrAlN [7]. Currently, it is well known that each coating system undergoes phase transition from cubic B1 to hexagonal B4 structure once Al composition exceeds certain value depending on the system. Experimental determination of phase boundary between B1 and hexagonal B4 have been reported for each system, TiAlN by Ikeda et al. [8], CrAlN by Sugishima et al. [9] and TiCrAlN by Yamamoto et al [7].

On the theoretical side, Makino predicted, by using band parameter method [10], maximum solubility of AlN into cubic lattice of transition metal nitride while maintaining B1 cubic structure. According to the calculation of Makino, maximum solubility of AlN into cubic TiN and CrN lattice is 65.3at% and 77.2 at% which shows good agreement with above mentioned experimental results.

Phase transition from B1 to B4 dose not only means change in crystal structure, but means change in critical property such as hardness and oxidation resistance. In this presentation, mainly experimental perspective of importance of controlling the phase and micro-structure of multi element nitride systems of TiAlN, CrAlN and TiCrAlN for cutting tool application will be presented.

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2:40pm **B6-2-MoA3 Maximum N Content in a-CN_x and other Amorphous Nitrides**, ***Jiri Houska (jhouska@kfy.zcu.cz)***, University of West Bohemia, Czech Republic

Structures of amorphous CN_x materials are predicted by extensive ab-initio molecular-dynamics simulations (more than 800 trajectories) in a wide range of compositions and densities [1]. The predicted lowest-energy densities are in agreement with the experiment. The main attention is paid to the formation of N_2 molecules, with the aim to predict and explain the maximum N content in stable CN_x networks. The results show that the maximum N content is of ≈42 at.%. From the kinetics point of view, higher N contents lead to steeply increasing rate of N_2 formation during materials formation. The preferred structures may contain some unbonded N_2 molecules at N contents above ≈37%, and that they contain many unbonded N_2 molecules at N contents above ≈42%. The content of N bonded in the amorphous networks only slowly increases above ≈42% with the overall N content (≈70% of the extra nitrogen leads only to N_2 formation). From the thermodynamics point of view, networks with more than ≈42% of N bonded in them may be temporarily stabilized by N_2 molecules sitting in voids around the network, but a subsequent N_2 diffusion into the atmosphere makes them unstable. Next, the methodology is applied to other amorphous nitrides such as SiCN and BCN. The results are important for the design of amorphous nitrides for various technological applications, prediction of their stability, design of pathways for their preparation, and identification of what may or may not be achieved in this field.

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3:00pm **B6-2-MoA4 Transition Metal Carbonitride based Thin Films: A Critical Review on Thermal and Elastic Properties of Group IV to VI $TMC_{1-x}N_x$**, *T. Glechner,* TU Wien, CDL-SEC, Austria*; P.H. Mayrhofer,* TU Wien, Austria*; S. Kodambaka,* University of California Los Angeles, USA*; R. Hahn,* TU Wien, CDL-SEC, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*;* ***Helmut Riedl (helmut.riedl@tuwien.ac.at)***, TU Wien, CDL-SEC, Austria

Cubic transition metal (TM) carbides and nitrides are well established in various industrial applications especially as thin films due to their refractory character including highest thermal stability, chemical inertness, as well as high hardness. Based on their bonding characteristics – dominated by mixtures of strong ionic, covalent, and metallic bonds between their metal and carbon/nitrogen atoms – these compounds are strongly limited with respect to ductility compared to metals and metallic alloys. Therefore, to overcome these limitations as well as further weak points, e.g. oxidation resistance or electrical properties, the formation of carbonitrides by substitutional alloying of non-metal sites is an interesting approach. Recent studies in the field of TM carbonitrides highlighted promising candidates as well as selection criteria [1,2]. Here the valence electron concentration (VEC) as well as structural defects such as point or Schottky defects play a prominent role.

Within this study, we therefore compared the thermal and elastic properties of selected carbonitride based coating materials of the group IV to VI (e.g. Hf-C-N or Ta-C-N) transition metals utilizing theoretical and experimental methods. Various coating materials, also including the binary base systems, have been deposited by reactive and non-reactive magnetron sputtering techniques and subsequently characterized with respect to structure, morphology, chemical composition, and mechanical characteristics – also including micro mechanical testing. These results have been correlated with ab initio calculations utilizing the Vienna Ab Initio Simulation Package. The obtained results clearly indicated that the synthesis of single phase structured fcc $TMC_{1-x}N_x$ structures gets more challenging from group IV to VI. Nevertheless, the enhancement of the fracture toughness through non-metallic alloying is an appropriate approach – e.g. an increase for K_{IC} from 1.8 to 2.9 MPam$^{1/2}$ for $TaC_{0.81}$ compared to $Ta_{0.47}C_{0.34}N_{0.19}$ [2]. In addition, thermal treatments suggest an enhancement of the hot hardness and oxidation resistance with deductions on the still high phase stability. In summary, $TMC_{1-x}N_x$ coatings depict an interesting alternative to other thin film materials but still require a more detailed scientific exploration.

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3:20pm **B6-2-MoA5 Kinetic Monte Carlo Simulations of Residual Stress Evolution**, ***Eric Chason (eric_chason@brown.edu)***, Brown University, USA; *A. Bower,* Brown University, USA, United States of America

Kinetic Monte Carlo (KMC) simulations have been a useful way to model the evolution of surface morphology during thin film growth. However, it has been difficult to include stress in KMC simulations because of the long range nature of stress fields. In this work, we have used an approximation that focuses on the stress development at the grain boundaries that allows us to overcome this problem. The results enable us to investigate how residual stress depends on the growth conditions (growth rate, temperature, particle energy) and microstructure (grain size) during thin film growth. . In particular, the KMC shows how the flux of deposited atoms on the surface leads to a supersaturation that creates compressive stress in the film.

3:40pm **B6-2-MoA6 Simulation for Compositional Variation in Reactive Magnetron Sputtered NiTi Films**, ***Indrani Banerjee (indrani.banerjee@cug.ac.in)***, Central University of Gujarat, India; *S.V. Haldar,* Harish-Chandra Research Institute, India; *S.K. Mahapatra,* Central University of Punjab, India

We demonstrate simulation of reactive magnetron sputtering of NiTi target using PIC MCC simulation model. The optimum operating pressure with a fixed target substrate distance for equiatomic deposition of NiTi (nitinol) films has been modeled. The compositional variation of Ni and Ti in the film has been simulated. An empirical relation between the Titanium to Nickel Vapor number density ratio (Y) and the pressure-(target substrate) distance product has been established. The nanoparticle distribution on the deposited film has also been simulated. This kind of compositional variation optimization of nitinol films will help in fabrication of low profile biomedical devices like artificial heart valves.

4:00pm **B6-2-MoA7 Electronic Structure based Design of Thin Film Metallic Glasses with Superior Fracture Toughness**, ***Simon Evertz (evertz@mch.rwth-aachen.de)*** [1], RWTH Aachen University, Germany; *I. Kirchlechner, R. Soler, C.K. Kirchlechner, P. Kontis,* Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany; *J. Bednarcik,* P. J. Safarik University, Kosice, Slovakia; *B. Gault, G. Dehm, D. Raabe,* Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany; *J.M. Schneider,* RWTH Aachen University, Germany

High fracture toughness is crucial for the application of metallic glasses as structural materials to avoid catastrophic failure of the material in a brittle manner. One fingerprint for fracture toughness in metallic glasses is the fraction of hybridized bonds, which is affected by alloying $Pd_{57.4}Al_{23.5}Y_{7.8}M_{11.3}$ with M = Fe, Ni, Cu, Os, Ir, Pt, and Au. It is shown that experimental fracture toughness data is correlated to the fraction of hybridized bonds which scale with the localized bonds at the Fermi level. Thus, the localized bonds at the Fermi level are utilized as a measure for fracture toughness. Based on *ab initio* calculations, the minimum fraction of hybridized bonds was identified for $Pd_{57.4}Al_{23.5}Y_{7.8}Ni_{11.3}$. According to the ansatz that the crystal orbital overlap population at the Fermi level scales with fracture toughness, a value of around 95 ± 20 $MPa.m^{0.5}$ is predicted for $Pd_{57.4}Al_{23.5}Y_{7.8}Ni_{11.3}$. Consistent with this prediction, in micro-mechanical beam bending experiments $Pd_{57.4}Al_{23.5}Y_{7.8}Ni_{11.3}$ thin films show pronounced plasticity and absence of crack growth.

Coatings for Biomedical and Healthcare Applications
Room Royal Palm 1-3 - Session D1-2-MoA

Surface Coating and Surface Modification in Biological Environments II

Moderators: Mathew T. Mathew, University of Illinois at Chicago, Rockford, USA, Phaedra Silva-Bermudez, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

2:00pm **D1-2-MoA1 Surface Coatings on Biodegradable Magnesium Alloys for Orthopaedic Applications**, ***Preeti Makkar (preeti.materials@gmail.com)***, *B.T. Lee,* Soonchunhyang University, South Korea

Biodegradable implants have been extensively studied for orthopedic regeneration. Magnesium seems as a potential candidate due to its unique combination of bone-like mechanical properties and being degradable in vivo. However, the rapid corrosion of magnesium and its alloys in physiological environment limits their clinical applications. Alloying and Surface coatings are the reliable ways to improve corrosion resistance by preventing its contact with the environment. The present paper details the state of the art in coating and surface modification technologies, applied to magnesium alloys for improved corrosion resistance and biocompatibility. The efficiency of single layered bioactive ceramic based coatings and dual layered ceramic-polymer based coatings are studied in this regard. The morphology, phase, chemical composition, wettability and performance in terms of in-vitro corrosion and biocompatibility using pre-osteoblast MC3T3 cells were discussed and compared with uncoated samples. In-vivo performance using rabbit model was also evaluated for the coatings with respect to magnesium substrate.

2:20pm **D1-2-MoA2 Analysis of a Drug Coated Polymer Stent with XPS and Argon Cluster Depth Profiling**, ***David Surman (dsurman@kratos.com)***, Kratos Analytical Inc., USA; *J. Counsell,* Kratos Analytical Ltd., UK; *M. Alexander,* University of Nottingham, UK

The application of cardiovascular stents for cardiovascular interventional therapy has emerged as the most effective method to treat coronary heart disease. Used to widen blocked or narrow coronary arteries by the insertion of a small tube into the vessels supplying blood to the heart, stents permanently allow blood to flow more freely. Cardiovascular stents were originally made from steel, however, they created issues for patients with thrombosis and hyperplasia being the usual pathological responses to the implantation of foreign devices. Despite recent advances in the field leading to the introduction of a new range of stents made from bioresorbable polymers, the undesirable problems associated with the original steel stents, such as thrombosis and hyperplasia, still remain. With these issues proving unavoidable despite the change in material, along with additional problems of overgrowth and subsequent restenosis, anti-inflammatory drugs are now loaded onto the surface of stent implants to suppress this immune response.

Here, we investigate the surface of a drug loaded polymer stent using X-ray Photoelectron Spectroscopy (XPS) and sputter depth profiling with Ar_n^+ clusters. The stents analyzed are composed of Polylactic Acid (PLA) where the outside surface has been doped with an anti-inflammatory drug. With the molecular structure of the drug being $C_{51}H_xNO_{13}$, nitrogen can be used as a marker to analyze the distribution of the drug across this stent surface. Quantitative XPS analysis concludes the drug distribution is higher on the abluminal (outer) surface than the luminal (inner) wall of the stent. Combining Argon cluster sputtering with XPS allows the distribution of the drug through the entire stent material to be fully characterized.

Conventional methods to study the effects of aging and drug mobility in these stents involve their immersion in a buffer solution for varying periods of time. Subsequent analysis of the solution with High Performance Liquid Chromatography (HPLC) can determine the extent of drug dissolution from the stent. Although this approach is accurate in determining the amount of drug dissolved, it is still unknown how much drug remains within the stent material and how it is subsequently distributed. These questions are addressed in this study where the bioresorbable stent had been immersed in PBS buffer solution for 1-3 months. Ar_n^+ cluster depth profiling of the stent materials was then used to determine the effects on simulated ageing and the propensity for the drug to migrate into the solution with time.

2:40pm **D1-2-MoA3 Biocompatibility Evaluation of TiZrNbTaFe High-entropy Alloy Thin Film Deposited by High Power Impulse Magnetron Sputtering**, ***Hsin Chao Chao (zz4444567@gmail.com)***, *Y.-C. Yang,* National Taipei University of Technology, Taiwan; *B.-S. Lou,* Chang Gung University & Memorial Hospital, Taiwan; *J.-W. Lee,* Ming Chi University of Technology, Chang Gung University & Memorial Hospital, Taiwan

High-entropy alloys (HEA) have various excellent performance such as high hardness, high temperature resistance and corrosion resistance, which have attracted attentions from academia and industries. In this study, the TiZrNbTaFe (HEA) thin film was fabricated cp-Ti and 304 stainless steel specimens using a high power impulse magnetron sputtering (HiPIMS) system. The chemical compositions, microstructures, surface roughness, mechanical properties, adhesion properties, corrosion resistance, and in-vitro biocompatibility test by MG-63 osteoblasts cell of the HEA thin film were investigated by means of FE-EPMA, FE-SEM, AFM, nanoindenter, scratch test, electrochemical analyses and MTT assay analysis. The in-vivo biocompatibility in terms of allergies, poisoning and possibly carcinogenic of the HEA film after the subcutaneous implantation animal test on SD rats was studied. The results showed that the HEA films had good biocompatibility and good corrosion resistance. The newly developed TiZrNbTaFe high-entropy alloy thin film exhibits a great potential for biomedical applications.

[1] **Student Award Nominee**

Keywords: TiZrNbTaFe high-entropy alloy thin films, high power impulse magnetron sputtering system, biocompatibility, MG-63 osteoblasts cell.

3:00pm **D1-2-MoA4 Behavior of fs-laser Micro-Patterend HDLC in Hyaluronic Acid**, ***Annett Dorner-Reisel (a.dorner-reisel@hs-sm.de)***, Schmalkalden Universtity of Applied Sciences, Germany; *S. Svoboda,* Schmalkalden University of Applied Sciences, Germany; *A. Engel,* University of Applied Sciences Mittweida; *C. Schürer,* Consultant Chemnitz; *S. Weißmantel,* University of Applied Sciences Mittweida, Germany

Surface micro-patterns like riffles, dimples, grooves can stimulate or supress special interaction with liquids and functionalize surfaces. They can act as reservoir for substances or trap undesired wear particles. In addition, laser treatment kill bacteria and clean surfaces, which is an important aspect in providing medical product to the market.

In nature, many surfaces are micro-patterned giving plant, like the lotus leave or cactus family special properties.

Micro-patterns are generated on hydrogenated diamond-like carbon films by Femtosecond-laser (fs-laser) irradiation (1028 nm, 220fs). Dimples with a spatial distance of 60 µm were generated. The parameters like fluences H (H: 0.78J/cm^2-6.63 J/cm^2) pulse repetition or duration were modified. In addition, a ripple structure (H: 3.03 J/cm^2; 220 fs) was generated. The structural changes are recorded by Raman spectroscopy, while nanotribology is performed for investigating the sliding properties of the micro-patterned HDLC surfaces. In addition to dry sliding for testing the emergency operation, hyaluronic acid is used as an intermediate substance during wear test against a zirconia ball. First impressions about potential of protein adhesion and cell interactions are discussed.

3:20pm **D1-2-MoA5 Embroidery of Conductive E-Threads: Opportunities and Challenges in Healthcare**, *Z. Dalisky, S. Alharbi, V. Mishra, A. Kiourti,* ***Katrina Guido (guido.26@osu.edu)***, The Ohio State University, USA **INVITED**

Rapid advances in bio-electromagnetics and flexible materials are opening unexplored opportunities in body area sensing. Next-generation wireless devices are envisioned that operate either upon or inside the human body and aim to break the state-of-the-art boundaries in terms of seamlessness, capabilities, and performance. To this end, embroidery of conductive threads (namely e-threads) is showing unprecedented potential. Technologies used to realize flexible conductors have long been reported (e.g., conductive inks, conductive fabrics, copper tape), but they exhibit numerous limitations in terms of electromagnetic and mechanical performance. By contrast, our e-textile technology brings forward numerous advantages: (a) the exhibited Radio-Frequency performance matches that of copper up to a frequency of ~4 GHz, (b) prototypes are mechanically and thermally robust, and (c) the printing resolution can be as high as 0.1 mm. Added to the above, polymer-based coatings can readily be integrated with such embroidered surfaces to serve numerous roles per applications requirements. For example, polymer-based substrates can be used to realize flexible multi-layer antennas, circuits, and transmission lines. In other cases, polymer-based superstrates can ensure biocompatibility of wireless textile-based implants or simply protect the exposed e-textile surface from corrosion and weathering. Finally, polymer-based coatings can help realize stretchable prototypes that stretch along with the polymer. Overall, embroidered e-textiles bring forward transformational opportunities in healthcare. Example applications explored to date include, but are not limited to, kinematics monitoring, medical imaging, deep brain sensing, recumbent height monitoring for infants, etc. This talk will present the current status on e-textile embroidered electronics, highlight opportunities in healthcare, and discuss challenges to be resolved in the future.

4:00pm **D1-2-MoA7 Flexible Plasma Jet Source for Biomedical Applications**, ***Carles Corbella (ccorberoc@gwu.edu)***, *S. Portal, L. Lin, M. Keidar,* George Washington University, USA

A new plasma source design that merges characteristics of capacitive dielectric barrier discharge (DBD) and cold atmospheric plasma jet (CAPJ) is presented. The DBD system consists of a porous ceramic material comprised between two planar electrodes. The supply of He flow, in combination with a sinusoidal voltage of ≈5 kV in amplitude and 12.5 kHz in frequency, provides a streamer that propagates beyond the DBD system. The plasma jet system can adopt different shapes with the aim of uniform surface treatment of 3D objects. Aspects like CAPJ extension, performance and lifetime of the plasma device are discussed in this paper. The composition and discharge parameters of the CAPJ are characterized by means of optical plasma diagnostics. Finally, we consider applications in plasma-based cancer surgery, as for example treatment of surgical margins. This novel source is also suitable for situations where plasma parameter adaptation to the environment (atmosphere and target surface) is required.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific Salon 6-7 - Session H1-2-MoA

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France, Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

2:00pm **H1-2-MoA1 The Spinodal Decomposition of Nanolamellar CVD $Ti_{1-x}Al_xN$ recorded by *in-situ* Scanning Transmission Electron Microscopy**, ***Christian Saringer (christian.saringer@unileoben.ac.at)***, *M. Tkadletz,* Montanuniversität Leoben, Austria; *I. Letofsky-Papst,* Institute of Electron Microscopy and Nanoanalysis, NAWI Graz, Graz University of Technology and Graz Centre for Electron Microscopy, Austria; *C. Czettl,* CERATIZIT Austria GmbH, Austria; *N. Schalk,* Montanuniversität Leoben, Austria

$Ti_{1-x}Al_xN$ deposited by chemical vapor deposition (CVD) exhibits an extraordinary microstructure consisting of alternating Al and Ti rich face centered cubic (fcc) lamellae with thicknesses in the range of only a few nanometers. This microstructure allows to stabilize the fcc modification of $Ti_{1-x}Al_xN$ up to exceptionally high Al contents above $x \approx 0.8$. Consequently, this leads to both, an increase of the onset temperature of spinodal decomposition as well as an enhanced oxidation resistance. In the present work we have used *in-situ* scanning transmission electron microscopy to track the spinodal decomposition of this nanolamellar material into fcc TiN and fcc AlN, as well as the subsequent formation of hexagonal wurtzitic AlN. In order to achieve that, an electron transparent sample was annealed inside the microscope up to a temperature of 1200 °C. Images were simultaneously collected using annular dark field (ADF) and high angle annular dark field (HAADF) detectors. Stacking the recorded images reveals a clear picture of the microstructural evolution taking place, enabling the observation of the spinodal decomposition *in-situ* during its occurrence. It can be seen that up to 975 °C the microstructure remains stable and the lamellar structure is preserved. At 1000 °C the pronounced elemental contrast achieved with the HAADF detector revealed first signs of spinodal decomposition in the Ti rich lamellae, while the Al rich lamellae remain stable. The decomposition process is completed at approximately 1150 °C and the material has entirely lost its lamellar structure. This is followed by a quick phase transformation and the formation of wurtzitic AlN, which is clearly visible from the recorded ADF images. Although the spinodal decomposition in $Ti_{1-x}Al_xN$ has been extensively investigated, the novel approach of recording the microstructural evolution using *in-situ* scanning transmission electron microscopy is able to shed new light on this and potentially on similar small scale processes.

2:20pm **H1-2-MoA2 UHV Specimen Transfer Systems for Analysis of Reactive Materials with Atom Probe Tomography**, ***Robert Ulfig (robert.ulfig@ametek.com)***, *K. Rice, T. Prosa, D. Reinhard, J. Shepard,* CAMECA Instruments Inc., USA; *U. Maier,* Ferrovac GmbH, Switzerland

Atom Probe Tomography is the highest sensitivity 3D analytical technique with nanoscale spatial resolution and has been used to study a wide variety of materials. APT however analyzes small volumes and requires specialized specimen preparation resulting in very high surface to volume ratios. For a wide variety of microscopies and associated applications, changes related to exposed surfaces, or the bulk temperature history have little or no effect on the goal of the analysis, e.g. characterization of stainless steel grain size. For other studies, especially when using atom probe tomography, a carefully controlled environment (temperature, pressure, atmosphere, etc.) may be critical. For example:

– Rapid oxidizers (e.g. uranium, lithium)

– Surface contamination (e.g. catalysts)

– Characterization of hydrogen content in steels, semiconductors, etc.

– Analysis of “soft” materials potentially encased in vitreous ice (e.g. biological)

– Transport between various microscopic analysis/treatments (e.g. FIB-SEM, reaction chambers)

Due to growing interest in the above applications that require this capability, a UHV/Cryogenic transfer system has been developed based on a collaboration between the Max Plank Institute for Steel Research in Germany, CAMECA in the United States, and Ferrovac in Switzerland. The transfer design is based on the mobile UHV Suitcase from Ferrovac, customized to transfer samples held in a standard LEAP specimen carrier. This system can be fully integrated to a specially modified LEAP 5000 system's hardware and software. Transfer can be completed in less than 1 minute to the LEAP or any system with a standard vacuum connection. This talk will describe the existing system and a new version of VCTM to FIB transfer system developed with cooperation from ThermoFisher Scientific for fast and easy transfer in/out of a standard FIB-SEM, to the LEAP, and to other systems such as reaction chambers.

2:40pm **H1-2-MoA3 Multicracking of Thin Films and Nanostructures on Stretchable Substrates; Impact on Magnetic Properties***, **Damien Faurie (faurie@univ-paris13.fr)**,* *F. Zighem, S. Merabtine,* LSPM-CNRS, Université Paris13, France*; P. Lupo, A. Adeyeye,* National University of Singapore, Singapore **INVITED**

Nanoscale systems fabricated on flexible or stretchable substrates are being studied more and more because of their ability to adapt to non-planar surfaces, particularly in confined environments. In addition, these systems have the advantage of being lighter and less expensive than their counterparts deposited on more conventional rigid substrates. In recent years, many magneto-electronic devices have been made on different polymer substrates. The ability of these magnetic thin films on polymer substrates to be folded or stretched is essential, but their use is still delicate, which is a brake on the industrialization of these systems.

The main issues are to understand how the applied strains to the flexible magnetic systems impact their magnetic properties. Obviously, when a thin film is deposited on a flexible substrate, it is usually submitted to high stresses due to the stretching or the curvature of the whole system and to the mechanical contrast between the film and the substrate. These stresses may have an important effect on the static and dynamic magnetic properties of thin films, especially on the resulting magnetic anisotropy. In particular, it is important that the large strains to which they are subject are not harmful to their functional properties. In fact, beyond the classical magnetoelastic effects observable at small strains, the phenomenon of multi-cracking and associated localized buckling observed for inorganic thin films on organic substrates tensily stressed lead to heterogenous strains must have effects on the magnetic properties. However, these are rarely discussed in the case of flexible magnetic systems, and have never been studied in depth.

In this work, we focused on experimentally identifying the cracking mechanisms for different magnetic alloys ($Co_{40}Fe_{40}B_{20}$, $Ni_{80}Fe_{20}$) deposited on Kapton® substrate. The phenomena of multicracking but also buckling of thin films have been studied. Thin films surface was probed by atomic force microscopy during *in situ* tensile tests to clearly identify these mechanisms. Subsequently, we have identified the effects of these irreversible phenomena on the magnetic properties of thin films (anisotropy and Gilbert damping coefficient).

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3:20pm **H1-2-MoA5 Tailoring Stress Evolution During Silver Thin Film Growth on Weakly-interacting Substrates by Addition of Nitrogen***, **Andreas Jamnig (andreas.jamnig@liu.se)**,* Linköping University, IFM, Nanoscale Engineering Division, Sweden*; K. Sarakinos,* Linköping University, Sweden*; G. Abadias,* Institut P', Université de Poitiers, France

The development of stress in vapor-deposited thin films is strongly correlated with the film morphological evolution. Metal films grown on weakly-interacting substrates (e.g., polar insulators, 2D materials) at conditions of high atomic mobility exhibit a pronounced 3D growth. *In situ* and real-time measurements of residual stresses have shown that this is accompanied by a compressive-tensile-compressive (CTC) stress evolution profile as a function of film thickness, which can—in combination with theoretical models and *ex situ* observations—be directly correlated with the stages of 3D island formation, coalescence and hole-filling, respectively. The presence of gaseous species during deposition (i.e., surfactants) has been shown to change the film growth, however, the effect of these morphological changes on the stress state of the film is not well understood. Here, we present a systematic study of the influence of the nitrogen partial pressure (p_{N2}/p_{tot} = 0.03 – 0.25 for a total pressure p_{tot} = 0.7 Pa) on the stress formation during the growth of magnetron sputter-deposited Ag thin films on weakly-interacting SiO_2. The stress evolution was measured *in situ* and real-time using wafer curvature technique. In pure Ar atmosphere, the Ag film develops a typical CTC stress behavior with a steady-state in the second compressive regime. Addition of nitrogen causes a shift of the tensile-to-compressive stress-transition (i.e., formation of a continuous film) to lower film thicknesses (e.g., decrease from 12 nm in Ar ambient to 7 nm for p_{N2}/p_{tot} = 0.25), and the formation of larger compressive stress. Moreover, no steady-state regime is observed but instead a turnaround towards tensile stress occurs at well-defined film thicknesses that decrease from 270 to 40 nm with increasing p_{N2}/p_{tot} from 0.05 to 0.25. Besides *in situ* stress measurements, we employ *ex situ* chemical (XPS) and structural (EBSD and TEM) analyses from which we find that nitrogen presence in the growth atmosphere: (i) leads to films with a larger density of grain boundaries relative to film grown in Ar ambient; and (ii) causes competitive growth for thicknesses above 30 nm. We show, how the presence of nitrogen leads to these morphological features, and discuss their correlation to the observed stress-changes.

3:40pm **H1-2-MoA6 The Nucleation, Bonding, and Radial Growth of Thin Film Coatings on Inert Surfaces***, **Carlos Guerra (carlos.guerra-nunez@empa.ch)**,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M. Li,* ETH Zürich, Switzerland*; R. Savu,* UNICAMP, Brazil*; Y. Zhang, R. Erni,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; S. Moshkalev,* UNICAMP, Brazil*; J. Michler, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

In this work, we present a comprehensive study to determine the lateral growth rate of atomic layer deposited (ALD) films on inert surfaces. Knowing the lateral growth allows for the precise control of the size of decorative particles or full film closure on these inert surfaces for very specific and tailored applications. We introduce the concept of radial-growth-per-cycle (rGPC) to quantify how thin films nucleate and grow from a defect site at the inert surface until eventual coalescence with neighboring nuclei. [1, 2]

In order to quantify the rGPC, we have monitored the deposition of TiO_2 (from TTIP and H_2O) on *non-functionalized* singled-walled carbon nanotubes (SWCNTs) via ALD using *in-situ* Raman measurements, which collects signals of hundreds of SWCNTs during deposition. For these experiments, we built a mobile-ALD system to be transported to the Raman spectrometer and fabricated a custom-made micro-reactor to fit under the Raman microscope, as shown in Figure 1.

The progression of adding precursor molecules in an ALD fashion allowed us to study the adsorption and eventual chemisorption of the precursor molecules at different substrate temperatures in order to determine the rGPC, as well as the film induced compressive stress on the SWCNTs from the frequency shifts. The gradual increase of the sp^2-to-sp^3 hybridization of carbon atoms and consequently the I_D/I_G ratio revealed the progression in which TiO_2 nuclei grow from the surface defects along the inert surface until nuclei coalescence, and hence, film closure occurred when the I_D/I_G ratio reached a plateau.

We then adapted the phenomenological model from Cançado et al. [3] to our experiments. We will discuss the experimental setup, the results, and analysis performed to obtain the radial GPC versus the 3D GPC, and the chemisorption vs. van der Waals bond of the TiO_2 film on the CNTs.

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Topical Symposia

Room Pacific Salon 3 - Session TS5-2-MoA

Thin Films on Polymer Substrates: Flexible Electronics and Beyond II

Moderators: Oleksandr Glushko, Montanuniversität Leoben, Leoben, Austria, Barbara Putz, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

2:00pm **TS5-2-MoA1 Flexible Electronics: From Interactive Smart Skins to In vivo Applications***, **Denys Makarov (d.makarov@hzdr.de),*** Helmholtz-Zentrum Dresden-Rossendorf e. V. (HZDR), Institute of Ion Beam Physics and Materials Research, Germany **INVITED**

Portable consumer electronics necessitates functional elements to be lightweight, flexible, and wearable [1-3]. The unique possibility to adjust the shape of the devices offered by this alternative formulation of the electronics provides vast advantages over the conventional rigid devices particularly in medicine and consumer electronics. There is already a remarkable number of available flexible devices starting from interconnects, sensing elements towards complex platforms consisting of communication and diagnostic components.

We developed shapeable magnetoelectronics [3] – namely, flexible [4,5], printable [6], stretchable [7] and even imperceptible [8-12] magnetosensitive elements, which were completely missing in the family of flexible electronics, e.g. for smart skin applications.

Here, we will review technological platforms allowing to realize not only mechanically imperceptible electronic skins, which enable perception of the geomagnetic field (e-skin compasses) [10], but also enable sensitivities down to ultra-small fields of sub-50 nT [11]. These devices allow humans to orient with respect to earth's magnetic field ubiquitously. Furthermore, biomagnetic orientation enables novel interactive devices for virtual and augmented reality applications. We showcase this by realizing touchless control of virtual units in a game engine using omnidirectional magnetosensitive skins. This concept was further extended by demonstrating a compliant magnetic microelectromechanical platform (m-MEMS), which is able to transduce both tactile (via mechanical pressure) and touchless (via magnetic field) stimulations simultaneously and discriminate them in real time [12]. This is crucial for interactive electronics, human-machine interfaces, but also for the realization of smart soft robotics with highly compliant integrated feedback system as well as in medicine for physicians and surgeons.

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2:40pm **TS5-2-MoA3 Electromechanical Behavior of Evaporated and Printed Thin Films and Devices on Compliant Substrates***, **Patric Gruber (Patric.Gruber@kit.edu)**, N. Mishra, S.-M. Yi, T. Haas, B.-Y. Kim,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WBM), Germany

Compliant substrates enable the fabrication of flexible electronics for numerous applications like flexible displays, solar cells, batteries or wearable/biocompatible electronics. However, the reliability of such devices is limited by the stretchability of the inorganic components. So far, little experimental work has been carried out to investigate the mechanical properties of thin inorganic films on compliant substrates at high strains and cyclic loading. Here, we present experimental results for the flow stress, fracture strain and fatigue behavior of evaporated and printed Ag films as well as printed thin film transistors on compliant substrates. The film systems have been tested by a synchrotron-based tensile testing technique (up to 10% total strain) as well as cycling loading (50 Hz, strain amplitude up to 2.5%) and have been characterized by SEM and FIB microscopy. The synchrotron experiments yield the stress evolution and strain transfer within the film systems whereas the cyclic tests give the fatigue lifetime. On the other hand, *in situ* electro-mechanical testing, *in situ* tensile tests in the SEM and stationary FIB investigations reveal the evolution of electrical performance, crack morphology and crack density as well as fatigue damage in the individual films. First, results of electro-mechanical testing of printed and evaporated Ag films will be presented. Electrical conductivity and mechanical reliability are investigated with respect to the inherently nanoporous microstructure, and are compared to those of evaporated Ag films of the same thickness. It is shown that there is an optimized nanoporous microstructure for inkjet-printed Ag films, which provides a high conductivity and improved reliability. It is argued that the nanoporous microstructure ensures connectivity within the particle network and at the same time reduces plastic deformation and the formation of fatigue damage. Furthermore, results on fully printed BST-PMMA capacitors will be presented. Here the evolution of the capacitance during loading will be discussed based on the sequence of crack formation and delamination within the individual layers of the capacitor structure.

3:00pm **TS5-2-MoA4 Fragmentation of ALD-PVD Multilayers on Flexible Substrates in Uniaxial and Biaxial Tension: Insights from in situ SEM and Synchrotron Diffraction Experiments***, **Barbara Putz (barbara.putz@empa.ch)**, T.E.J. Edwards, T. Xie, E. Huszar, L. Pethö,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P. Kreiml,* Montanuniversität Leoben, Department of Material Physics, Austria*; M.J. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; D. Thiaudiere,* Synchrotron SOLEIL, France*; D. Faurie,* LSPM-CNRS, Université Paris13, France*; P.O. Renault,* Université de Poitiers, France*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Brittle layers are often dominating the deformation behavior of flexible thin film multilayer structures, where the modulation period ($t_{brittle} + t_{ductile}$) as well as the modulation ratio ($t_{brittle}/t_{ductile}$) influence the extent of embrittlement [1].

In this work, a unique combination of atomic layer (ALD) and physical vapor deposition (PVD) is used to fabricate model multilayers of Al and Al2O3 and study fundamental deformation mechanisms in brittle/ductile multilayers on flexible polymer substrates (Polyimide, 50 µm, Upilex-S®). The ability of operating the ALD/PVD process without breaking vacuum opens up a wide range of otherwise unachievable modulation and thickness ratios. For Al2O3 layers thickness control with precision down to 0.1 nm can be achieved. The investigated individual layer thicknesses are 50nm for Al (PVD) and 0.1 nm – 10 nm for Al2O3 (ALD) layers. Constant oxide thicknesses (50/2/50/2…) and cross-sectional thickness variations (50/1/50/3…) are used to determine crack onset and propagation as a function of oxide layer thickness during *in situ* uni- and biaxial tensile experiments. Uniaxial fragmentation is studied *in situ* with scanning election microscopy (SEM) and focused ion beam cross-sectioning. This *in situ* approach avoids crack closure due to relaxation of the polymer substrate after unloading. Biaxial tensile experiments, performed at the Synchrotron Soleil (Paris, France), reveal the evolution of Al film stresses as a function of applied strain from X-ray diffraction and sin^2psi analysis. Digital image correlation is used to measure true strains on the thin film surfaces. All multilayer structures have good adhesion between individual layers as well as to the polymer substrate. Grain growth of Al is limited by the Al2O3 layers, allowing for easy discrimination of individual Al layers. The Al2O3 layers show increasing stretchability with decreasing film thickness, as a result of being extremely well defined and practically defect free. In biaxial tension, fracture of 8nm Al2O3 at 2.2% strain induces through thickness cracking. Crack onset correlates to a relaxation of the Al film stresses. In contrast, samples with 2nm oxide layers do not exhibit a pronounced crack pattern or stress relaxation within the tested strain regime.

The possibility to manipulate Al grain sizes by ultrathin ALD layers and the observed deformation behavior of the multilayers highlights the potential of the combined deposition technique for designing flexible thin film systems with improved strength and damage tolerance.

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3:20pm **TS5-2-MoA5 HiPIMS Metallization of Polymers: Titanium on PEEK***, **Aarati Chacko (aarati.chacko@empa.ch)**, K. Thorwarth, R. Crockett, U. Müller, H.J. Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Metallized polymers are becoming a prevalent part of our world, be it in electronic, medical or transport applications, and the performance requirements for these metal-polymer systems are becoming more demanding. Meeting these requirements means gaining a better understanding of plasma-polymer and metal-polymer interactions, both of which can occur in coating processes. High Power Impulse Magnetron Sputtering (HiPIMS) is a physical vapor deposition method characterized by a large fraction of ionized metal species in the coating discharge, which allows for a high level of control over film-forming species. This makes HiPIMS a method of choice to study and tailor the substrate-film interphase region responsible for ‘good’ and long-lived thin film adhesion. However, prior to HiPIMS metallization, the polymer must be ‘activated’ such as to raise its surface energy.

In this work, we evaluate the chemistry of a polymer surface before and after plasma activation using XPS, ToF-SIMS and ATR-FTIR. We then relate this to HiPIMS-metallized surfaces and interfaces using the same techniques. The test metal-polymer system for this study is titanium on Polyetheretherketone (PEEK), a system that has shown exemplary adhesion in a former study.

3:40pm **TS5-2-MoA6 Carbon Containing Multicomponent Alloys with High Hardness, Ductility and Corrosion Resistance**, ***León Zendejas Medina (leon.zendejas.medina@kemi.uu.se)***, Uppsala University, Sverige; *G. Lindwall,* KTH - Royal Institute of Technology, Sweden; *E.M. Pascalidou,* Uppsala University, Sweden; *L. Riekehr,* Uppsala University, Angstrom Laboratory, Sweden; *M. Tavares da Costa,* Uppsala University, Sweden; *S. Fritze,* Uppsala University, Angstrom Laboratory, Sweden; *K. Gamstedt,* Uppsala University, Sweden; *L. Nyholm, U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden

The development of fuel cells has created the need for new multifunctional materials for corrosive environments, as the cell components need to withstand the high potentials and low pH in the cell while simultaneously meeting a range of additional material requirements. In this study, we focus on finding coatings for corrosion protection of bipolar plates in PEM fuel cells. The high demands on the corrosion resistance must be combined with high mechanical stability and formability, to allow for roll-to-roll deposition followed by stamping to a customized pattern of flow channels. The coatings must, therefore, meet high demands on three points: corrosion resistance, hardness, and ductility.

To achieve this we have explored multicomponent materials deposited by magnetron sputtering. The customizable composition of these alloys, in combination with their typically high strengths, makes them excellent candidates for this study. The Cantor alloy, CrMnFeCoNi, was used as a starting point and modified in two ways. Firstly, by the addition of carbon at different concentrations, as this is a known way to overcome the hardness-ductility trade-off of thin films.[1] Secondly, some of the metallic elements of the base alloy were replaced to optimize the corrosion resistance.

The selection of new compositions was first explored by thermodynamic calculations using CALPHAD. The films were characterized using a range of techniques, from XRD, SEM, EDS, TEM, XPS to HAXPES and XAS at a synchrotron. Electrochemical measurements and mass spectrometry were used to understand the corrosion mechanisms. For the mechanical tests, nanoindentation was used to obtain mechanical parameters, while fragmentation tests on polyimide substrates were performed to investigate the strength distribution and specifically the fracture energy at crack onset.[2]

The addition of carbon to the alloy resulted in the amorphization of the material, starting from 6 at-% C, with no evidence of free carbon or a segregated carbide phase. The change in structure was accompanied by an increase in both corrosion resistance and hardness with increasing carbon, as shown by polarization experiments and nanoindentation respectively. The fracture energy of the coating almost doubled from 2.7 kJ/m for the carbon-free sample to 5.5 kJ/m for the sample at 11 at-% carbon. In the second part of the study, Mo and W were added to the alloy as a way to increase the corrosion resistance further. The effects on structure and material properties will be presented in more detail.

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Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B5-1-TuM

Hard and Multifunctional Nanostructured Coatings I

Moderators: Tomas Kozak, University of West Bohemia, Czech Republic, Vincent Moraes, Institute of Materials Science and Technology, TU Wien, Austria

8:00am **B5-1-TuM1 HPPMS (Ti,Al,Cr,Si)N - Influence of Substrate Bias and Pulse Frequency on Cutting Performance***, K. Bobzin, T. Brögelmann, N.C. Kruppe,* ***Marco Carlet (carlet@iot.rwth-aachen.de),*** Surface Engineering Institute - RWTH Aachen University, Germany

Machining of powder metallurgical high speed steel leads to thermal and mechanical loads, which cause damages such as abrasive and adhesive wear as well as oxidation of the tool. Due to the high hardness and thermal resistance of hard coatings, their application on cutting tools, is state of the art. In order to improve the tool lifetime and performance of the cutting process and to fulfill the increasing requirements in machining, the complex coating (Ti,Al,Cr,Si)N was developed. The embedding of the nanocrystalline (Ti,Al,Cr)N grains in an amorphous Si_3N_4 matrix is expected to result in advantageous properties in comparison to the monolithic coating (Ti,Al,Cr)N. The thermal resistance and elastic-plastic properties, for example, are enhanced. Furthermore, the addition of aluminum and chrome improves the oxidation resistance. The coating deposition was conducted in an industrial coating unit using a hybrid process consisting of direct current Magnetron Sputtering and High Power Pulsed Magnetron Sputtering (dcMS/HPPMS). Indexable inserts made of tungsten carbide were used as substrate material. By using this hybrid process, the advantages of HPPMS, such as a dense morphology and high indentation hardness, are combined with the higher deposition rate of dcMS. In this work, the influence of the bias voltage and the pulse frequency of the HPPMS cathodes during the hybrid process are investigated. On the one hand, the coating properties such as morphology, chemical and phase composition are examined by scanning electron microscope, electron probe micro analysis and X-ray diffraction. Additionally, the elastic-plastic properties are investigated by nanoindentation. On the other hand, the compound properties between the different coatings and the hard metal substrates are investigated. Scratch tests are carried out for this purpose. Finally, the coatings are tested by milling of powder metallurgic produced high speed steel 1.3345. Thereby the flank wear at the flank face is measured over the cutting length. In addition, damage analyses were subsequently carried out using scanning electron microscope. The coatings show a fine crystalline morphology with a cubic crystal structure and a smooth surface. The chemical and phase composition is only slightly influenced by the bias voltage and the pulse frequency. By increasing the pulse frequency and the bias voltage, it was possible to improve the surface quality and the compound properties on tungsten carbide. During the milling tests, the coatings prove to be suitable for improving the performance of cutting processes.

8:20am **B5-1-TuM2 Improved Ti–Al–Ta–N Coatings by Doping with LaB_6 and $CeSi_2$***,* ***Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at),*** *S. Kagerer,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The ever-growing need for improved mechanical and thermal resistance of protective coatings ask for their continuous enhancement and optimization. Recently, we showed that $CeSi_2$ or LaB_6 doping (<2 mol%) of well-known and used Ti–Al–N coatings leads to a considerable enhancement of their thermomechanical properties and oxidation resistance. The very positive effects of Ta for Ti–Al–N (with Ta/Ti ratios of ~1/3) are already well documented. Within this study, we further follow the alloying concept by preparing sputtered nitride coatings using $Ti_{0.45}Al_{0.45}Ta_{0.10}$ composite targets alloyed with 2 mol% $CeSi_2$ or 1 mol% $CeSi_2$ plus 1 mol% LaB_6. The thereby developed single-phase face centered cubic LaB_6 and $CeSi_2$ doped Ti–Al–Ta–N coatings outperform the previously studied Ti–Al–Ta–N coatings considerably.

In their as-deposited condition, the LaB_6+$CeSi_2$-doped $Ti_{0.44}Al_{0.42}Ta_{0.13}N$ coatings exhibit a hardness (H) of 37.8±1.5 GPa and an indentation modulus (E) of 498±14 GPa (on polished sapphire substrates). Although the hardness after vacuum-annealing at 1100 °C is with 30.7±1.8 GPa below that of the solely LaB_6-doped $Ti_{0.43}Al_{0.57}N$ (39.6±1.3 GPa), the oxidation resistance is simply outstanding. Even after exposure to ambient air at 900 °C for 25 h, the oxide scale thickness is only 800 nm. Thus, easily outperforming the solely LaB_6-doped $Ti_{0.43}Al_{0.57}N$, but also the already excellent oxidation resistance of $Ti_{0.44}Al_{0.44}Ta_{0.12}N$ and $Ti_{0.43}Al_{0.42}Ta_{0.14}Ce_{0.01}N$, which showed 2.4 and 1.9 µm thick oxide scales after 25 h exposure at 900 °C in ambient air, respectively.

Based on our results we can conclude that knowledge-based alloying design is a powerful tool to meet the ever-growing demands of highly-sophisticated applications.

8:40am **B5-1-TuM3 Impact of Nitrogen Deficiency on the Phase Transformation of (Ti,Al)N Thin Films at Elevated Temperatures*, Isabella Schramm (isabella.schramm@sandvik.com),*** Sandvik Coromant R&D, Sweden **INVITED**

The work presented here contributes to the understanding of the effect of nitrogen vacancies (nitrogen deficiency) on the phase transformations of cathodic arc–evaporated cubic (Ti,Al)N thin films at elevated temperatures. It experimentally confirms theoretical predictions by Alling *et al.* on the effect of N vacancies on the decomposition pathway of *c*- $(Ti,Al)N_y$ (y < 1) [1]. For the low/medium N deficient alloys (1 > y > 0.74), special attention is paid to the evolution of the beneficial spinodal decomposition into *c*-TiN and *c*-AlN, the detrimental formation of wurtzite AlN, and the potential application as hard coating in cutting tools [2, 3]. For the highly nitrogen-deficient solid solution cubic $(Ti_{1-x}Al_x)N_y$ (0.58 ≥ y ≥ 0.40) alloys, the decomposition pathway was investigated with an emphasis on the formation of Ti_4AlN_3 (MAX phase) in thin films via solid state reactions [4] .

Solid solution cubic$(Ti_{0.52}Al_{0.48})N_y$ thin films with low/medium N content (y = 0.93 to 0.75) show a substantial improvement of the thermal stability with lower nitrogen content. This results in a significant delay in the spinodal decomposition when increasing the amount of N vacancies, and consequently in a 300 °C increase in the age hardening temperature maximum [2, 3]. Highly N-deficient $(Ti_{1-x}Al_x)N_y$ thin films (y = 0.58 to 0.40) showed formation of *c*-TiN, w-AlN, and additional phases such as intermetallic and MAX phases (Ti_4AlN_3, Ti_2AlN, Al_5Ti_2, and Al_3Ti) during annealing. This is the first study showing the formation of Ti_4AlN_3 (MAX phase) in thin films via solid state reaction in nitrogen deficient cubic$(Ti_{1-x}Al_x)N_y$ alloys. A transformation mechanism from Ti_2AlN to Ti_4AlN_3 via intercalation of Al layers for N layers along Ti_2AlN basal plane is proposed [4].

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[2] I. C. Schramm et al., *Acta Mater.***119** (2016) 218.

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9:20am **B5-1-TuM5 Thermal Stability of Nanostructured TiAl(Si,B)N Coatings Deposited by HiPIMS with Positive Pulses*, Álvaro Méndez Fernández (alvaro.mendez@nano4energy.eu),*** *J.A. Santiago, I. Fernández-Martínez, A. Wennberg,* Nano4Energy SL, Spain*; M. Panizo-Laiz,* Universidad Politecnica de Madrid, Spain*; M.A. Monclús, J.M. Molina-Aldareguia,* IMDEA Materials Institute, Spain

In recent years, due to the advancement of high-speed machining (HSM), more demanding specifications on cutting tool coatings' hardness, chemical inertness materials, wear resistance, anti-abrasion, and also thermal and oxidation resistance are required. In order to overcome the detrimental effects associated with high temperatures during HSM on tool life and workpiece surface finishing, nanostructured coatings based on multilayers or nanocomposites have been proposed [1, 2]. In this work, we present nanostructured TiAlSiN and TiAlBN coatings deposited by HiPIMS with positive pulses. The optimization of the coatings was carried out by tailoring metal ion fluxes and energies. More energetic process conditions have been provided by adjusting height and width of positive pulses. Coatings' microstructure has been studied and related to HiPIMS parameters. The influence of Si and B from 0 to 15% at. content on stabilizing fcc-AlN phase results has also been studied. The formation of nanocrystalline grains (TiAlN) embedded in an amorphous phase (a-Si_3N_4, a-BN) provides enhanced toughness and wear resistance. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained in nanoscratch testing. High temperature nanoindentation and micropillar splitting were used to evaluate toughness and thermal resistance of the coatings.

[1] J. Musil, Surface and Coatings Technology 125 (2000) 322–330

[2] P. Mayrhofer et al., Progress in Materials Science 51 (2006) 1032–1114

9:40am **B5-1-TuM6 Development and Evaluation of Ultra-thick CrAlAgN Coatings for High Temperature Wear Resistance*, Jianliang Lin (jlin@swri.org),*** Southwest Research Institute, USA*; X.H. Zhang,* Southeast University, China*; R. Wei,* Southwest Research Institute, USA

There are needs to develop advanced coating systems to provide sufficient oxidation resistance and self-lubrication for high temperature tribological applications. One of the approaches is to dope traditional hard transition metal nitride coatings with solid lubricants, e.g. Ag, Au, which diffuses towards coating surface to provide lubrication at elevated temperatures. The long term performance of these coatings at high temperatures in ambient air is limited by the oxidation resistance of the coating and the rapid out diffusion of Ag, which is strongly affected by many factors, e.g. the fraction of the dopant and the density of the coating. It is expected that dense coating structure combined with increased coating thickness is helpful for achieving long term lubrication performance. In this paper, CrAlAgN coatings with thickness of 50 µm are deposited on steel and cement carbide substrates using high power impulse magnetron sputtering (HiPIMS) with hot filament assistance. The structure and composition of the coatings were first tailored to achieve a combination of good adhesion, high density and good mechanical strength. The Ag concentration in the coatings is about 8-10 at.%. For the coating performance, the oxidation resistance of the coating was studied in ambient air using isothermal test. The high temperature wear resistance of the CrAlAgN coating was evaluated using a high temperature pin-on-disc tribometer in the ambient air from 500 °C to 900 °C. It was found that the Ag content in the coating was well maintained up to 800 °C. The coefficient of friction (COF) of the coating sliding against a sapphire ball dropped from 0.77 to 0.3 while the wear rate increases as the temperature increases from 500 ºC to 800 ºC. At 900 ºC, although Ag rapidly depleted on the coating surface, the COF of the coating remained at 0.3 due to the formation of oxides. The coating exhibited robust wear resistance and showed a maximum wear rate of 7.98×10^{-5} $mm^3N^{-1}m^{-1}$ at 900 ºC after a travel length of 1018 m at 300 rpm sliding speed.

10:00am **B5-1-TuM7 On the Structure and Mechanical Properties of X_2BC Coatings Prepared by High Power Impulse Magnetron Sputtering at Different Temperatures**, ***Pavel Soucek (soucek@physics.muni.cz)**, M. Polacek, L. Zabransky, M. Stupavska, P. Vasina,* Masaryk University, Brno, Czech Republic

As the demands for the quality and speed of machining increase, the application of protective coatings on cutting or forming tools becomes increasingly important. Currently used protective coatings exhibit sufficient hardness, but this trait is often coupled with distinct brittleness. Recently a material combining seemingly mutually exclusive high hardness and moderate ductility has been theoretically predicted [1]. This material contains atoms of a transition metal (X), boron (B) and carbon (C) in X_2BC stoichiometry ordered in a complex high aspect ratio unit cell. The arrangement of the unit cell provides for high hardness of the material due to strong ionic-covalent bonds together with enhanced ductility owing to planes with only metallic bonds providing for plastic deformation of the cell. The properties of X_2BCs with different transition metals were calculated; however, experimental synthesis of only crystalline Mo_2BC was reported so far [2,3]. Apart from post-deposition annealing [3], HiPIMS was shown to be an effective way to prepare crystalline Mo2BC at industrially relevant deposition temperatures [2]. Other X_2BC such as W_2BC have been predicted to exhibit better mechanical properties compared to Mo_2BC, however, this comes at the cost of near-zero formation enthalpy predicting problems with the crystallization of this phase. On the other hand, systems such as Nb_2BC should exhibit lower hardness and ductility, but they should be significantly easier to be synthesized in the correct crystalline form.

This contribution reports on HiPIMS driven deposition of different X_2BC systems covering systems with low as well as higher negative formation enthalpies. Coatings prepared at ambient temperature as well as those prepared elevated temperatures > 700 °C will be compared. The correlation between the deposition parameters, the structure of the coatings and their mechanical properties will be shown.

This research has been supported by the project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of Czech Republic, project CZ.1.05/2.1.00/03.0086 funded by the European Regional Development Fund and GACR project 15-17875S.

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10:20am **B5-1-TuM8 Molecular Dynamics Simulations of Dislocation Confinement Effects in Core-Shell Nanostructures**, ***Drew Fleming (rofleming@AState.edu)**,* Arkansas State University, USA

Recently, a novel nanostructured surface composed of patterned arrays of Al/a-Si core-shell nanostructures (CSNs) has been shown to have a desirable combination of ultra-low friction (COF ~0.015 against a diamond counter face) and high durability. When subjected to instrumented nanoindentation, the individual CSNs show an unusual mechanical response characterized by almost complete deformation recovery, even beyond the elastic limit. Fundamentally, this mechanical behavior is hypothesized to be a result of a back-stress that develops in the confined Al core during compression loading that causes nucleated dislocations to retrace their paths or otherwise annihilate during unloading. In this study, molecular dynamics simulations are utilized to investigate the role that geometry and material properties play on the unique mechanical behavior of CSNs, with special attention paid to the core-shell interface structure, the core size/shape, and supporting stress calculations. Knowledge of the physical mechanisms that contribute to the deformation-resistant properties of Al/a-Si will potentially allow for control of dislocation dynamics in confined volumes and will further enable the development of novel material systems.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B8-1-TuM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

Moderators: Jon Tomas Gudmundsson, University of Iceland, Iceland, Tiberiu M. Minea, LPGP, Universite Paris-Sud, France

8:00am **B8-1-TuM1 Fabrication of AlTiSiN Nanocomposite Coatings with High Hardness and Low Internal Stress**, ***Zhengtao Wu (wuzhengtao5@163.com)**, Q.M. Wang,* Guangdong University of Technology, China*; G. Greczynski,* Linköping University, Sweden

Introducing a interfacial tissue phase such as amorphous SiN_x into AlTiN to fabricate AlTiSiN nanocomposite coating is wildly used to increase both hardness and oxidation resistance. However, the introduction of Si favors the growth of soft w-AlN. Based on ion flux incident investigations, both segregation and dissolution of Si and Al components in cubic Ti-N can be controlled by adjusting ion energy and ion-to-metal flux ratio. In this work, a HiPIMS/DCMS hybrid configuration is employed to fabricate AlTiSiN nanocomposite coatings with 7.6~10.3 at.% Si. Solid solution-type AlTiSiN coatings can be obtained with the maximum (Al+Si)/(Al+Ti+Si) atomic ratio of 0.67. The cubic coating exhibits a unique combination of high hardness and low internal stress.

8:20am **B8-1-TuM2 Measurements and Modeling of Residual Stress in Sputtered Nitride Films: Dependence on Growth Rate and Gas Pressure**, ***Zhaoxia Rao (zhaoxia_rao@brown.edu)**,* Brown University, USA, United States of America*; E. Chason,* Brown University, USA

Transition metal nitride films (e.g. TiN, ZrN and TaN) are often used as coatings because of their exceptional physical and mechanical properties. However, the residual stress induced during deposition can significantly alter their performance and reliability, leading to failure by cracking or buckling. Therefore, it is of critical importance to understand and control the stress evolution during deposition in nitride films. In this work, we investigate the stress evolution in nitride coatings deposited by physical vapor deposition. We report on the dependence of stress on the growth rate and gas pressure coupled with microstructure characterization. The experimental data is interpreted in terms of a kinetic model which includes the effects of film growth kinetics and energetic processes. The ultimate goal is the development of a model for predicting and optimizing stress in sputtered nitride films.

8:40am **B8-1-TuM3 Plasma Chemistry, Crystal Growth and Mechanical Properties of CrAlYN / CrN Nanoscale Multilayer Coatings Deposited by High Power Impulse Magnetron Sputtering**, ***Arutiun Ehiasarian (a.ehiasarian@shu.ac.uk)**, A.A. Sugumaran, P.Eh. Hovsepian,* Sheffield Hallam University, UK

Nanoscale multilayer coatings based on CrAlYN / CrN find applications in manufacturing, automotive components, power generation turbines and petrochemical industry. To perform well in these different environments, the coating microstructure must be tailored via the deposition process. In High Power Impulse Magnetron Sputtering (HIPIMS), which provides a high degree of ionisation of the metal flux and activation of the reactive gas, the relation between process parameters, microstructure and coating properties is not well understood.

We report on the effect of unbalancing magnetic field on species-dependent transport of metal and gas species to the substrate and its influence on film growth, texture formation and mechanical performance of nanoscale multilayer CrAlYN/CrN films. Experiments were carried out in an industrial-sized coater with four cathodes arranged in a closed magnetic field configuration, two of which were operated in HIPIMS mode and two in conventional sputtering.

In a balanced configuration, the magnetic null height was h_m = 12 cm and the volume of plasma near the target was the greatest and resulting in a high metal-to-gas ion ratio (J_{Me}+ / J_G+) observed by optical emission spectroscopy. The transport to the substrate, as measured by the ion saturation current (J_i), was the lowest due to the absence of magnetic field lines connecting to the substrate. The 4-micrometre-thick films exhibited competitive growth and a strong [111] texture evidenced by XRD due to the relatively low flux of dissociated nitrogen to the surface. SEM observations showed that the [111] texture resulted in dome-shaped column tops and clearly defined column boundaries where vacuum impurities were segregated.

As the magnetic field grew more unbalanced, the confinement volume decreased whilst transport to the substrate was enhanced, resulting in both J_{Me}+ / J_G+ and J_i reaching their maximum values. Weakly unbalanced fields with h_m = 10 cm provided sufficient flux of activated species to cause the grains to switch to [220] and then to [200] texture and allowing them to absorb impurities interstitially. This resulted in the elimination of dome-shaped morphology, drastic reduction in roughness, parallel column boundaries and increase in grain size.

Highly unbalanced fields (h_m = 4 cm) constricted the height of the confinement volume, reducing the ionisation of metal and dissociation of nitrogen as evidenced by the significant reduction in J_{Me}+ / J_G+. The loss of dissociation switched the texture back to a strong [111]. Grain sizes were significantly larger than for the balanced configuration due to a higher J_i.

The hardness and dry sliding wear rates are discussed.

9:00am **B8-1-TuM4 Fabrication of TiN Coatings using Superimposed HiPIMS and MF: Effect of MF Power and Synchronized Substrate Bias***, **Wun-Sian Yang (yang850620@outlook.com)**, J.-W. Lee,* Ming Chi University of Technology, Taiwan

The high power impulse magnetron sputtering (HiPIMS) technique has been widely studied due to its ability to generate high density plasma and high ionization rate for deposition of thin films with denser microstructure and good mechanical properties. However, the lower deposition rate of HiPIMS limits its application in industry. In this study, a superimposed HiPIMS and medium frequency (MF) power supply coating system was used to deposit TiN coatings under 50% target poisoning status controlled by a plasma emission monitoring (PEM) system. The MF power was adjusted to deposit TiN films under 50% target poisoning status with a synchronized substrate bias. Effects of MF powers and synchronized substrate bias on the deposition rate, microstructure, mechanical properties and adhesion of TiN thin films were investigated.

9:20am **B8-1-TuM5 Advantages of HIPIMS and Positive Kick Pulse***, **Jason Hrebik (jasonh@lesker.com)**,* Kurt J. Lesker Company, USA, United States of America

HIPIMS technology is currently one of the hottest thin film technologies in the industry. It's recent emergence into the R&D market has played a significant role in both advancements in the technology and general market interest for more potential applications. The ability to optimize HIPIMS to specific applications in order to realize it's full benefit is a key factor in both development and integration. Having control of parameter adjustment and being able to run processes at completely different parameter sets can result in significant performance improvements that are all application specific. This talk will define the critical parameters involved in HIPIMS, share data and review performance from different applications, and show how system integration has been enhanced to realize the benefits of the technology.

9:40am **B8-1-TuM6 The Effect of Metal Transition Dopents on Mechanical Properties TiBCN Based Coatings Deposited by CFUBMS-HiPIMS***, **Ihsan Efeoglu (iefeoglu@atauni.edu.tr)**,* Ataturk University, Turkey*; N.A. Aksakalli,* Atatürk University, Turkey*; B.G. Gumus,* Aselsan Inc., Turkey

Ternary and quaternary hard coatings based on carbonitrides of transition metals with amorphous matrix have many advantages; these are high hardness, adhesion, abrasion, oxidation and corrosion resistance. Functional properties can be gained by adding definite amounts of different transition elements to carbonitride based coatings**.** In this study, mechanical properties were investigated by adding Zr and Nb transition elements to TiBCN based coatings. Coatings were deposited on 4140 tool steel and silicone wafer using Taguchi experimental design. TiBCN-based coatings with high adhesion and dense microstructure were synthesized with CFUBMS-HiPIMS using Cr, Ti, TiB_2, Nb, Zr targets and Ar_2, N_2, C_2H_2 gases. Microstructural properties of the coatings were obtained from the coatings on the silicone wafer using SEM, XRD, XPS. Mechanical properties were obtained from the coatings on 4140 steel base with Microhardness and Scratch tests. The hardness and adhesions of TiBCN-based coatings, which were grown by adding Zr and Nb, respectively on Cr:CrN graded structure (~200nm) as the transition layer, were optimized depending on the process parameters. Scratch resistance test showed that the adhesion strength was changed as function of the Zr and Nb target negative bias voltages. The highest adhesion strength was obtained as Lc:95N at -800V with adding Zr. In case of the Nb adding, the highest adhesion strength was obtained as Lc:54N. The adhesion and microhardness test results indicated that bias voltage was the most effective coating parameter related to the critical load and hardness. As a result, it was found that adding a Zr instead of adding an Nb into the TiBCN coating significantly improved adhesion and hardness values of the coating films.

Coatings for Biomedical and Healthcare Applications
Room Royal Palm 1-3 - Session D2-TuM

Bio-corrosion, Bio-tribology and Bio-Tribocorrosion-Additive Manufacturing Impact

Moderators: Steve Bull, Newcastle University, UK, United Kingdom of Great Britain and Northern Ireland, Hamdy Ibrahim, University of Tennessee at Chattanooga, USA, Jessica Amber Jennings, University of Memphis, USA

8:00am **D2-TuM1 Sputtered Thin Film Systems As Anode Materials for Biodegradable Battery***, **Waseem Haider (haide1w@cmich.edu)**,* Central Michigan University, USA

The biodegradable battery is a promising choice to provide power to implantable medical devices. However, the anode material in such batteries, usually Mg or its alloys, suffer from parasitic hydrogen evolution and faster discharge kinetics that limits the lifet ime of these devices. In the pursuit of finding a better anode material, herein, the idea of combinatorial development is employed to fabricate a material having a good combination of corrosion resistance properties and discharge characteristics by exploring a wider $Mg_{100-x}Zn_x$ (0 < x < 50 at.%) system. Structural characterization of the Mg-Zn systems via X-Ray Diffraction manifests range of microstructures dictated by percent species and sputtering conditions. The corrosion investigation of the systems is done using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a conventional three-electrode configuration. Additionally, the discharge performance of the Mg-Zn anode systems is investigated, coupled with sputtered iron as the cathode in Phosphate Buffered Saline (PBS) solution as the electrolyte. The EIS and galvanostatic discharge tests reveal that discharge performances of the anode materials can be effectively tailored via a prudent design of alloy composition and microstructure.

8:20am **D2-TuM2 Corrosion Resistance of Cerium Oxynitride Thin Films for Use in Implants and Prothesis***, G.C. Numpaque Rojas, **Brian Felipe Mendez Bazurto (bfmendezb@unal.edu.co)**, G.I. Cubillos Gonzalez,* Universidad Nacional de Colombia - Bogotá, Colombia

Due to its chemical properties and high corrosion resistance, the cerium oxide has been widely used in aeronautical and naval industry as coating of aluminium alloys [1, 2]. The CeO is deposited mainly by suspended techniques, clean high vacuum techniques deposit of cerium oxide has not been studied since being a pyrophoric solid, and the films obtained are porous and easily delaminated. In this work, we determine the conditions of pressure, temperature and nitrogen flow to deposit homogeneous films on stainless steel AISI 316L surgical grade and corrosion resistance cerium oxynitride was evaluated. CeO_xN_y/ZrO_xN_y coatings were obtained from a 4 in. ×1/4 in. Zr-Ce (99.9%) target (Stanford Advanced Materials). RF reactive sputtering technique, in atmosphere of N_2/O_2, with a flow ratio $\Phi N_2/\Phi O_2$ of 20 was used. The structural analysis carried out through X-ray diffraction (XRD) showed that the CeO_xN_y/ZrO_xN_y coatings had a cubic polycrystalline structures preferencial growth for CeOxNy, while ZrO_xN_y is amorphous. The SEM analysis evidenced that the films grew with homogeneous morphology and exhibited a columnar growth. Corrosion resistance evaluated from the potentiodynamic polarization curves in Hank's solution [3], showed that the coating increases the corrosion resistance of steel by two orders of magnitude. CeO_xN_y/ZrO_xN_y coatings deposited on surgical grade stainless steel could be a promising candidate to be used in osteosynthesis processes.

8:40am **D2-TuM3 Crevice Tribocorrosion of Additively Manufactured Stainless Steels in Ringers Solution**, *Mobin Salasi (mobin.salasi@curtin.edu.au)*, *E Hornus,* Curtin University, Western Australia, Australia*; C Schulz,* University of South Australia*; M Salem,* Ecole de Mines Albi, France*; Z Quadir, W Rickard,* Curtin University, Western Australia*; P Lours,* Ecole de Mines Albi, France*; M Iannuzzi,* Curtin University, Western Australia **INVITED**

Additively manufacturing (AM) of stainless steels facilitates the fabrication of custom-built components for biomedical applications. Parts and components can be three-dimensionally modelled and designed, followed by production on-demand, specific to the patient and surgical requirements.

Among the various AM techniques, the powder-bed selective laser melting (SLM) method is a widely used technique to produce a large variety of engineering alloys. Localised melting of the metallic powder during SLM and resulting possible residual stresses, however, can distort the microstructure of manufactured parts and is usually associated with different levels of porosity. When exposed to physiological conditions, the components must present excellent crevice and tribocorrosion resistance. While crevice and tribocorrosion of wrought 316L stainless steel have been extensively studied, there is little and contradictory information about AM fabricated 316L which requires further research.

Although implant materials used in-vivo usually undergo a combination of chemo-mechanical damage mechanisms, the main issues are crevice and tribocorrosion. A recent investigation by the Curtin Corrosion Centre (CCC) revealed that SLM-fabricate 316L has a complex three-body tribocorrosion behaviour in 0.6 M NaCl solution when compared to that of wrought specimens. Additionally, a custom test rig was developed by CCC researchers to elucidate the tribocorrosion behaviour of surgical-grade stainless steels in a dynamic crevice geometry. It was found that the combined action of interrupting movement (wear) and crevice formation reduced the localized resistance of stainless steel implants due to the effect of passive film disruption under a two-body tribo-contact.

This study first reviews the state-of-the-art on SLM-fabricated 316L corrosion performance. The pitting, crevice, and tribocorrosion behaviour of these alloys are then discussed. The effects of porosity on dynamic crevice corrosion of SLM fabricated 316L in Ringer's solution are compared to wrought samples, based on the results of an original investigation. Characterization methods such as scanning electron microscopy focused ion beam, and transmission electron microscopy are used to gain a better understanding of the combined action of crevice and tribocorrosion.

9:20am **D2-TuM5 In Vitro Degradation of ZrO_2 Coated Magnesium Alloys**, ***Benjamin Millan (bmillan@ciencias.unam.mx)***, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; O. Depablos-Rivera,* Universidad Nacional Autónoma de México, México*; P. Silva-Bermudez,* Instituto Nacional de Rehabilitación Luis Guillermo Ibarra, Mexico*; S.E. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, México

The main limitation of the Mg-based alloys as a biodegradable implant material for bone repair application is

their rapid corrosion rate, especially in solutions containing chloride, including human body fluid and blood plasma. The initial fast degradation lead to the production of H2 bubbles and pH changes that affect the surrounding tissue. The long-term degradation of Mg-based implant materials induces a loss of their mechanical strength and integrity before the recovery of newly formed bone.

Different strategies have been applied to improve the corrosion resistance of Mg-based alloys, and some s urface modifications, such as the use of thick polymeric or ceramic-based coatings, have proven to be effective.

In this work, we evaluated the effect of dense but thin ZrO_2 coatings on optimized MgZnCa alloys. ZrO_2 coatings were chosen due to their excellent biocompatibility, good corrosion resistance and potential to induce osteoblasts differentiation.

The ZrO_2 coatings were deposited on 2 x 2 cm^2 MgZnCa pieces by reactive magnetron sputtering under Ar/O_2 atmosphere, at a deposition pressure of 4 Pa and RF power of 200 W. Thicknesses between 100-300 nm were evaluated. The in vitro corrosion of the uncoated and coated samples was evaluated by measurement of the open circuit potential at long immersion times, potentiodynamic polarization and electrochemical impedance spectroscopy in a 0.89 wt% NaCl solution. A reduction in the corrosion current density of 50% was achieved, without observing significant changes in the corrosion potential. The electrochemical response was compared to the degradation rate measured by immersion tests.

9:40am **D2-TuM6 Prognosis of Hip Implant Tribocorrosion Processes: Acoustic Emission Technique**, ***Christine Lee (clee146@uic.edu)***, *L. Zhang,* University of Illinois at Chicago, USA*; D. Morris,* University of Illinois at Chicago, Rockford, USA*; KY. Cheng,* University of Illinois at Chicago, USA*; M. Barba,* Orthoillinois, Rockford, USA*; D. Bijukumar,* University of Illinois at Chicago, Rockford, USA*; D. Ozevin,* University of Illinois at Chicago, USA*; M.T. Mathew,* University of Illinois at Chicago, Rockford, USA

Total hip replacements (THR) are becoming increasingly common in the United States (332K/year in 2017) to relieve pain and improve the mobility of those that are affected by osteoarthritis, ankylosing spondylitis, or injury [1]. However, complications induced by biological response caused by introducing biomaterials into the human body may lead to implant failure. Implants are prone to tribocorrosion, or material degradation due to friction and corrosion, that may lead to THR complications. Unfortunately, few strategies to noninvasively diagnose early-stage complications are reported in literature, leading to implant complications being detected after irreversible damage. Therefore, by using Acoustic Emission (AE), the status of an implant can be continuously monitored, and the abnormalities are identified by correlating them to AE activity prior to severe damage [2]. The model utilized a hip simulator [3] which can maintain the physiological conditions closer to in vivo. Located in this chamber exists a pin-on-ball schematic that mimics the head-cup interface of a hip implant. The ball was made of Alumina, and two pin materials were tested in the experiment: Cobalt Chromium Molybdenum (CoCrMo) and Titanium alloy (Ti6Al4V). The experiment consisted of monitoring friction, corrosion, and acoustic emission data with a specific protocol that consisted of human activities, such as rest/sleep, stand and walk (3 times 900 steps) with a total duration of 7,500 seconds. The results showed that the electrochemical potential of the titanium sample was higher throughout the experiment than the CoCrMo sample during all cycles of standing, walking, and sleeping. Organic substances were found on the surface of both samples to suggest the formation of protective films (oxide or tribolayer). The passivation layer may have aided in the exponential increase in potential in the titanium samples. During the walking cycles in the experiment, the potential for both CoCrMo and Ti6Al4V samples dropped, indicating that mechanical exposure negatively impacted the tribocorrosion behavior [2]. In addition, in both samples, the absolute energy detected with acoustic emission displayed higher fluctuations during applications of load and friction. This infers the correlation between worsening structural degradations of a sample with increasing AE stress waves. Our model proposes an innovative method to continuously monitor the performance of a hip implant and noninvasively detect complications at early stages. Therefore, acoustic emission can be utilized to identify the deformations and failure modes of implant materials caused by tribocorrosion.

10:00am **D2-TuM7 A Bio-Tribocorrosion Appraisal of a Dual Layer PVD Coated CoCrMo Alloy Tribopair**, *A. Mazzonello, R. Chetcuti,* University of Malta, Malta*; P.A. Dearnley,* Boride Services Ltd, UK*; J. Buhagiar,* ***Bertram Mallia (bertram.mallia@um.edu.mt)***, University of Malta, Malta

CoCrMo alloys have been widely applied for the protection of bearing surfaces in orthopaedic implants owing to their optimal mechanical properties and excellent corrosion resistance. However, several concerns on the synergy of corrosion and mechanical wear have arisen since this has been identified as the prime source of implant degradation that stimulates adverse reactions in the human body. Consequently, the aim of this work was to investigate the tribocorrosion performance of a surface engineered CoCrMo alloy in a corrosion-wear environment exposed to simulated body fluids. A dual layer PVD coating consisting of a CrN layer on top of a CoCrMo(C) S-phase underlayer (CrN/S) was investigated. The corrosion-wear response of the uncoated CoCrMo discs versus uncoated CoCrMo balls tribopairs and coated CrN/S tribopairs was studied using a reciprocating sliding tribotester in Ringer's solution and in diluted Foetal Bovine Serum (FBS) solution under passive potential conditions.

Results have shown that, while abrasive damage was observed for the uncoated tribopairs due to third body wear, CrN/S has successfully mitigated oxidation-related material losses and catastrophic-type failures in all corrosion-wear tests. For tests performed in diluted FBS, the effect of proteins resulted in the formation of a bio-tribolayer with optimal lubricious properties, which acted as a barrier to charge transfer, and improve d the corrosion-wear resistance. This renders the application of dual layer CrN/S to CoCrMo metal tribopairs a potential solution to existing concerns of metal implants, deserving of further investigation.

10:20am **D2-TuM8 In Solution, A New Representation to Link the Corrosion Degradation Consistent with Wear: Smooth and Hard Coatings are Well Discriminated.**, ***Jean Geringer (geringer@emse.fr)***, *A. Boyer,* Mines Saint-Etienne, France*; H. Ding, V. Fridrici, P. Kapsa,* Ecole Centrale de Lyon, Ecully, France*; T. Tayler, L. Semetse, P.A. Olubambi,* University of Johannesburg, South Africa

Prosthetic hip joints are nowadays common issues due to people aging. Restoring gait is a heath issue from the patient benefits and the economical one. Due to taper junction manufacturing process some corrosion and fretting corrosion (friction under small displacements, lower than 100 micrometers) issues are appearing concerning the implants lifetime. In this study we are suggesting a not well used representation concerning the efficiency of connections under fretting corrosion solicitations. The usual wear volume vs. Dissipated energy might be investigated but highlighting protective coatings is failing. Wear volume vs. open circuit potential drop (first hundred seconds of fretting) is classifying clearly every coating on metallic material. However another issue is coming related to stick/slip during the fretting process. Finally the wear volume is replaced by the A ratio, dissipated energy over total energy. When some stick, even under high normal load, is occurring, A ratio is decreasing and there is no relative displacement between materials in contact. Various combinations of materials/coatings have been investigated and the evolutions seem evoluate consistently. Some improvements are needed to confirm the tendency.

10:40am **D2-TuM9 Anodizing on 3D Printed Mesh Structure for Bone Reconstruction**, ***Yong-Hoon Jeong (yonghoonj186@kbiohealth.kr)***, *T.G. Jung, J.W. Yang, K.M. Park,* Osong Medical Innovation Foundation, Republic of Korea*; S.H. Woo, T.H. Park,* Medyssey Co. Ltd.

Three-dimensional Additive manufacturing (3D-printing) is already well established within engineering technology which is popularly utilized for rapid prototyping, small series, and unique component manufacturing with specific 3D structures. Recently, a demand of 3D-printing in medical application has been increased, the ability to fabricate complex biomedical devices is powerful with patient customized for the restoration of anatomic defects and the reconstruction of complex organs. 3D-printing also allows to design various mesh structures with computer software aid which act to reduce the elastic modulus of bone defect implant. Regarding with surface topology of implant, it has required to be more compatible to promote bone bonding or formation with their structure, anodization is one of bio-active modification method can fabricate nano pores on micro level of 3D-printed structure. Therefore, the purpose of this study was to investigate the material characteristics of 3D printed implant by effect of their mesh structure and surface modification by anodization.

The Arcam® EBM (electron beam melting, Mölndal, Sweden) system used with Ti-6Al-4V-ELI (extra low interstitial) medical-grade powder in this study for the manufacture of specimens. To produce structured, three-dimensional solids or mesh arrays defined with different density by MATERIALISE and 3-Matic/MAGICS (www.materialise.com) software. The surface modification was performed by anodization at 120~200 V in H3PO4 electrolyte on 3D-printed mesh structure. The surface morphology and 3 dimensional stereology were analyzed by field emission-scanning electron microscopy (FE-SEM) and micro-computed tomography (μCT) to make sure mesh shape and size, and potentiodynamic measurements were carried out in saline solution to verify their corrosion characteristics with In-Vitro body condition, respectively.

As a preliminary result, 3D-printing mesh structure could be effected for the formation degree of oxide porous surface, higher density of mesh structure showed more corrosion resistance at In-Vitro body potential (300 mV) and more stable anodic polarization curves at region of passivation current.

Acknowledgement: This research was supported by a grant of the Korea Health Technology R&D Project through the Korea Health Industry Development Institute (KHIDI), funded by the Ministry of Health & Welfare, Republic of Korea (grant number HI18C1224).

Keywords: 3D-printing, Ti-6Al-4V, Lattice structure, Anodization, Corrosion

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room San Diego - Session E1-1-TuM

Friction, Wear, Lubrication Effects, and Modeling I

Moderators: Nazlim Bagcivan, Schaeffler AG, Germany, Tomáš Polcar, University of Southampton, UK, Manel Rodriguez Ripoll, AC2T Research GmbH, Austria

8:00am **E1-1-TuM1 Efficiency Improvement Along the Stribeck Curve through Pvd Coatings - From Minimum Quantity Lubrication to Full Fluid Lubrication**, ***Tobias Brögelmann (broegelmann@iot.rwth-aachen.de)***, *K. Bobzin, C. Kalscheuer, M. Welters, M. Thiex,* Surface Engineering Institute - RWTH Aachen University, Germany **INVITED**

Legislative regulations to minimize greenhouse gas and pollutant emissions and growing environmental awareness are forcing the automotive sector to increase the energy efficiency of the powertrain and seek solutions for sustainable mobility concepts. The application of physical vapor deposition (PVD) coatings on tribological components combining a low coefficient of friction with a low wear rate has been established since the mid-1990s with the introduction of diamond-like carbon (DLC) coatings in the mass production of diesel injection systems. Since then, the process and material development, in addition to the technological progress in machine equipment has enabled PVD coatings to improve the tribological performance along the entire Stribeck curve from minimum quantity lubrication to full fluid lubrication.

In this talk, highlights of application-oriented process and material development for rolling/sliding contacts from basic research to particular coating development for specific components of industrial partners will be presented. At low lubricating film thickness under periodic or continuous operation in boundary or mixed lubrication, the interaction between the coating and the lubricant dominates the performance of the coated component. Triboactive and tribocatalytic CrAlMoCuN coatings are developed, which form tribochemical reaction layers consisting of elements provided by the coating and by the additives of the lubricant. Pulsed high performance plasmas such as high power impulse magnetron sputtering (HiPIMS) and cathodic arc evaporation (CAE) using industrial-scale coating machines are applied for coating deposition on complex shaped components such as spur gears or chain pins. Nitride hard coatings CrAlN+Mo:S and DLC coatings a-C:H:Zr with solid lubricant properties are presented as a promising alternative. Under tribological loads, solid lubricants are formed in situ so that the friction-reducing effect of the additives can be successfully integrated into the coating. This enables the use of novel lubricants, e.g. water-based lubricants with low viscosity for e-mobility. Even under full fluid lubrication, PVD coatings contribute to friction reduction despite the complete separation of the functional surfaces by the load-bearing lubricating film. Experimental investigations of DLC coated rolling contacts and numerical simulations of the TEHL temperature distribution are conducted to explain the decisive influence of the thermophysical properties of the coatings on the heat transfer. The resulting increase in the TEHL contact temperature leads to a decrease in the effective viscosity of the lubricant and a reduction in fluid friction.

8:40am **E1-1-TuM3 From Surface to Sub-surface Contributions to Friction at the Nanoscale**, *C Menezes,* UFSC, Brazil*; V Pavinato, L Leidens,* UCS - Caxias do Sul University, Brazil*; F Echeverrigaray, F Alvarez,* UNICAMP, Brazil*; A Michels,* ***Carlos Figueroa (carlos.cafiguer@gmail.com)***, UCS - Caxias do Sul University, Brazil

The friction phenomenon is a complex manifestation of the nature originated in energy dissipation events owing to the lost work of non-conservative forces. In spite of different surface mechanisms describing the friction phenomenon at the nanoscale, the involved energy in such surface events is not enough to explain friction forces in wearless regime. Indeed, phononic, electronic and magnetic effects are not capable of providing a sufficient energy to explain friction forces. Thus, new contributions are mandatory to reach a satisfactory energy balance among friction mechanisms and lost work by non-conservative friction forces. The aim of the work is to establish sub-surface contributions to friction at the nanoscale. In this study, we report the friction forces at the nanoscale on iron nitride and oxide by nanoindentation followed of unidirectional sliding (NUS) and friction force microscopy (FFM). Two different experimental setups are reported. Moreover, the sub-surface elastic deformation due to indentation was modeled following the classical contact theory from Hertz by using the ABAQUS software. Firstly, the elastic deformation leads to reach elastic energies in the order of lost work of friction forces. Secondly, the sub-surface contributions seem to be more important than the surface contributions to friction at the nanoscale. We discuss these surface and sub-surface mechanisms by dissipation effects associated with surface phonon coupling and sub-surface energy-releasing due to elastic energy dissipation.

9:00am **E1-1-TuM4 Computer Simulations of FCC Alloys Subjected to Dry Sliding as Basis for a Near-Surface Deformation Mechanism Map**, ***Stefan Eder (stefan.eder@ac2t.at)***, *M. Rodríguez Ripoll, U. Cihak-Bayr,* AC2T Research GmbH, Austria; *D. Dini,* Imperial College London, United Kingdom of Great Britain and Northern Ireland; *C. Gachot,* TU Wien, Austria

We study the microstructural response of five FCC CuNi alloys subjected to sliding with large-scale molecular dynamics simulations. The initial grains measure approximately 40 nm in diameter to ensure that plasticity is not dominated by grain boundary sliding, so our polycrystalline aggregate exhibits dislocation pile-up, twinning, and grain refinement analogous to polycrystals with much larger grains. We analyze the depth-resolved time development of the grain size, shear, twinning, and the stresses in the aggregate to produce a deformation mechanism map for CuNi alloys. This map captures the predominant microstructural phenomena occurring for a given composition and normal pressure, and will aid engineers in optimizing materials/surfaces to work within a required operating range. We compare tomographic visualizations of our atomistic model with focused ion beam images of the near-surface regions of real CuNi alloys that were subjected to similar loading conditions.

9:20am **E1-1-TuM5 Multi-sensing Nano-wear with Electrical Contact Resistance and Friction Measurement**, ***Ben Beake (ben@micromaterials.co.uk)***, Micro Materials Ltd, UK; *T.W. Liskiewicz,* Manchester Metropolitan University, UK; *A.J. Harris,* Micro Materials Ltd.; *S.J. McMaster, A. Neville,* University of Leeds, UK

Wear begins at the asperities but typically the contact pressures acting on these are unknown in a standard macro-scale tribological test. In contrast, testing at the nano-/micro-scale (“single asperity tribology”) enables the onset of wear to be studied conveniently and correlations with friction forces investigated to aid the design of surfaces with improved wear resistance.

Reciprocating contacts occur in a wide variety of practical wear situations including hip joints and electrical contacts. In optimising materials for improved durability in these contacts it is important that the contact conditions (e.g. sliding speed) can be reproduced. Hence, a capability for rapid high-cycle linear reciprocating nano-scale wear tests has been developed (NanoTriboTest) with automatic recording of friction loops, cumulative energy dissipation and electrical contact resistance. The design has high level of lateral rigidity providing the necessary stability to perform nano- or micro-scale wear tests for extended duration (e.g. several hours, up to 300 m sliding).

In this study, high cycle, up to 40 mm long track length reciprocating nano-wear tests have been performed on multilayer DLC coatings, and the biomedical alloys Ti6Al4V and 316L stainless steel. Stainless steel showed ductile response throughout the load range but an abrupt transition to higher friction and fracture-dominated wear after ~20 cycles occurred on Ti6Al4V. Friction and wear evolution in the test was compared to that in nano-fretting (gross slip) and nano-scratch (unidirectional) tests [1-3].

Improved detection of the onset of wear and the subsequent failure mechanisms was achieved by a multi-sensing approach where changes to electrical contact resistance were shown to correlate directly with the measured friction. Nano-wear tests of noble metal-noble metal contacts (Au-Au and Ag-Ag) showed much longer endurance than gold vs. steel contacts although occasional isolated failures were observed in 35000 cycle tests.

[1] Short note on improved integration of mechanical testing in predictive wear models, TW Liskiewicz et al, Surf Coat Technol 237 (2013) 212.

[2] Comparison of nano-fretting and nano-scratch tests on biomedical materials, BD Beake and TW Liskiewicz, Tribol Int 63 (2013)

[3] Development of DLC coating architectures for demanding functional surface applications through nano- and micro-mechanical testing, BD Beake et al, Surf Coat Technol 284 (2015) 334-343.

9:40am **E1-1-TuM6 PTFE Coating on Nanoscale Polymer Structures: Role in Tribological Characteristics**, *P. Pendyala,* Hanyang University, Republic of Korea; *H.N. Kim,* ***Eui-Sung Yoon (esyoon@kist.re.kr)***, Korea Institute of Science and Technology, Republic of Korea

Nanoscale tribology is complex due to the role of material and surface size effects. Studying and engineering nanoscale tribological surfaces was difficult due to limitations in generating surfaces with well-defined chemistry and geometry. In this work, we study the role of nanoscale polytetrafluoroethylene (PTFE) coatings in controlling the adhesion and friction characteristics of well-defined nanoscale cylindrical, mushroom-shaped, and hierarchical tribological surfaces. The nanoscale structures were generated on polystyrene (PS) and polymethylmethacrylate (PMMA) thin films using capillary force lithography and nano-drawing techniques. A 20 nm thick PTFE coating was applied to the patterned structures using plasma enhanced deposition process. We studied the relative importance of coating and structure in tribology. We show how the PTFE coating primarily influences tribology by controlling the interaction volume and stiffness of the contact by altering the van der Waals and capillary forces. Overall, we show that real contact area dominated by surface coating curvature, surface coating and pattern density predominantly affected adhesion. While effective lateral stiffness dominated by structure, surface coating and capillary forces affected friction. Importantly, we discovered a correlation between nanoscale adhesion and friction for our patterned surfaces. A master curve in the graph of adhesion vs. friction that defines this correlation was dependent on the effective lateral stiffness of the contact. Our correlation results brought out the role of coatings in controlling tribology at nanoscale.

10:00am **E1-1-TuM7 Analysis of Coating Layers and Defects Using Atomic Force Microscopy**, ***Stefan Kaemmer (stefan@parksystems.com)***, *G.M. Mendoza,* Park Systems Corporation, USA

Coatings provide important roles in industrial environments. They can protect the underlying material from harsh environments or improve the tribological properties of machine parts as an example [1]. Even small defects or imperfections can act as a failure center. The inspection of the coating quality becomes therefore an important step during the development and production of the coating process.

Atomic Force Microscopy (AFM) is a well-established technique for analysis of surface morphology with sub-nanometer resolution. It has become a routine tool in material research and semiconductor manufacturing for quality control of surfaces. For standard morphological analysis, the AFM is generally operated in Non-Contact mode, which allows for non-destructive, quantitative, three-dimensional analysis of the surface topography (figure 1). However, AFM does not only allow for the morphological analysis of surfaces. By combining AFM with other techniques information like the frictional properties, electrical conductivity, surface charges, magnetic properties etc. can be extracted and mapped with nanometer resolution as well. A recent development leverages the AFM resolution capabilities and enables the determination of the nanomechanical properties, like modulus and adhesion. This so called ‘PinPoint” mode is based on fast force-distance curves that are executed at each pixel [3]. Figure 2 depicts a basic force curves and some of the information that can be extracted.

We will discuss applications and highlight how PinPoint AFM can help to determine the difference between a scratch before and after coating.

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Comprehensive Materials Processing, Vol 7, 191-241

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10:20am **E1-1-TuM8 Mo-Se-N Low-Friction Coatings Prepared by High Target Utilisation Sputtering (HiTUS) Technology**, ***Tomáš Hudec (t.hudec@soton.ac.uk)***, University of Southampton, UK; *V. Izaii, L. Satrapinskyy, T. Roch,* Comenius University in Bratislava, Slovakia; *T.H. Huminiuc,* University of Southampton, UK; *M. Mikula,* Comenius University in Bratislava, Slovakia; *T. Polcar,* University of Southampton, UK

Solid lubricant thin films produced by physical vapour deposition (PVD) techniques represent modern approach to reduce friction in highly demanding situations where traditional liquid lubricants cause problems (environmental, excessive costs, frequent maintenance) or cannot be used at all (vacuum, extremely high/low temperatures and contact pressures). Transition metal dichalcogenides (TMDs), such as MoS_2 and WS_2, are the most known and applied solid lubricant coatings; however, its use is limited by environmental sensitivity and low hardness. Metal selenides, such as $MoSe_2$, are much less studied than sulphides although it has been shown they have comparable or even better self-lubricant properties and lower sensitivity to humidity than sulphides, which is for instance of particular interest for space components that require testing or storage periods on Earth.

To improve mechanical and tribological properties, in the presented work, $MoSe_2$ coatings were doped with nitrogen, denoted as Mo-Se-N. All coatings were prepared by state-of-the-art High Target Utilisation Sputtering (HiTUS) technology. The biggest advantage of HiTUS to the conventional magnetron sputtering is the possibility to independently control plasma density and sputtering ion energy due to the remote plasma source. Moreover, to this date, Mo-Se-N coatings have never been reported before.

$MoSe_x$ films with Se/Mo ratio 1.9 outperformed MoS_x with the average COFs in the range of 0.1 – 0.025 for loads 2 - 45 N. Mo-Se-N films were prepared with nitrogen contents in a range of 11 to 40 at. %. As expected, pure $MoSe_2$ coatings exhibited extremely low values of hardness ~ 0.5 GPa. Hardness increased with N doping up to 8 GPa. Friction behaviour in humid air was evaluated using a ball-on-disk tribometer. Globally, the doping with N resulted in hardness of Mo-Se-N films one order of magnitude higher and wear rate two orders of magnitude lower than in an undoped one, keeping the friction coefficient at the same level or even lower. These coatings showed remarkable friction coefficients in humid air from 0.2 to 0.015 with loads from 2 to 45 N. TEM images confirmed that the excellent friction properties were attributed to the formation of a thin molybdenum diselenide tribofilm on the top of the wear track. We can conclude that emerging HiTUS technology represents a very promising way of depositing low-friction coatings even onto the temperature sensitive bearing steels.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific Salon 2 - Session G2-TuM
Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications

Moderators: Etienne Bousser, Polytechnique Montreal, Canada, Satish Dixit, Plasma Technology Inc., USA, Tetsuya Takahashi, Kobe Steel, Ltd., Japan

8:00am **G2-TuM1 Enhancing TiAl Oxidation Resistance at High Temperature: A Challenge for the Aerospace Industry***, **Marjorie Cavarroc (marjorie.cavarroc@safrangroup.com),*** Safran Tech, France **INVITED**

The 21st century is one of major importance for the aerospace industry because of the important increase in flight demands from the Asian market. Evaluated at 3.8 billion in 2016 by the International Air Transport Association (IATA), the number of airplane passengers is predicted to double by 2037. To supply to the rising demand, to mitigate operation costs, and to reduce the environmental impact of such air traffic, aircraft designs are pushed to technological limits. This is particularly true for the engines, whose efficiency is dictated by their thrust-to- weight ratio. Judicious weight reduction combined with the elevation of engines' operating temperatures will therefore improve their efficiency.

In this context, titanium aluminides (TiAl) attract immense interest because of their low weight and their high specific strength at high temperature compared to conventional titanium or nickel alloys. This allows for the manufacture of lighter blades and the reduction of the mass of other components.

TiAl are intermetallic compounds. Their ordered structure and strong atomic bonds give them good mechanical properties and good oxidation resistance. These properties are almost of the same order of magnitude as the ones of Nickel-based alloys. They also have a lower density than Nickel based alloys (3.9 to be compared to 8.3), that could allow a significant weight reduction of the engines. However, intermetallic compounds are known to be brittle and to have low toughness.

Presently, TiAl is used for application parts exposed to temperatures lower than 750°C. Above this temperature, mechanical properties are severely reduced. The range of temperature at which severe oxidation appears is between 750 °C and 850 °C, depending on the alloy.

The oxygen embrittlement and the ductility loss of TiAl alloys are commonly considered as a subsurface effect due to the uptake of oxygen into the $\alpha 2$ phase. The γ phase has a low oxygen uptake, can act as a barrier against oxygen and has better mechanical properties than the $\alpha 2$ phase.

Up to now the most promising approach to protect γ-TiAl-based alloys against environmental degradation at temperatures as high as 1000 °C is surface engineering. By decoupling bulk and surface properties, it allows the protection of various types of materials against environmental degradation without impacting their carefully designed composition.

A large study, including PVD, PECVD and electrochemical deposition, was performed in order to find a way to protect efficiently TiAl at high temperature. A review of this study will be presented and performances of the different coatings will be compared.

8:40am **G2-TuM3 Mechanical and Optical Properties of Si doped ta-C Anti-reflective Coatings for Satellite Solar Cell Applications***, **HoeKun Kim (ndkim2@naver.com)**, S.Y. Lee,* Korea Aerospace University, Republic of Korea

The improvement of radiation resistance in the space solar cells(SC) is still of great importance. The main reason for space SC efficiency degradation under the action of solar wind is a reduction in carrier concentration of the base region, so that the space SC must be protected by coverglass with good protective and optical properties. However, it is very important to reduce SC weight, especially for interplanetary application. To achieve this aim relatively thin protective coating should be applied. For the decade, it has been shown that diamond-like carbon (DLC) coatings are very promising anti-reflection (AR) and protective coatings for solar cell. The advantages of DLC include high chemical stability, radiation stability and high hardness with the possibility of changing their optical properties by varying the deposition conditions. Especially, tetrahedral amorphous carbon (ta-C) coatings with extremely high hardness, smooth surface, excellent wear resistance, and better thermal stability than DLC have been paid much attention to an alternative protective coating materials. Additionally, optical properties of the ta-C coating could be improved by various metals doping. In this study, various contents of Si were doped in the ta-C coating to improve the mechanical and optical properties of the ta-C coatings. Filtered cathodic vacuum arc (FCVA) and sputter hybrid system was co-deposited to synthesize the metal doped ta-C coating. Microstructure of the Si doped ta-C coatings showed a columnar "moth-eye" structure that is especially useful for reducing reflections and increasing transmission between materials by the roll of light absorption. Raman spectroscopy analysis showed that all the coatings had high sp3/sp2 fraction over 65%, and the hardness showed high values of 52 GPa. The ta-C coating with high Si content showed improved transmittance than other carbon based coatings, and these results indicate that the metal doped ta-C top-coating could be applied for protective & AR coating of satellite solar cell.

9:00am **G2-TuM4 Cobalt-based Thin Films as Electrocatalysts for Water Recombination Applications***, **Clara Linder (clara.linder@liu.se)**,* Linköping University, IFM, Nanostructured Materials, Sweden*; S. Gangaprasad Rao, A. Le Febvrier,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; S. Munktell,* Swerim AB, Sweden*; P. Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; E. Björk,* Linköping University, IFM, Nanostructured Materials, Sweden

Catalysts and electrocatalysts are crucial for energy production and storage solutions. Water recombination is one important reaction for these applications, but due to sluggish kinetics, an electrocatalyst is required. Cobalt oxides have presented good performances for the oxygen reduction reaction (ORR) [1], and in some cases as good as noble metal-based catalysts [2]. To develop cost efficient systems and functionalized surfaces, the catalysts can be synthesized as nanomaterials or thin films.

In this work, cobalt thin films were deposited on low alloyed steel using magnetron sputtering. The thickness of the film was estimated to 200 nm with cross-section scanning electron microscopy (SEM) analysis. Co-films were then electrochemically oxidized at room temperature in an alkaline solution. The final material was a multi-layered mix of cobalt oxides, one of them being Co_3O_4 identified with X-Ray Diffraction (XRD). The catalytic performances of the oxidized films were evaluated in 1M KOH electrolyte saturated with oxygen. Cathodic currents in 10-50 mA/cm^2 range, corresponding to ORR activity, were measured with linear scan voltammetry. Different characterization techniques (SEM, XRD and X-ray photoelectron spectroscopy) were used to define the material properties of the thin films and its catalytic activity.

This work has shown that thin films can be used as electrocatalysts, after electrochemical modification, efficiently for oxygen reduction reaction for energy production and storage solutions.

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9:20am **G2-TuM5 Data-driven Colliding Surface Enhancement using Coated Ceramic in Shot Peening**, ***Benjamin Levy (benjamin.levy@ensam.eu)***, Arts et Métiers ParisTech d'Aix-en-Provence, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France; *M. El Mansori,* Arts et Métiers ParisTech d'Aix-en-Provence, France, Texas A&M University, USA, France; *S. Mezghani, M. EL HADROUZ,* Arts et Métiers ParisTech de Châlons-en-Champagne, France; *A.-L. BEAUDONNET,* Saint-Gobain Research Provence, France

Surface enhancement is a key process stage for improving the functionality, performance, and longevity of a component. Ceramic shots are hence used in a large range of industrial peening applications focusing on fatigue life improvement [1] where surface finishing enhancement processes can still be improved, especially in terms of surface roughness and deformation levels. One way to provide complete surface enhancement solution is to apply a coating on the beads. Coated ceramics shots with various features were hence fully characterized and compared with traditional ceramic beads. To that extent, a special mono-peening process has been developed. It consists in making indentation on an aluminum alloy specimen by impacting it with one coated particle. The observation of the resulted plastic deformation of the target was followed by systematic multiscale texture characterization [2] and analysis of resulting indentation pattern. The processing parameters such as incident and rebound kinetic energies were also computed. The induced effects of these parameters were related to characteristics of the coatings designed for shots in order to identify the intensity and pattern [3] of transferred signature from coated ceramics beads to Al 6063-T6 surface properties, under similar peening conditions. Furthermore, the interactions between coated ceramic beads and Al 6063-T6 specimens were also studied, following the cinematic aspect. Coating may allow reducing the transfer of energy between beads and target (elastic absorption) decreasing the creation of residual stress while maintaining the surface functionalization. All experimental data were used to construct a robust numerical model.

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9:40am **G2-TuM6 The Benefits of Using Functional Coatings to Improve Performance of Components in Conventional Mobility and E-Mobility**, ***Mahdi Amiriyan (amirimhd@schaeffler.com)***, *R. Farahati,* Surface Technology, Schaeffler Group USA, Inc., USA **INVITED**

The continuous need for greater energy efficiency in modern means of transportation is accompanied by ever-increasing demands on the tribological load-carrying capacity of their components. Surface coatings can be applied to components to provide unprecedented low friction, as well as additional highly desirable features and benefits such as wear protection. Application methods such as physical vapor deposition (PVD) or plasma-assisted chemical vapor deposition (PACVD) can produce coatings with a hardness of > 2 000 HV. Meanwhile, applying such coatings on some engine components has been shown to lower frictional torque by up to 50%, which can correspond to a reduction in automotive CO2 emissions. Under certain conditions, stray electrical current can pass through rolling bearings in electric motors or axles. This can damage and degrade the lubricant inside the bearing, which can cause the entire e-motor to fail prematurely. Current-insulated bearings, which feature coated inner or outer rings, offer cost-effective protection against electrical arcing damage—especially when they are specified at the design stage. Schaeffler Insutect® coatings offer excellent adhesion to a bearing's base material and at the same time can provide insulation up to 3,000 V DC under dry or humid conditions.

10:20am **G2-TuM8 Laser Cladding NiTi on the Magnesium Alloy Substrate with the Intermediated Aluminum Layer**, ***Chiyike Zhang (2014105228@hrbeu.edu.cn)***, *Y. Yang, X. Cui, G. Jin, W. Zheng,* Institute of Surface/Interface Science And Technology, China

Magnesium and its alloys are the most promising green engineering structural materials in the 21st century, have the advantage of low density, high damping intensity etc. While the major obstacles of the magnesium alloy in widespread applications are poor corrosion resistance and low hardness. Laser cladding, an effective surface modification approach, is a kind of high energy beam technology. Nickel titanium alloy has excellent corrosion resistance and high hardness, which is a favorable coating system of magnesium alloy surface strengthening. Aluminum is compatible with both magnesium and titanium, so the introduce of intermediated aluminum layer makes it feasible to cladding NiTi alloy coating on magnesium alloy.

Aluminum intermediated layer was developed on the surface of AZ91D substrate by using laser cladding, the pre-set aluminum powder system on the surface of substrates. Laser power is set as 1,000W at the scanning speed of 30mm/s. Then a top layer of NiTi alloy on the intermediated layer is obtained with the laser power of 1300W and 30mm/s of scanning speed. Microstructure of the coating section morphology was observed by optical microscope and the scanning electron microscope (SEM). X-ray diffraction (XRD) and energy dispersive spectroscope (EDS) are employed to verify the presence of Ti_2Ni, NiTi, Ni_3Ti, Ni_2TiAl and the elements distribution. Hardness-depth profile of the layer was measured by microhardness tester, and the measured hardness value of the NiTi alloy layer is over 7 times of the AZ91D substrate. Weight loss and friction coefficient are evaluated by the tribological wear tester, and the result of the test shows that NiTi alloy layer presents superior wear resistance properties compared with that of magnesium alloys. Corrosion resistance in simulated seawater environment was tested on an electrochemical workstation, and the enhanced corrosion resistance of the NiTi layer is gained on the surface of magnesium alloy substrate.

High energy beam surface modification technology greatly expands the application range of magnesium alloy. With this technology, magnesium alloy will be able to adapt to worse working environment, and higher performance requirements applications, such as aerospace, military aircraft, and car industry etc.

Keywords: Laser cladding; Magnesium alloy; Nickel titanium alloy; Intermediated aluminum layer

Acknowledgements

This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.

10:40am **G2-TuM9 Laser-clad Induced Reaction Synthesis of TiC/WC Reinforced Co-based Composite Coatings on Copper Alloy**, ***Hua Yan (yanhua@foxmail.com)***, Shanghai University of Engineering Science, China

Co-based composite coatings reinforced by nickel coated WC (Ni/WC) and in-situ synthesized TiC particles has been fabricated from precursor mixtures of HG-Co01(Co-based alloy), Ni/WC, graphite and pure titanium powders by laser cladding on Cr-Zr-Cu alloy substrate. The microstructure, phase and wear properties were investigated by means of optical microscopy (OM), X-ray diffraction (XRD) and scanning electron microscopy (SEM), as well as dry sliding wear test. Results show that reinforcements dispersed uniformly in the Co-based matrix. TiC showed the morphology of dendritic and particle. During laser-clad processing, the laser heating effect caused inter-diffusion action between the precursor mixtures and generated TixCy and some Ti element diffused into Ni/WC particles formation of TiWC2 alloyed layer. The laser-clad TiC/WC reinforced Co-based composite coatings exhibited higher microhardness and better wear resistance than copper alloy. The highest microhardness was up to 1007 HV0.2 which was improved 8 times comparing to the Cr-Zr-Cu substrate. The friction coefficients of the laser-clad composite coatings were reduced significantly to about 0.15 and relatively smooth wear surface could be observed.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific Salon 6-7 - Session H2-1-TuM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes I

Moderators: Olivier Pierron, Georgia Institute of Technology, USA, Timothy Rupert, University of California, Irvine, USA

8:00am **H2-1-TuM1 Characterization of the Onset of Delamination in Thin Films Coatings using Advanced Nanoindentation Techniques**, ***Marzyeh Moradi (Marzyeh.Moradi@kla-tencor.com)***, *B. Faulkner, K. Johanns,* KLA-Tencor, USA

Adhesion energy and onset of delamination in Low K thin film materials was characterized using nanoindentation. Advanced measurements methods were developed to combine fast indentation techniques with extremely high data acquisition rate to capture the early stages of failure and short temporal events during crack propagations. This enabled to statistically examine the interfacial toughness and controlling failure mechanisms in different stages of fracture. The analysis was extended to study the effect of residual stress in the film where there is a high probability of defects concentration.

8:20am **H2-1-TuM2 Development and Application of a Multifunctional Nanoindenter: Coupling to Electrical Measurements and Integration in-situ in a Scanning Electron Microscope***, **Fabien Volpi (fabien.volpi@grenoble-inp.fr)**, S. Comby-Dassonneville, C. Boujrouf, M. Verdier,* SIMaP – Univ. Grenoble Alpes, CNRS, SIMaP, France*; D. Pellerin,* CSI/Scientec, France

Nanoindentation is a well-known characterisation technique dedicated to local mechanical testing of materials at small scales. In the past decades, numerous efforts have been made to expand the capabilities of nanoindentation technique [1]: real-time electron imaging, coupling with multifunctional characterisation tools, high temperature measurements,...

The present submission reports the development of a home-made multifunctional characterisation device based on a commercial nanoindenter. This device combines mechanical to electrical characterisations, and can be integrated in-situ in a Scanning Electron Microscope (SEM):

- Electrical characterisations cover both resistive and capacitive measurements.
- In-situ SEM integration allows precise positioning of nanoindentation tests (precision better than 100nm) as well as the positioning of electrically-coupled indentation maps.

Selected applications will be shown:

- Dielectric permittivity determination under mechanical load: an experimental procedure and a data-processing method have been set up to quantitatively extract the dielectric permittivity of insulating films from capacitive-nanoindentation (Fig.1) [2].
- Leakage current through insulators under mechanical load: Insulating films are know to degrade when subjected to mechanical stresses. The present device allows the real-time monitoring of this insulation degradation. Leakage mechanisms with or without mechanical load will be discussed.
- Multifunctional property mapping: The combined mapping of mechanical and electrical properties is also possible (Fig.2). An illustration will be shown on a multiphase alloy developed for its compromise between high tensile strength and high electrical conductivity.
- Real-time monitoring of the contact area: a three-step procedure applied to resistive-nanoindentation has been developed to precisely monitor the tip-to-sample contact area. This approach is expected to be an experimental alternative to analytical models for contact area determination.

Prospects are numerous : capacitive-nanoindentation can fill a gap between quantitative characterisations at macro-scales and relative characterisations at nanoscale; leakage measurements under mechanical loads should help the understanding of oxide degradations; SEM-integration opens to multifunctional property mapping;...

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3. S. Comby-Dassonneville, F. Volpi, G. Parry, D. Pellerin, M. Verdier, MRS Communications, 9(3), 1008-1014 (2019)

8:40am **H2-1-TuM3 Characterization of Defects and their Dynamics using Transmission Scanning Electron Microscopy***, **Daniel Gianola (gianola@engr.ucsb.edu)**,* University of California Santa Barbara, USA **INVITED**

The past several years has witnessed a surging popularity of scanning transmission electron microscopy (STEM) for defect characterization using diffraction contrast imaging. Advantages of these methods over conventional TEM include the suppression of dynamical effects and spurious contrast, as well as the ability to image relatively thick specimens. In parallel, the use of transmission modalities in the scanning electron microscope (SEM) has attracted recent attention.

Here, we link these capabilities by employing an field emission SEM equipped with an annularly-segmented STEM detector for defect characterization – termed transmission SEM (TSEM). Stacking faults and dislocations have been characterized in commercially pure aluminum, strontium titanate, a polycrystalline nickel-base superalloy, several multi-principal-element alloys, and a single crystal cobalt-base material. Imaging modes that are similar to conventional CTEM bright field (BF) and dark field (DF) and STEM are explored, and some of the differences due to the varying accelerating voltages highlighted. Defect images have been simulated for the TSEM configuration using a scattering matrix formulation, and diffraction contrast in the SEM is discussed in comparison to TEM. Interference effects associated with conventional TEM, such as thickness fringes and bending contours, are significantly reduced in TSEM by using a convergent probe (similar to a STEM imaging modality) enabling individual defects to be imaged clearly even in high dislocation density regions.

We further show that TSEM provides significant advantages for high throughput and dynamic *in situ* characterization. We employ location-specific *in situ* tensile experiments to study the nature of dislocations dynamics in several structural alloys. By selecting specific crystallographic orientations relative to the tensile axis, we observe the underpinnings of several plasticity mechanisms including shear localization, cross-slip, and dislocation junction formation and evolution. To demonstrate the power of this new method for defect-contrast studies, we further show the ability to deduce reciprocal space mapping, and thereby, Burgers vector determination.

9:20am **H2-1-TuM5 Measurement of hardness and elastic modulus by depth sensing indentation: Further advances in understanding and refinements in methodology***, Phani Pardhasaradhi,* ARCI, India*; **Warren Oliver (Warren.Oliver@kla.com)**,* KLA Corporation, USA*; G.M. Pharr,* Texas A&M University, USA, United States of America

Depth sensing indentation technique has been widely used to measure small scale mechanical properties over the years. Starting from the seminal work of Oliver & Pharr, there have been many improvements / modifications to the test methodology and also significant advances in measurement electronics / testing instrumentation. These advancements provide opportunities to not only develop novel testing capabilities but also further improve the precision and accuracy of the most common measurement parameters – hardness and elastic modulus.

Several steps are involved in a typical depth sensing indentation test, viz., surface approach, surface detection, load-time history including superimposing an oscillatory force on broad band load, unloading and drift rate measurement. The effect of each of these steps on the accuracy and precision of the hardness and elastic modulus measurement will be discussed with specific focus on frequency specific testing techniques such as continuous stiffness measurement. A simple model is developed to simulate a depth sensing indentation test that incorporates the material and instrumentation parameters to help visualize the overall process and provide new insights for pushing the limits of the currently available instrumentation for improved precision and accuracy. This involves performing tests beyond the traditional boundaries of parameter space such as increased oscillation amplitude, strain rate, oscillation frequency, etc. For instance, if the indentation strain rate gets high compared to the oscillation frequency, inaccuracies can occur. This work presents the critical experimental parameters and the associated first order corrections for the potential errors. The model predictions and corrections are validated on different classes of materials. Finally, guidelines for measuring hardness and elastic modulus using a depth sensing indentation test with significantly improved precision and accuracy within the limitations of the currently available instrumentation will be discussed.

9:40am **H2-1-TuM6 Strength and Fracture Toughness at Elevated Temperature of Monolithic and Multilayered Hard Coatings***, **Jon Molina-Aldareguia (jon.molina@imdea.org)**,* IMDEA Materials Institute, Spain **INVITED**

Hard coatings for the cutting tool industry experience high temperatures under service conditions. However, the characterization of their mechanical properties relies traditionally on nanoindentation tests, commonly at room temperature. With the current development of novel nanomechanical testing techniques, in combination with FIB milling, it is now possible to test these materials under compression, tension and/or bending, and to determine their strength and toughness, even at elevated temperature.

These novel testing methodologies open new opportunities to explore microstructural effects on the mechanical behavior of hard coatings. In particular, the use of controlled loading configurations at the micrometer scale allows elucidating anisotropic effects in strength and toughness of hard coatings, and to identify weak microstructural features that can compromise their mechanical response. The ultimate objective is to generate the knowledge required to design new coatings with superior strength and toughness. In this talk, examples of application of micropillar compression, cantilever bending, microtensile testing and micropillar splitting tests to understand the mechanical behavior of hard coatings will be shown. Examples will include monolithic and multilayered nitride coatings, as well as nanoscale multilayer systems, combining metallic and ceramic layers.

10:20am **H2-1-TuM8 Influence of the Bonding Nature on the Fatigue Resistance of Cr-based Thin Films***, Lukas Zauner (lukas.zauner@tuwien.ac.at), R. Hahn,* TU Wien, CDL-SEC, Austria*; M. Alfreider,* Montanuniversität Leoben, Department of Materials Science, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; D. Kiener,* Montanuniversität Leoben, Department of Materials Science, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Innovative coating materials and architectural concepts extending the fatigue-life of modern high-performance components throughout their operating spectrum by controlled, and hence predictable crack propagation are of major interest for various industrial fields. Consequently, a fundamental knowledge on the decisive failure criteria of PVD deposited coatings – generally associated with an intrinsic lack in ductility – under long-term mechanical and/or thermal loading is paramount in order to enhance the limited bulk material properties utilizing protective thin films. Literature reports on fatigue resistance, of especially hard ceramic coating materials [1] but also thin films in general, are relatively rare. Thus, an in-depth analysis of different coatings – meaning prevalent bonding states, *i.e.* altered ratio of ionic, covalent, and metallic bonds – with respect to fatigue phenomena (e.g. LCF, HCF, strain rates or extrusion formation) is of great interest.

Within this study we present a methodical approach towards a general understanding on the failure behaviour of PVD deposited thin films from the aspect of the bonding structure between the atomic constituents making use of a model system containing Cr and Cr-based compounds, respectively. The DC magnetron sputtered thin films have been analysed with respect to phase formation, thermo-mechanical properties, and morphology by means of nanoindentation, X-ray diffraction, as well as electron imaging techniques. The influence of the stress state was quantified through high-temperature wafer-curvature measurements. Microcantilever tests were used to calculate the fracture toughness K_{IC} and the fracture stress σ_f by introducing a pre-notch as well as bending the cantilevers in the as received state, respectively. Low (LCF) and high cycle fatigue (HCF) tests of unstrained micro-cantilever geometries were subsequently performed under various loading conditions based on the critical stress intensities observed during quasi static tests. Through this comprehensive approach we are able to identify the most critical aspects with respect to fatigue life of different coating material classes.

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10:40am **H2-1-TuM9 New Models and Advancement in Measuring the Elastic Behaviour of Thin Films using Impulse Excitation Technique***, Akram Alhussein (akram.alhussein@utt.fr),* University of Technology of Troyes (UTT), France*; E. Zgheib,* University of Technology of Troyes (UTT) and Lebanese University (UL), France*; M.F. Slim, M. François,* University of Technology of Troyes (UTT), France

The deposition of Micro layer thin films is developed more and more to meet the industrial and society needs. Coatings are considered as a solution to protect a material and giving it some functionalities. The elasticity behaviour of theses layers is the mean issue to be controlled. The film performance almost depends on its elastic behaviour (e.g. hardness, residual stress, wear resistance, oxidation resistance, etc.).

The goal of our project is to develop a new methodology to measure the elastic constants of films using impulse excitation technique (IET). IET is based on the analysis of vibrational frequencies of an excited sample. Different kinds of films were deposited using magnetron sputtering technology. Mono and multi layer films, isotropic and anisotropic materials, were deposited on glass and steel substrates. The parameters influencing the elasticity of the coatings were identified. The error factors and the measure uncertainty were evaluated.

Missing data in the literature to determine the elastic constants values of films at different scales motivates the development of the IET. The methodology used is based on a multi-scale approach and an inverse method for mono and multilayer films. The correlation between the microstructural state and the properties of the coating was established after performing experiments (Film deposition, IET measurements, Nanoindentation, XRD, …) and numerical and analytical developing using Abaqus, Mathematica and Matlab software. These analyses allowed us to develop new models to get Young's and shear moduli of films and understand the relation between the deposition parameters, the physicochemical properties, the microstructures and the elastic constants of the materials [1-4].

Keywords: Coatings, Elastic constants, Multilayers, Impulse Excitation Technique, Magnetron sputtering.

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Topical Symposia
Room Pacific Salon 3 - Session TS2-1-TuM

New Horizons in Boron-Containing Coatings: Modeling, Synthesis and Applications I

Moderators: Marcus Hans, RWTH Aachen University, Germany, Helmut Riedl, TU Wien, CDL-SEC, Austria, Johanna Rosen, Linköping University, Sweden

8:00am **TS2-1-TuM1 Enhanced High-temperature Oxidation Resistance of Hard TiB_2-rich $Ti_{1-x}Al_xB_y$ Thin Films***, B. Bakhit (babak.bakhit@liu.se),* Linköping University, Sweden*; **Ivan Petrov**, J.E. Greene,* University of Illinois, USA, Linköping University, Sweden, USA*; L. Hultman, J. Rosen, G. Greczynski,* Linköping University, Sweden

Ultra-high-temperature refractory transition-metal (TM) diborides are considered as promising candidates for extreme environments. However, they typically do not exhibit sufficiently high oxidation resistance required for harsh environmental conditions. Here, we study the effect of Al addition on the high-temperature oxidation resistance of TiB_2-rich $Ti_{0.68}Al_{0.32}B_{1.35}$ thin films. The films, grown by hybrid high-power impulse and dc magnetron co-sputtering (Al-HiPIMS/TiB_2-DCMS) in pure Ar atmosphere at ~475 °C, exhibit hexagonal columnar nanostructure. While the column boundaries of $TiB_{2.4}$ layers grown by DCMS are B-rich, the $Ti_{0.68}Al_{0.32}B_{1.35}$ alloys consist of Ti-rich columns surrounded by an Al-rich $Ti_{1-x}Al_xB_y$ tissue phase which is highly B deficient. The observed transition in the nanostructure is attributed to the lower formation enthalpy of AlB_2 than TiB_2 together with enhanced atomic mobility caused by intense Al^+ ion bombardment during HiPIMS pulses. $TiB_{2.4}$ films readily oxidize at temperatures above ~300 °C, as evidenced by X-ray photoelectron spectroscopy, with oxidation products consisting of a tetragonal rutile-TiO_2 structure filled with an amorphous BO_x phase. Air-annealing at 700 °C for 1 h results in the formation of a thick double-layer oxide scale on $TiB_{2.4}$, ~510 nm, where the outer layer is composed of sub-micrometer crystallites and the inner layer has a porous and V-shape columnar structure. Compared to $TiB_{2.4}$, $Ti_{0.68}Al_{0.32}B_{1.35}$ alloys show significantly higher oxidation resistance, while retaining high hardness. In addition, the Ar content is significantly reduced, from 1.2 to 0.5 at.%, due to the use of pulsed substrate bias synchronized to the Al-rich phase of the HiPIMS pulses.

8:20am **TS2-1-TuM2 Design of Under/Overstoichiometric Superhard $TaB_{2\pm x}$ Films**

***Viktor Šroba (viktor.sroba@gmail.com)**, T. Fiantok, M. Truchlý,* Comenius University in Bratislava, Slovakia*; P. Švec, Jr.,* Slovak Academy of Sciences, Slovakia*; T. Roch, L. Satrapinskyy, M. Zahoran, B. Grančič, P. Kúš, M. Mikula,* Comenius University in Bratislava, Slovakia

Transition metal diborides (TMB_2) are very interesting due to their high temperature chemical stability and excellent mechanical properties. Growth of diboride films by physical vapor deposition (PVD) methods, such as magnetron sputtering from stoichiometric compounds, is accompanied by several interesting aspects. Different angular distribution of sputtered elements plays an important role leading to the formation of under/overstoichiometric nanocomposite films. The best-known superhard overstoichiometric TiB_{2+x} film consists of oriented α-TiB_2 hexagonal filaments embedded in the boron-rich tissue phase. In addition, thermodynamically non-equilibrium PVD processes lead in Nb-, Mo-, WB_2 to the synthesis of metastable structures by incorporating point defects such as vacancies. Understoichiometric $MoB_{1.6}$ and $NbB_{1.7}$ films form despite boron deficiency vacancy-containing α-nanofilaments surrounded by a boron matrix. In the case of slightly understoichiometric α-WB_{2-x} films, boron vacancies promote α-type of the structure exhibiting more ductile behavior in comparison with brittle character of stoichiometric ω-WB_2. Tantalum is probably the most interesting metal of the abovementioned transition metals of VB and VIB group due to its superior oxidation resistance and mechanical properties. Grančič et al. [1] sputtered TaB_{2-x} films from a stoichiometric compound. They drew attention to the significant impact of reflected Ar neutrals from heavy Ta atoms in the target toward the growing film. This led to a large re-sputtering of boron and formation of a significantly understoichiometric amorphous $TaB_{1.2}$ film. Only the maximum decrease in acceleration voltage reduced the energy of Ar neutrals resulting in the nanocrystalline $TaB_{1.7}$ film, but without the typical nanocolumnar character as in the other diborides. Here, we grow under/overstoichiometric $TaB_{2\pm x}$ films using High Target Utilisation Sputtering (HiTUS) technology where it is possible to independently change the kinetic energy of the argon particles accelerated towards the target (target voltage) while maintaining the same amount (target current). We used SRIM (Stopping and Range of Ions in Matter) simulation of sputtering processes and experiments supported by density functional theory (DFT) calculations to investigate the effect of reflected Ar neutrals on the chemical composition, structure and mechanical properties of tantalum diboride films.

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8:40am **TS2-1-TuM3 Thermomechanical Properties and Oxidation Resistance of Ternary $W_{1-x}Ta_xB_{2-z}$ Coatings**

***Christoph Fuger (christoph.fuger@tuwien.ac.at)**,* TU Wien, CDL-SEC, Austria*; V. Moraes,* Institute of Materials Science and Technology, TU Wien, Austria*; R. Hahn,* TU Wien, CDL-SEC, Austria*; H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P.H. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Future tasks in many different fields of academia and industry are directed towards environmental sustainability, asking also for new advance in the field of protective coating materials. Especially, transition metal diboride based thin films exhibit a great potential to be applied in various applications because of their extreme refractory character as well as interesting electrical properties. Latest studies on various diborides emphasized their strong and weak points being on the one hand high hardness and phase stability in a wide range but on the other limited fracture and oxidation resistance. Alloying concepts involving transition metals (TM) such as W, Ta, or Zr forming ternary diborides ($TMI_{1-x}TMII_xB_{2-z}$) suggest to be a proper solution to overcome these restriction [1-3].

Therefore, within this study we provide a detailed insight on the thermomechanical properties and oxidation resistance of ternary $W_{1-x}Ta_xB_{2-z}$ thin films prepared by DC magnetron sputtering utilizing diboride based target materials. Based on theoretical investigations using density functional theory, we classified the two binary systems α-WB_{2-z} and α-TaB_{2-z} as highly ductile materials according to semi-empirical criteria e.g. Pettifor and Pugh. On behalf of structural investigations, we could confirm that single phased structured α-$W_{1-x}Ta_xB_{2-z}$ thin films are formed up to Ta contents of x=0.26. The addition of Ta also clearly enhances the phase stability in inert atmosphere shifting the decomposition of the metastable α- into the thermodynamically more stable ω-structure from 800 to 1400 °C for x=0.26. During oxidation treatments up to 800 °C the high Ta alloyed coatings outperform its counterparts, forming dense and stable oxide scale also after long exposure times (1000 min). In addition, these films were investigated by nanoindentation and in-situ micromechanical bending tests to evaluate the mechanical properties. The fracture toughness only slightly decreases with increasing Ta content from 3.7 to 3.0 $MPam^{1/2}$. In summary, the study highlights the potential of Ta alloyed WB_{2-z} coatings and confirms the strategy to form ternary or multinary diborides to expand the limitations in specific material properties.

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[3] B. Bakhit, D.L.J. Engberg, J. Lu, J. Rosen, H. Högberg, L. Hultman, I. Petrov, J.E. Greene, G. Greczynski, J. Vac. Sci. Technol. A. 37 (2019) 031506.

9:00am **TS2-1-TuM4 Configurational and Vibrational Thermodynamics of Metastable Ternary $Ti_{1-x}Al_xB_2$ Alloys with Age-Hardening Potential, and their Constituent Binaries**

***Erik Johansson (erik.johansson@liu.se)**,* Linköping Univ., IFM, Theoretical Physics Div., Sweden*; N. Nedfors,* Linköping University, IFM, Thin Film Physics Division, Sweden*; F. Eriksson,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; A. Ektarawong,* Linköping Univ., IFM, Theoretical Physics Div., Sweden*; J. Rosen,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; B. Alling,* Linköping Univ., IFM, Theoretical Physics Div., Sweden

$Ti_{1-x}Al_xB_2$ metastable ceramic alloys were predicted in [1] to exhibit a tendency for isostructural decomposition despite the fact that binary TiB_2 and AlB_2 belong to the same hexagonal space group and have very similar lattice parameters. Due to the reported high hardness of TiB_2 and the prospect of age-hardening through isostructural clustering, these alloys could be good candidates for hard protective coatings on industrial cutting tools. In this work, we present theoretical predictions regarding phase stability and temperature dependence of structural parameters, based on first-principles density functional theory. The phase diagram for this ternary system is derived and shows an isostructural miscibility gap that closes only at temperatures beyond the melting temperatures of TiB_2 and AlB_2.

Out of the constituent binaries, TiB_2 is a well-studied line compound that has received more focus than AlB_2. In this work, initial phonon calculations of stoichiometric AlB_2 indicates that the thermal expansion trend does not follow experimental measurements as closely as TiB_2. Furthermore, it is known in the literature that there is an inherent metal deficiency present in AlB_2. Therefore, special attention is put on AlB_2 to further our fundamental understanding of the compound. We investigate configurational thermodynamics of metal vacancies, their origin in the electronic structure and their interplay with lattice vibrations. Through the use of cluster expansion, effective cluster interactions are obtained and used in Monte Carlo simulations in order to study vacancy order-disorder transition temperature and to derive a phase diagram. For a subset of vacancy structures, phonon vibrational contributions in the quasiharmonic approximation are calculated to obtain volume expansion for metal deficient AlB_2, and are compared with experimental measurements performed by our partners.

[1] B. Alling et al. “A theoretical investigation of mixing thermodynamics, age-hardening potential, and electronic structure of ternary $M^1_{1-x}M^2_xB_2$ alloys with AlB_2 type structure". Scientific Reports 5 2015, 09888.

9:20am **TS2-1-TuM5 Stoichiometry, Structure and Mechanical Properties of Co-Sputtered $Ti_{1-x}Ta_xB_{2\pm\Delta}$ Coatings**

***Branislav Grancic (grancic@fmph.uniba.sk)**, K. Viskupova, M. Mikula,* Comenius University in Bratislava, Slovakia*; M. Caplovicova,* Slovak University of Technology in Bratislava, Slovakia*; L. Satrapinskyy, T. Roch, M. Truchly,* Comenius University in Bratislava, Slovakia*; M. Sahul,* Slovak University of Technology in Bratislava, Slovakia, Slovak Republic*; M. Gregor,* Comenius University in Bratislava, Slovakia*; P. Svec Sr.,* Slovak Academy of Sciences, Slovakia*; M. Zahoran, P. Kus,* Comenius University in Bratislava, Slovakia

Ternary transition metal diborides $M^1_{1-x}M^2_xB_2$ represent a promising class of materials for hard wear-resistant coatings [1]. By using co-deposition from two binary stoichiometric targets, it is possible to prepare a ternary system in a wide x range. However, the varying boron-to-metal ratio often embodies obstacles/difficulties in the evaluation of the effect of x on coating properties. The mechanisms that determine the resulting boron-to-metal ratio are dependent on the target material and may significantly alter the resulting coatings' properties [2].

We use magnetron co-sputtering from TiB_2 and TaB_2 stoichiometric targets to prepare AlB_2-prototype ternary $Ti_{1-x}Ta_xB_{2\pm\Delta}$ solid solution, with x in the range from 0 to 1. Using this technique, the boron-to-metal ratio (B/Me) varies with the actual Ti and Ta content. The boron-to–tantalum ratio can be increased by decreasing the TaB_2 target voltage, which has a considerable effect on the coating structure. Coatings with B/Me > 2 reveal highly textured nanocolumnar structure, while the coatings with B/Me < 2 tend to be nanocrystalline (without any preferred crystallite orientation) or amorphous. All the deposited coatings have a hardness higher than 32 GPa. The under-stoichiometric (B/Me < 2) coatings show material pile-up around the cube-corner indent edges, an indication for plastic flow and increased ductility.

[1] B. Alling, et al. Scientific Reports 5 (2015)

[2] B. Grančič, et al. Surface & Coatings Technology 367 (2019) 341–348

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9:40am **TS2-1-TuM6 Fracture–Microstructure Relations of W-diboride Thin Films***, **Rainer Hahn (rainer.hahn@tuwien.ac.at)**, C. Fuger,* TU Wien, CDL-SEC, Austria*; G. Habler,* University of Vienna, Austria*; H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P.H. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Physical vapor deposited transition metal borides are an emerging class of materials. Their inherent promising properties range from ultra-low compressibility, highest thermal stability to chemical inertness, allowing an application as protective coating in quite harsh environments. Our recent ab initio calculations [1] suggest an attractive combination of high stiffness and appropriate high ductility for α-structured WB_{2-z} (space group 191, AlB_2-prototype, P6/mmm). This leads to an interesting combination of high hardness while maintaining a sufficient fracture toughness. The stabilization of the α-structure over the intrinsically favored ω-structure (space group 194, W_2B_5-prototype, $P6_3/mmc$) is based on omnipresent growth defects (e.g. various types of 0-dimensional vacancies) in the PVD process. However, next to the stabilized phases (hence prevalent bonding nature) also the morphology, especially column size and grain boundary interior, has a huge impact on the mechanical response.

Therefore, within this study we deposited various WB_{2-z} coatings using different deposition techniques as well as parameters to modify the crystallite size and grain boundary constitution but also predominating phases. Subsequently, the mechanical properties of these coatings in the as deposited and annealed state have been analyzed by means of nanoindentation, microcantilever bending tests, and micropillar compression testing. Depending on the coating morphology, which varies from nanocrystalline (amorphous) to crystalline fibrous grown structures, the hardness, indentation modulus, and fracture toughness obtains a strong variation. Hardness and indentation modulus can be varied between 31±2 to 42±2 GPa and 440±30 and 560±30 GPa, respectively. The most significant variation though was found in the fracture toughness of these coatings: We calculated values within the framework given by Matoy et al. [2] between 2.5 and 4.7 MPa√m. Furthermore, we critically evaluate the comparability of distinct micromechanical testing techniques assessing the fracture behavior also with respect to the residual stress state.

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[2] K. Matoy, H. Schönherr, T. Detzel, T. Schöberl, R. Pippan, C. Motz, G. Dehm, Thin Solid Films 518 (2009) 247–256.

10:00am **TS2-1-TuM7 Design of Novel Boride-based Hard and Tough Coatings for Engineering Applications***, **Michael Stueber (michael.stueber@kit.edu)**,* Karlsruhe Institute of Technology (KIT), Inst. for Applied Mat. (IAM-AWP), Germany*; H. Riedl,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Özbilen,* Gazi University, Ankara, Turkey*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Inst. for Applied Mat. (IAM-AWP), Germany*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal diboride hard coatings are attractive material candidates for a huge variety of high performance applications in engineering. Due to their chemical nature these materials exhibit interesting multifunctional properties. However, their mechanical properties (i.e. toughness and ductility) like the achievement of stoichiometric composition or adhesion onto various substrates in physical vapor deposition processes make their utilization often a challenge. Thus, such materials experience currently a strong revitalization of research efforts. In this presentation, we will discuss three design concepts for novel boride-based hard and tough coatings for engineering applications. These are all based on the model thin film material TiB_2 which is by far the most detailed characterized PVD diboride. The first approach describes the alloying of TiB_2 with the intention to design novel ternary solid solutions, $(Ti,X)B_2$ where X is another metal such as Al, Cr, Zr, V or others. We will discuss exemplarily the impact of low Al content on phase formation, microstructure and mechanical properties of magnetron-sputtered $(Ti,Al)B_2$ thin films. The second approach refers on the formation of TiB_2-metal composite thin films, which covers the objectives of designing thin film material composed either of a boride matrix with dispersed metal nanoclusters or of a metal matrix with dispersed diboride cluster phase. The metal phase used in this part of the description is the superalloy B2 structured NiAl. We will discuss phase formation and microstructure evolution of magnetron co-sputtered TiB_2-NiAl thin films, both in as-deposited and vacuum annealed state. The third approach deals with the integration of TiB_2 layers into nanoscale multilayers when the second layer constituent is also a metal layer. We focus again on the combination of TiB_2 with NiAl. We consider multilayers with variation of the bilayer period and discuss their structure and properties.

10:20am **TS2-1-TuM8 A Progress Report on Bulk MAB Phases***, **Michel Barsoum (barsoumw@drexel.edu)**,* Drexel University, USA, United States of America*; J. Kota,* Drexel University, USA **INVITED**

The MAB phases are atomically layered, ternary or quaternary transition metal (M) borides

(TMBs), with the general formula $(MB)_{2z}A_x(MB_2)_y$(**z** = 1–2; **x** = 1–2; **y** = 0–2), whose structures

are composed of a transition M-B sublattices interleaved by A-atom (A = Al,Zn) mono- or bilayers. Most of the MAB phases were discovered prior to the year 2000, but recent discoveries of intriguing magnetocaloric properties and high-temperature oxidation resistance has led to their **'**re-discovery**'**. Herein, bulk MAB phase synthesis is reviewed and their magnetic, electronic, thermal, oxidation and mechanical properties will be overviewed with an eye on applications. Because the M-B layers in the MAB phases are identical to their corresponding binaries of the same M:B stoichiometry, the effects of the A-layers on properties are discussed. Fruitful avenues for future research are proposed; potential limitations are also considered.

Topical Symposia
Room Pacific Salon 1 - Session TS4-TuM
Photocatalytic and Superhydrophilic Surfaces

Moderators: Peter Kelly, Manchester Metropolitan University, UK, Carlos Jose Tavares, University of Minho, Portugal, Glen West, Manchester Metropolitan University, UK

8:00am **TS4-TuM1 Photocatalytic Activity of a ZnO/Bi_2O_3 Thin Film Heterojunction***, **Sandra E. Rodil (srodil@unam.mx)**,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, México*; A. Hernandez-Gordillo, M. Bizarro,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; J.C. Medina,* Instituto de Ciencias Aplicadas y Tecnologias, Universidad Nacional Autonoma de Mexico, Mexico

Zinc oxide (ZnO) has been known as an outstanding photocatalyst in water treatment with an important performance in the degradation and mineralization of several organic pollutants with the use of UV radiation. Unfortunately, UV radiation only represents a small part of the solar light spectrum. A possible method to extend the functionality of ZnO into the visible light is the formation heterostructures with another semiconductor material. An adequate candidate is bismuth oxide (Bi_2O_3) which has appeared recently as a photocatalytic material with the advantage of working in the visible range. In this work, bilayers of ZnO/Bi_2O_3 were produced combining spray pyrolysis and magnetron sputtering techniques aiming to produce a visible-light active photocatalyst for the degradation of organic compounds. Firstly, ZnO thin film was sprayed on glass substrates and subsequently Bi_2O_3 dots were sputtered on this surface. The structural, morphological and optical properties were studied and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis spectroscopy as well as the chemical composition by X-ray photoelectron spectroscopy (XPS). The photocatalytic response was evaluated following the degradation of indigo carmine (IC) under UV and visible light. The results show that the photocatalytic activity under white light irradiation of the ZnO film was improved with the coupling of the Bi_2O_3 dots, attaining a superior mineralization degree compared with ZnO and Bi_2O_3 films separately. It was found that depending on the irradiation source, the production of hydroxyl or superoxide radicals is affected which promotes different degradation mechanisms of the IC molecule.

8:40am **TS4-TuM3 Photocatalytic Bismuth Oxide Coatings and their Potential for Water Treatment Applications**, ***Marina Ratova (m.ratova@mmu.ac.uk)***, *J. Redfern,* Manchester Metropolitan University, UK*; C.C. Amorim,* Universidade Federal de Minas Gerais, Brazil*; P.J. Kelly,* Manchester Metropolitan University, UK **INVITED**

As the levels of industrialization and urbanization in the modern world increases, so will the amount of waste, with increasing potential to contaminate water, air and soil. Consequently, there is an urgent requirement for reliable and efficient methods to treat persistent organic pollutants as well as microbial contamination. Bismuth-based oxides, and in particular bismuth oxide and bismuth tungstate, have recently attracted attention as promising photocatalytic materials for water treatment processes. In the present work, novel photocatalytic narrow band gap semiconducting films were prepared by pulsed direct current (DC) reactive magnetron sputtering of Bi (and W) targets in an Ar/O2 atmosphere onto spherically-shaped glass beads. The uniform coverage of the substrate was enabled by the use of oscillating bowl placed underneath the magnetrons. The deposited films were extensively analysed by the range of analytical techniques. The photocatalytic properties of the films were studied via the various dyes degradation process under artificial (fluorescent light) and natural (sunlight) irradiation, and compared to the photocatalytic performance of conventional photocatalytic material, titanium dioxide, deposited onto identical substrates. However, for efficient water treatment processes, disinfection is as important as decontamination. Therefore, antimicrobial efficiency of the coatings was tested via inactivation of E. coli; additionally, bacterial adhesion experiments were performed for all types of the studied coatings. It was found that the performance of bismuth oxide for both dye degradation and bacterial inactivation experiments under visible light was superior to that observed for either bismuth tungstate or titanium dioxide. Moreover, bismuth oxide coatings (and to a lesser extent – bismuth tungstate), due to its hydrophobic nature was able to inhibit bacterial adhesion to the surface. The latter phenomenon is likely to afford bismuth oxide coatings additional antifouling properties compared to conventional titanium dioxide-based photocatalytic coatings. These findings, along with the follow-up studies on bismuth oxide antimicrobial efficiency against common water-borne pathogens and other microbiology-related factors including the effect of bismuth oxide photocatalysis on the presence of genomic DNA, bacteriophage and human hepatotoxicity of treated water, are likely to be of interest to those involved in visible or solar light-irradiated water treatment systems, where effective disinfection of the treated media is as important as degradation of the pollutants.

9:20am **TS4-TuM5 Preparation of Bismuth Titanate Thin Films by Co-sputtering for Photocatalytic Water Treatment Application**, ***Matthieu Grao (matthieu.grao@stu.mmu.ac.uk)***, *M. Ratova, P.J. Kelly,* Manchester Metropolitan University, UK

Bismuth titanate (BIT) photocatalysts have recently caught researchers' attention, as a possible replacement for the well-established TiO_2, whose weaknesses have yet to be overcome. Herein, BIT thin films were produced by pulsed DC magnetron co-sputtering of metallic titanium and bismuth targets, in an argon/oxygen atmosphere. To the best of our knowledge, such synthesis process has not been reported in the literature. BIT films were coated onto soda-lime glass slides with different bismuth and titanium content, until a mixture of $Bi_4Ti_3O_{12}$ and $Bi_{12}O_{20}Ti$ was obtained. This was achieved by varying the power applied to each target. The samples were then annealed at 600C in air to obtain a crystalline structure. The crystallinity of the samples was assessed by X-ray diffraction, Raman spectroscopy and Transmission Electron Microscopy. The samples' photocatalytic activity was assessed by methylene blue degradation tests under UV and compared to bespoke TiO_2 thin films. On average, BIT decomposed methylene blue ~23% faster than TiO_2. Furthermore, reusability tests revealed a 5-fold increase in photocatalytic activity after 15 consecutive tests. PL, UV-Vis and XPS analysis hinted toward oxygen vacancies, forming in the BIT thin films during the tests, as responsible for this uncanny performance enhancement. This newly found property could make bismuth titanate a compelling candidate to replace TiO_2 as the most efficient photocatalyst.

9:40am **TS4-TuM6 Hematite and Titania Thin Films: Energy and Environmental Applications**, ***Josef Krysa (Josef.Krysa@vscht.cz)***, University of Chemistry and Technology, Prague, Czech Republic **INVITED**

Titania (TiO_2) and hematite (α-Fe_2O_3) have potential applications as semiconducting photoanodes for either hydrogen production *via* photoassisted water electrolysis or photoelectrochemical (PEC) oxidation of water pollutants. The advantages of TiO_2 are high stability, nontoxicity, and low price. However, it absorbs only a very small part of sunlight (3% of the total power). On the other hand, iron oxide (α-Fe_2O_3) has a favourable band gap (2.0 – 2.2 eV), which enables absorption of a substantial fraction of solar light, resulting in the theoretical maximum power conversion efficiency of 27 %. This has created much interest in the past, which has been rekindled by the advent of new thin film preparation and texturization methods. Limitations are the non-ideal position of the conduction band, *i.e.* too large an electron affinity for spontaneous water reduction, low minority carrier diffusion length, surface states that can mediate recombination, low stability in acidic media, and photocorrosion. We have recently fabricated Sn-doped hematite (Fe_2O3) films by aerosol pyrolysis (AP) on fluorine doped tin oxide (FTO). P hotosensitivity had an onset around 650 nm and maximum incident photon to electron conversion efficiency (IPCE) was 0.21 at 400 nm. T he aim of the present work was to check whether the capping with TiO_2 can be used for corrosion protection of such films.

AP hematite films on FTO were covered by titania films fabricated by spray-pyrolytic coating. Spray pyrolysis of TiO_2 used as precursor a 0.2 M ethanolic solution of titanium di-isopropoxide bis-acetylacetonate. AP hematite layers coated with TiO_2 show that with increasing thickness (increasing number of passes of the spray nozzle) of the TiO_2 coating the photoelectrochemical response decreased. This is due to TiO_2 increasingly taking part in the solid liquid interface. This is also reflected in the photocurrent onset shifting to more negative potentials. The Faradaic efficiency (f) of the photocorrosion reaction in 1 M sulphuric acid decreased from 0.47 % (for an unprotected hematite electrode) to 0.17 % for that covered with spray coated TiO_2 layer (but decreased photoresponse).

10:20am **TS4-TuM8 Ultrasonic-assisted Supercritical Fluid Exfoliated and Modified by Chlorine Intercalation Synthesis of P3HT/ g-C_3N_4 Composite for Photocatalyst**, ***Hong-Shen Chen (archerchenhs@gmail.com)***, *J.-M. Ting,* National Cheng Kung University, Taiwan

In the paper, we report a new composite photocatalyst based on exfoliated g-C_3N_4 which was synthesized using a facile method. g-C_3N_4 was first prepared from bulk carbon nitride using a partial oxidation assisted supercritical fluid (SCF) method with or without Na doping. In selected experiments, various amounts of P3HT nanotubes were included for the formation of P3HT/g-C_3N_4 composites. The resulting samples were examined for the material characteristics and then used as photocatalysts in water splitting cell. We demonstrate enhanced photocatalytic performance due to the doping and/or the use of P3HT nanotubes. The performance will be discussed in terms of the material characteristics and optical/electronic properties.

Keywords: P3HT/g-C_3N_4, supercritical fluid, water splitting cell, exfoliation

10:40am **TS4-TuM9 Bixbyite-based Ta-N-O film: A Promising Candidate for Water Splitting?**, ***Jiri Capek (jcapek@kfy.zcu.cz)***, *S. Batkova, S. Haviar, M. Matas, J. Houska,* University of West Bohemia, Czech Republic*; F. Dvorak,* University of Pardubice, Czech Republic

The Ta–O–N materials are an interesting group of materials that may provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). However, it is still a big challenge to prepare highly crystalline Ta–O–N materials in a form of a thin film mainly due to their very high crystallization temperature (800–900 °C).

In our research we utilize the advantages of high-power impulse magnetron sputtering in combination with film post-annealing in a vacuum furnace to prepare single-phase Ta–O–N thin films. Recently, during our work[1] dealing with monoclinic TaON films, fine-tuning of the elemental composition of the films led to a successful preparation of bixbyite-based Ta_2N_2O films. To the best of our knowledge, this material has not been yet reported. In this work, we present the way of preparation of the films and we investigate their properties with respect to the water splitting application. The optical band gap width of this material is 2.0 eV, allowing absorption of visible light up to 620 nm and the band gap is also well aligned with respect to the water splitting redox potentials (based on the ultraviolet photoelectron spectroscopy data). Furthermore, in this work we present and discuss results of carried out ab-initio calculations providing a closer insight into the band structure of this material. Finally, we also present preliminary results of the activity of these films based on electrochemical measurements.

[1]J. Čapek, Š. Batková et al., *Effect of annealing on structure and properties of Ta-O-N films*

prepared by high power impulse magnetron sputtering, Ceram. Int. 45 (2019) 9454.

Exhibition Keynote Lecture
Room Town & Country - Session EX-TuM

Exhibition Keynote Lecture

Moderator: Christopher Muratore, University of Dayton and Air Force Research Laboratory, USA

11:00am **EX-TuM1 Carbon based Coatings in Industrial Scale for Sustainable Surface Solutions*, Jörg Vetter (joerg.vetter@oerlikon.com),*** Oerlikon Balzers Coating Germany GmbH, Bergisch Gladbach, Germany **INVITED**

The attractive properties of carbon based hard coatings include high hardness, chemical inertness, tuneable electrical resistivity and optical properties, biocompatibility, excellent tribological behaviour in many engineering applications, show a high potential for use in anti-corrosion and electrochemical applications, and have a potential for sensory applications and for fuel cell applications. The main coatings in use are amorphous carbon coatings consisting of a disordered network of carbon atoms with sp2 and sp3 coordinated C-C bonds. The family of amorphous carbon films is called "diamond like carbon": DLC. However also diamond coatings with nearly 100% sp3 carbon bond hybridization are in application. Oerlikon Balzers develops and applies industrial solutions to deposit amorphous carbon coatings based on PACVD processes, vacuum arc evaporation (direct and filtered), magnetron sputtering including newer developments of HiPIMS (e.g. S3p®). The diamond coatings are deposited by a special PACVD process or by a hot filament process. Tailored batch coating systems with different sizes are used both for large scale and small lot applications. Selected industrial coating systems will be briefly described (a-C:H:Me, a-C:H, a-C:H:X, a-C, ta-C, diamond). Typical dedicated applications of the carbon based coatings and diamond coatings including surface solutions for green car developments (e.g. ICEV, HEV, FCEV) and green manufacturing are presented.

Coatings for Use at High Temperatures
Room Pacific Salon 1 - Session A2-1-TuA

Thermal and Environmental Barrier Coatings I

Moderators: Sabine Faulhaber, University of California, San Diego, USA, Kang N. Lee, NASA Glenn Research Center, USA, Pantcho Stoyanov, Pratt & Whitney, USA

1:40pm **A2-1-TuA1 Influence of the Microstructural Evolution of YSZ TBCs on their Thermal Insulation Potential**, ***Germain Boissonnet* (germain.boissonnet@univ-lr.fr)**, *G. Bonnet, F. Pedraza,* Université de La Rochelle, France **INVITED**

Keywords Thermal Barrier Coatings (TBCs), Thermal Diffusivity, CMAS, Oxidation

Abstract. In aeronautical gas turbine engines, the metallic materials employed in the hottest sections are subject to very harsh chemical environments at high pressures and temperatures. Thermal barrier coating (TBC) systems (ceramic yttria-stabilized zirconia (YSZ) / MCrAl or NiPtAl bond coatings / inner cooling system) are employed to lower the temperature at the surface of the components, which ensures an adequate thermomechanical behaviour and reduces the oxidation/corrosion rates. However, the increase of the turbine inlet temperature for enhanced engine performance brings about new degradation phenomena (e.g. CMAS) and loss of efficiency of the TBCs [1-4]. Therefore, understanding the evolution of the insulation ability of TBCs in such harsh environments is key from both the scientific and technological perspectives to estimate the lifetime of these coatings, hence that of the engines.

Based on current plasma-sprayed (PS) and electron-beam physical vapour deposited (EB-PVD) YSZ coatings, this work seeks to provide a better comprehension on the relationships between the intrinsic properties of the current TBCs and their thermal insulation capacity as a basis for the development of future coatings. Thermal ageing, in the presence or absence of CMAS, was performed on both type of coatings and showed that the sintering of the YSZ, the evolution of crystal phases, the reactions between YSZ and CMAS and the growth of thermal oxides alter the thermal diffusivity to different extents.

References

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3. G. Boissonnet, G. Bonnet, A. Pasquet, N. Bourhila, F. Pedraza, J. Eur. Ceram. Soc. 39, 2019, pp. 2111-2121.

4. G. Boissonnet, C. Chalk; J. R Nicholls; G. Bonnet; F. Pedraza, accepted in J. Eur. Ceram. Soc.

2:20pm **A2-1-TuA3 Effect of Varying APS Flash Bond Coating Thickness on Furnace Cycle Lifetime**, ***Michael Lance* (lancem@ornl.gov)**, *K Kane, A Haynes, B Pint,* Oak Ridge National Laboratory, USA, United States of America*; E Gildersleeve, E Sampath,* Stony Brook University, USA, United States of America

The addition of an air plasma sprayed (APS) "flash" bond coating layer on top of a high velocity oxy-fuel (HVOF) bond coating has been found to significantly extend the lifetime of APS yttria stabilized zirconia (YSZ) top coatings on rod and disk specimens. In order to test the hypothesis that the flash coating forms a crack-inhibiting mixed metal-oxide zone and the HVOF layer acts as an Al reservoir, a set of superalloy 247 disks were coated with 0, 25, 50 and 100% APS layers using NiCoCrAlY powder. Groups of five specimens of each coating type were cycled to failure using 1-h cycles in air+10%H_2O at 1100°C. Residual stress in the thermally-grown Al_2O_3 scale was measured using photo-luminescence piezospectroscopy (PLPS) as a function of time for one specimen of each coating variation. Principal component analysis (PCA) of both Raman and x-ray spectroscopy maps were conducted to determine the phases present within the oxide and the bond coating. The results of furnace cycling testing and analysis of the compositions and microstructures will be presented.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy's Turbine Program.

2:40pm **A2-1-TuA4 Volcanic Ash Infiltration of Plasma Sprayed Lanthanum Zirconate based Thermal Barrier Coatings at 1250 °C**, ***Praveen Kandasamy* (mkpraveen89@gmail.com)**, *S. Govindarajan,* International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI)*; S. Gurusamy,* Bharathiar University

Yttria stabilized zirconia (YSZ) is the state-of-the-art thermal barrier coating (TBC) material, but it is highly susceptible to the reaction of calcium-magnesium-alumino-silicate (CMAS) and volcanic ash (VA) deposits in advanced aero-engines at high temperature. The limitations with YSZ have led to quest for new materials, wherein zirconates and cerates have attracted more attention due to their superior thermophysical properties. Lanthanum-zirconium-cerium oxide ($La_2(Zr_{0.7}Ce_{0.3})_2O_7$, LZC) is one such candidate TBC material with interesting thermophysical properties deemed better than YSZ for thermal barrier applications. In the present study, LZC composite phase of pyrochlore-fluorite based new ceramic material was synthesized and its coatings were generated by air plasma spraying. VA infiltration and its mitigations at two different time periods were carried out. Phase and microstructure of the coatings were evaluated before and after VA interaction and their results were discussed. Additionally, the role of ceria doping is studied by comparing with plasma sprayed pyrochlore based lanthanum zirconate ($La_2Zr_2O_7$, LZ) coating.

3:00pm **A2-1-TuA5 Electrodeposited Thin La_2O_3 Based Chromium Barrier Coating for Interconnectors in Solid Oxide Electrolysis**, ***Vladislav Kolarik* (vladislav.kolarik@ict.fraunhofer.de)**, *M. Juez Lorenzo, E. Walschburger,* Fraunhofer Institute for Chemical Technology ICT, Germany

Solid oxide steam electrolysis (SOE) using electric power from renewable sources is a promising technology to produce hydrogen for energy storage or for industrial purposes. Ferritic stainless steels are used for interconnectors between the SOE cells offering good mechanical properties and forming at high temperatures an electrically conductive Cr_2O_3 scale. In presence of water vapor however, the highly volatile and toxic $CrO_2(OH)_2$ is formed poisoning the SOE cell. To mitigate the Cr(VI) evaporation protective coatings are used.

To reduce the costs of an SOE stack, cost efficient coating processes are required. Electroplating was applied to deposit a $La(OH)_3$ layer on a Crofer 22 APU substrate with a subsequent heat treatment to transform the $La(OH)_3$ to a La_2O_3 coating. The coating thickness and morphology is controlled directly by the electroplating parameters. The electrodeposited layers are well adherent and exhibit thicknesses around 1 µm and a needle-like nano-crystalline structure. With higher layer thickness a network of thin cracks is observed. The heat treatment was followed is situ by high temperature X-ray diffraction both on heating as well as isothermally in order to adjust the parameters.

For investigating the chromium evaporation rate the coated samples as well as an uncoated reference sample were subjected in a closed furnace system to humid air with a mass flow of 2000 ml/min and a water content of 130 g/m^3 at 850°C for 500 h. On the furnace outlet the humid air was cooled to condense the water. The chromium content in the condensed water was detected by a colorimetric quick test as well as by ICP-OES analysis. The evaporation rate as a function of time was determined in time intervals of 24 h. Samples were taken out of the furnace for SEM analysis after 100 h, 200 h, 300 h and 500 h.

Chromium evaporation was found in all time intervals during the whole exposure duration. At the beginning lower chromium evaporation rates were measured with the coated samples than without coating. With longer exposure times the evaporation rate values are closer to those for uncoated steel. Areas with partial coating spallation were observed in the micrographs after longer exposure periods, probably originating from cracks that formed due to the thermal expansion mismatch. An oxide scale consisting of Cr_2O_3 and Cr-Mn-spinel formed beneath the coating as well as in the areas with coating spallation. Electrodeposition is a possible cost efficient method to produce chromium barrier coatings on interconnector steels. The process parameters however, need to be further investigated.

4:00pm **A2-1-TuA8 Avoiding Amorphous Phases with Solution Precursor Plasma Spray in YAG TBC s and Yb Silicate EBCs**, ***Eric Jordan* (eric.jordan@uconn.edu)**, *C. Jiang, R. Kumar, M. Gell,* University of Connecticut, USA **INVITED**

Atmospheric plasma spray (APS) using powders are known to produce amorphous phases for both YAG TBC s and rare earth silicates including Yb silicates. For the silicates APS processing results to selective loss of silicon. Results will be presented that show that the solution precursor plasma spray process (SPPS) produces minimal amorphous phases in both cases. In addition for Yb silicates the flexibility of the SPPS process allows accurate compensation for selective silicon loss. In addition APS produced Yb disilicates yields significant contiguous regions of mono silicate. The SPPS process yields much more nearly phase pure Yb silicates with finer regions of the second phase.

4:40pm **A2-1-TuA10 Laser Processing of Freeze Casted Yttria Stabilized Zirconia / Gadolinia Thermal Barrier Coatings to Mitigate CMAS Attack**, ***Said Bakkar (SaidBakkar@my.unt.edu)****, M. Pantawane,* University of North Texas, USA*; A. Ghoshal, M. Walock, M. Murugan,* Civ Usarmy Rdecom Arl, USA*; M.L. Young, D. Berman, N.B. Dahotre, S.M. Aouadi,* University of North Texas, USA

Yttria-stabilized zirconia and Gadolinia blend (YSZ/Gd_2O_3) ceramics with unidirectionally-aligned pore channels were created using the freeze-casting method. Preforms were prepared by freezing 70 wt% YSZ and 30 wt % Gd_2O_3 after ball milling for 15 hours /distilled water/polyvinyl alcohol (PVA) slurry under a freezing temperature of -196 °C. The frozen preform was sublimated using afreeze-drying system in vacuum (0.05 mTorr) at -85 °C. The sublimated preforms were subsequently sintered at 1600°C for 9 h in air. The surface of the sintered samples was modified using a laser process to seal its surface to mitigate CMAS (calcium–magnesium–aluminum–silicon oxide) attack. Scanning electron microscopy (SEM) revealed that the pore channels consisted of columns, which act to decrease the thermal conductivity of the (YSZ/Gd_2O_3) blend. Also, SEM confirmed that the surface treatment successfully sealed the surface. Laser processing was used to create a dense layer of sandphobic YSZ/Gd_2O_3 blend. The performance of the different surface treatment systems was compared by conducting CMAS infiltration studies. The newly designed fabrication process that combines freeze casting with laser modification was shown to be a viable technique to significantly reduce CMAS infiltration in porous thermal barrier coatings.

5:00pm **A2-1-TuA11 A Parametric Study on Optimal Design of Double-ceramic Thermal Barrier Coating**, ***JangGyun Lim****, M.K. Kim (mkkim@me.skku.ac.kr),* Sungkyunkwan University, Republic of Korea

Thermal barrier coating (TBC) is an essential system for gas turbine engine to protect hot components against impinging environment. Its thermal insulation ability can bring many benefits but there is a limitation of temperature increase because yttria-stabilized zirconate (YSZ), a conventional top coating material for TBC, experiences the harmful phase changes at a surface temperature of 1300 C. To overcome this problem, double-ceramic TBC (DT) has been suggested. DT has additional top-coats on the YSZ based top-coats to keep the temperature of YSZ lower than the operating temperature. Although many lifetime prediction models have been established based on the numerous empirical parameters, they focus on the conventional TBC. Therefore, a new lifetime prediction model is required for DT.

In this study, a finite element model for DT was constructed to evaluate the durability by considering underlying physics. Here, the durability can be quantitatively expressed by a failure index including thermal stress and intrinsic fracture strength implicitly. To verify this index, a lot of experimental data were used as references for four different top-coats in DT such as $La_2Zr_2O_7$, $La_2Ce_2O_7$, $LaTi_2Al_9O_{10}$, and $Sr(Zr_{0.8}Yb_{0.1})O_{2.95}$. As a result, the calculated failure index was correlated with the real lifetime obtained from references. Furthermore, a parametric study was carried out to optimize the specifications of DT. The parameters are material of additional top-coats and thickness ratio of two top-coats. Total 64 cases were tested for four operating temperature between 1200-1500 C. First, the minimum thickness was determined to guarantee sufficient insulation of YSZ and substrate against the critical temperatures. Then, the failure indexes were calculated and compared to suggest the optimal thickness ratio and material at each operating condition. Consequently, the proposed lifetime prediction method will be a useful design guideline of double-ceramic TBC.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B5-2-TuA

Hard and Multifunctional Nanostructured Coatings II

Moderator: Vincent Moraes, Institute of Materials Science and Technology, TU Wien, Austria

1:40pm **B5-2-TuA1 PVD of Hard Nanocomposite Coatings Using Multiphase SHS Cathodes - Evolution and New Horizons**, ***Philipp Kiryukhantsev-Korneev (kiruhancev-korneev@yandex.ru)****, E. Levashov,* National University of Science and Technology "MISiS", Russian Federation, Russia **INVITED**

The development of PVD technologies is often related with creation of new multicomponent materials that are used as precursors in deposition process. Particularly relevant is the manufacture of cathodes made of ceramics & composite materials. Since the doping of coatings by structure modifiers, such as B or Si, for example, is a non-trivial task. Among the methods of ceramic cathodes manufacturing can be noted the pressing+sintering & hot pressing technology. Self-propagating high-temperature synthesis (SHS) is the cost effective & convenient method for manufacturing of composite cathodes [1].

The SHS method allows obtaining a wide range of materials & cathodes have a high density & a low content of impurities due to self-cleaning effect in the combustion wave. In present review, the several types of advanced coatings deposited with the SHS-materials were demonstrated.

It was shown that the follow nanocomposite coatings can be produced in various energy regimes, including rigid, due to the use of functionally graded & reinforced SHS-materials (FGM & RM):

a) hard oxidation resistant MoHfSiB, MoZrSiB, & TaZrSiB coatings were obtained by DC magnetron sputtering (MS) & pulsed MS of ($MoSi_2$-HfB_2-MoB)/Mo, ($MoSi_2$-ZrB_2-MoB)/Mo, & (ZrB_2-$TaSi_2$)/Mo FGM disk targets [2] b) hard optically transparent TaSiCN coatings - by MS of $TaSi_2$-TaC-SiC-Si_3N_4 RM disk targets c) hard corrosion resistant CrB_2 & TiAlNiCN coatings - by HIPIMS using CrB_2 & TiC-NiAl disk targets [3]. d) hard wear resistant TiCrBN coatings - by ion implantation (MEVVA) or pulsed cathodic arc evaporation (PCAE) of (TiB-Cr_4Ti_9B-Cr_2Ti)/(Ti+TiB) ring FGM targets [4]. e) hard oxidation & corrosion resistant coatings - by PCAE method using CrB_2 & Cr_3C_2-NiAl rod targets. f) hard TiAlSiCN & TiCrSiCN coatings with high thermal stability/oxidation resistance - by MS of $TiAl_3$-TiC-Ti_5Si_3-AlN & TiC-Cr_3C_2-Ti_5Si_3 disk targets at high currents [5]. g) hard wear resistant soft magnetic FeTiB films - by MS of Fe/TiB_2 segment target [6] h) hard oxidation resistant SiBCN films - by ion sputtering (IS) & MS of SiC-B_4C disk SHS-targets [7].

The research was carried out under the financial support of the Russian Science Foundation in the framework of project No. 19-19-00117.

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2:20pm **B5-2-TuA3 Ti-Si-B-C-N PECVD Nanocomposite Coatings for Tribological Applications at Elevated Temperatures**, ***Alexander Nienhaus (alexander.nienhaus@ist-extern.fraunhofer.de)****,* Technical University of Braunschweig, Germany*; H. Paschke,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany

With increased demands for service lifetime of tools in hot forming applications, e.g. extrusion molding and die-casting, surface modifications of hot working steels play an important role to improve its tribological properties under thermal load. Especially the machining of aluminum (Al) and copper (Cu) is challenging, considering its tendency to stick at the tools surface, which is increasingly problematic at elevated temperatures. Developing nanocomposite Ti-Si-B-C-N coatings is a promising approach, because with an adequate Si-content, the thermal stability and oxidation resistance can be increased by forming a thin, amorphous (a-) Si_3N_4 tissue layer between the nanocristalline (nc-) grains, mostly nc-TiN, nc-TiC and nc-TiCN. High temperature (T = 750, 800 and 900 °C) in-situ XRD-measurements with synchrotron radiation showed, that, despite its high C–content of > 30 at.-%, the coatings are thermally stable up to at least 800 °C. The C-content should lead to lower coefficients of friction (CoF), as investigated by Ma et.al. (2007) for comparable Ti–Si–C–N nanocomposite coatings at room temperature, as well as at elevated temperatures (T = 550 °C). Chemically stable TiB_2 phases are formed by adding the precursor BCl_3 to the PECVD coating deposition process. These phases are not observed in XRD-diffraction patterns, which indicates a-TiB_2 rather than nc-TiB_2, e.g. in contrast to Ti–B–N nanocomposite coatings. In contact with molten or almost molten Al or Cu, B-containing nanocomposites are expected to reduce the adhesive wear on the tools surfaces. The multiphase coatings form compositionally complex nanostructures, leading to universal hardness of up to 32 GPa. So-called "superhardness" (> 40 GPa) was not observed, yet. This is due to either a high a-C content or high impurities of > 2.0 at.–% O and > 2.0 at.–% Cl. Further work will focus on reduction of impurities in the coating process, before pin-on-disc tests at T = 750 °C with Al_2O_3 counterparts will be carried out.

2:40pm **B5-2-TuA4 Erosion Properties of TiAlVSiCN Coatings Prepared by Plasma Enhanced Magnetron Sputtering***, X. Huang,* Beijing Sanju Enviro. Protect. & New Matls., China*; **Ronghua Wei (rwei@swri.org)**, J. Lin,* Southwest Research Institute, USA

A series of TiAlVSiCN coatings have been prepared on Type 304 stainless steel coupon samples using plasma enhanced magnetron sputter (PEMS) deposition by employing a design of experiment (DOE) method in order to obtain erosion resistant coatings for valve stems，valve seats and other components used in chemical industry. Erosion tests were conducted using a solid particle blaster at different incidental angles. Nanoindentation and scratch tests were used to measure the nanohardness and critical loads, while the coatings were analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) to characterize the surface morphologies 、 phase formation and microstructures. The thick coatings (>20 μm) were found to be a nanocomposite structure with nanocrystalline Ti(Al,V)(C,N) dispersed in a matrix of amorphous SiC. The nanohardness of the coatings reached to 34.6±14.1 GPa, while the coatings exhibited excellent adhesion to the substrate with a critical load of >65N. The erosion rates at 90° and 30° angles decreased by up to 7.4 and 26 times from those of uncoated tungsten carbide.

3:00pm **B5-2-TuA5 Tribocorrosion Behaviors in Seawater of TiSiCN Coatings Deposited by High Power Impulse Magnetron Sputtering: In-situ Electrochemical Response***, **Yixiang Ou (ouyx16@tsinghua.org.cn)**,* Beijing Radiation Center, China*; H.Q. Wang,* Beijing Normal University, China*; J. Luo,* Beijing Radiation Center, China*; B. Liao, X. Zhang,* Beijing Normal University, China*; W. Wang,* Beijing Radiation Center, China*; X.P. Ouyang,* Northwest Nuclear Technology Institute

To meet the requirement and needs of seawater lubrication for mechanical components in marine industry, nanostructured coatings with simultaneously high hardness and toughness are expected to deposit on component surface to enhance working performance and lifetime. Hence, in this work, TiSiCN nanocomposite coatings were deposited on Si (100) and AISI 316L stainless steel wafers by high power impulse magnetron sputtering (HiPIMS) at various peak power of 4-8 kW and negative substrate bias of 0--200V. Metal Ti and MAX phase Ti_3SiC_2 layers serve as adhesion and transition layers, respectively. Nanocrystalline (*nc*)-(TiN,TiC,TiCN)/amorphous (*a*)-(Si_3N_4, SiC, sp^2-C) nanocomposite structure is obtained in TiSiCN nanocomposite coatings, which exhibits high surface/interface integrity and dense microstructure without distinctly preferred orientation. At 7 kW and -60 V, TiSiCN/ Ti_3SiC_2/Ti coatings with high H, H/E*, H^3/E^{*2} and adhesion exhibit high open circuit potential of -0.07 V, low COF of 0.25 and specific wear rate of $6.1\times10^{-7}mm^3N^{-1}m^{-1}$, resulting from mild abrasive wear without the occurrence of pitting corrosion in 3.5 wt.% NaCl aqueous solution. Moreover, cycling tribocorrosion tests exhibit that passive films possess strong abilities of regeneration and repairation on sliding contact surface thanks to high surface/interface integrity and dense microstructure.

4:00pm **B5-2-TuA8 Synthesis and Thermomechanical Properties of Hf-C-N Coatings***, **Thomas Glechner (thomas.glechner@tuwien.ac.at)**, S. Lang,* TU Wien, CDL-SEC, Austria*; V. Moraes,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Primetzhofer,* Uppsala University, Sweden*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* TU Wien, CDL-SEC, Austria

Hafnium and Hf-based compounds such as HfC, HfB_2, or HfO_2 are highly interesting materials based on their outstanding thermal properties indicated through melting points (TM) being individually nearly the highest within their material families. This makes these Hf based systems extremely interesting for ultra-high-temperature applications such as protective coatings applied on high-performance components. Except the metallic Hf itself, all other Hf based compounds lack particularly on their low fracture tolerance. Nevertheless, for transition metal (TM) carbides serval literature reports suggest that substitutional alloying of the non-metallic sublattice by exchanging C with N atoms enhance various properties, e.g. T_M, Young's modulus, as well as fracture tolerance [1,2]. Furthermore, the enhancement of the ductile character was in detail proven for the Ta-C-N system [2]. Along with these facts and a suggested increase in oxidation resistance with respect to the binary carbides, TM-carbonitrides can be a promising alternative for protective thin film materials.

Therefore, within this study the impact of the composition on the non-metallic sublattice for the Hf-C-N system has been explored systematically with respect to thermo mechanical properties, ranging from phase stability, fracture parameters, as well as oxidation resistance. We therefore applied a combined theoretical and experimental approach using density functional theory based calculations and PVD based synthesis techniques. Hf-C thin films were deposited via non-reactive magnetron sputtering, while ternary Hf-C-N coatings have been deposited in mixed N_2/Ar atmospheres. Furthermore, to also compare the phase formation route with respect to chemical composition and grain boundary interior a Hf-C-N compound target was sputtered non-reactively. The chemical composition and morphology of all coatings deposited has been studied via ERDA and SEM/TEM, respectively. Mechanical characteristics such as hardness, Young's modulus, or fracture toughness have been accessed by different micromechanical testing techniques. The phase evolution in inert and oxidizing atmospheres was analysed by DSC/TG.

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4:20pm **B5-2-TuA9 Optimization of TiSiCN Coating Properties Obtained by RF Magnetron Sputtering and High Power Impulse Magnetron Sputtering***, **Joël Matthey (joel.matthey@he-arc.ch)**,* Haute Ecole Arc Ingenierie HES-SO, Switzerland Ecole Arc Ingenierie, Switzerland*; O. Banakh, R. Constantin, F. Bisoffi, M. Erard,* Haute Ecole Arc Ingenierie HES-SO, Switzerland

Recently, remarkable properties of the TiSiCN coatings namely low friction and good wear protection have been reported. Our study aimed at a comparison between different technologies (RF Magnetron Sputtering and High Power Impulse Magnetron Sputtering) used for the coating depositions. Operating in RF mode, a composite target Ti-Si-C was sputtered in Ar + N_2 atmosphere. In HiPIMS mode, the coatings were obtained from alloyed TiSi targets with different Si contents (15 and 25 at.%) in a gas mixture containing Ar + N_2 + C_2H_2. Tailoring the coating properties can be successfully performed with a help of the target ion-induced secondary electron emission (ISEE). Technical aspects of both technologies will be discussed in order to set a relationship between thin film properties and process parameters. Physicochemical analyses (XRD, SEM, XPS and RBS) were carried out to evaluate the coating composition, morphology and crystalline structure. Residual stresses were determined by the curvature method on glass plates. Nanohardness values up to 28 GPa and Young's modulus values up to 216 GPa were obtained while the coefficient of friction exhibited values below 0.35 against steel in an unlubricating pin-on-disk setup. The process parameters have been optimized to maximize the ion bombardment of the substrate surface by a monitoring the bias current signal with a Rogowski coil probe. The coating thickness was set to one micron onto polished steel substrates.

4:40pm **B5-2-TuA10 Ammonium Thiosulfate Precursor for Coating Molybdenum Disulfide onto the Surface of Porous Metal for High Anti-Wearing Application in the Machinery Industry***, **Lung-Hao Hu (lunghhu@mail.nsysu.edu.tw)**,* National Sun Yat-Sen University, Taiwan*; PC. Chen,* Southern Taiwan University of Science and Technology, Taiwan

High anti-wearing capability of friction coating is extremely important to any low friction and machinary industry, especially for highly automated production era coming, "Industry 4.0". Molybdenum disulfide (MoS_2) belongs to Transition-metal dichalcogenids, TMDs . It is composed of layered structures, providing excellent wear resistance due to layer sliding . In this study, a cheap and massive producible ammonium thiosulfate precursor ($(NH_4)_2MoS_4$) has been developed for coating MoS_2 layer onto the nano-porous anodic aluminum oxide (AAO) layer on the surface of 7003 series aluminum alloy. MoS_2 layer on the aluminum alloy surface is detected by scanning electron microscope (SEM). The ammonium thiosulfate precursor is pyrolyzed at 280, 375, 400 and 550°C, respectively to form the MoS_2 layer. The wearing experiment is tested by using the Surface Hardness Abrasion Tester. After 1440 m wear test, the wear rates (weight loss/original weight) of pure 7003 aluminum alloy, AAO and MoS_2 coated aluminum alloy pyrolyzed at 400°C are 0.339%, 0.017%, 0.0109%, respectively. The thickness of the molybdenum disulfide film sliced and observed by focused ion beam-transmission electron microscope (FIB-TEM) is about 40 nm. The surface hardnesses of AAO and MoS_2 coated aluminum alloy are 3~4 GPa and 5~6 GPa, respectively, measured by nanoindentation. As the result of the test, the coating of MoS_2 layer on the surface of aluminum alloy substantially enhances anti-wear capability and hardness. This coating technique is expected to be used in all kind of metal parts for improving the lifetime of automated equipment .

Hard Coatings and Vapor Deposition Technologies
Room California - Session B8-2-TuA

HiPIMS, Pulsed Plasmas and Energetic Deposition II

Moderators: Jon Tomas Gudmundsson, University of Iceland, Iceland, Tiberiu M. Minea, LPGP, Universite Paris-Sud, France

1:40pm **B8-2-TuA1 Optimizing Ionization and Deposition Rate in High Power Impulse Magnetron Sputtering***, **Daniel Lundin (daniel.lundin@liu.se)**,* Linköping University, Sweden **INVITED**

Quantification and control of the fraction of ionization of the sputtered species are crucial in magnetron sputtering. This is especially important in high power impulse magnetron sputtering (HiPIMS), since the presence of significant amounts of material ions during film growth has resulted in very smooth and dense films, control over their phase composition and microstructure, as well as enhanced mechanical and electrical properties. Yet proper definitions of the various concepts of ionization are still lacking. In this contribution, we distinguish between three approaches to describe the degree (or fraction) of ionization: the ionized flux fraction F_{flux}, the ionized density fraction F_{density}, and the fraction α of the sputtered metal atoms that become ionized in the plasma (sometimes referred to as probability of ionization). By studying a reference HiPIMS discharge with a titanium target, we show how to extract absolute values of these three parameters and how they vary with peak discharge current. Using a simple model, we also identify the physical mechanisms that determine F_{flux}, F_{density}, and α as well as how these three concepts of ionization are related. This analysis identifies ion back-attraction β as a key parameter in the ion balance between the target and the bulk plasma and finally explains why a high ionization probability does not necessarily lead to an equally high ionized flux fraction or ionized density fraction. In the second part of this contribution we seek to decrease ion back-attraction by exploring the effect of magnetic field strength $|\mathbf{B}|$ and geometry (degree of balancing) on the deposition rate and ionized flux fraction in dc magnetron sputtering and HiPIMS when depositing titanium. By investigating HiPIMS discharges operated in fixed voltage mode as well as fixed peak current mode in seven different magnetic field configurations, we relate the measured quantities, the deposition rate and ionized flux fraction, to the ionization probability α and the back-attraction probability β of the sputtered species and show that it is indeed possible to simultaneously increase both deposition rate (up to 40%) and ionized flux fraction (up to 50%).

2:20pm **B8-2-TuA3 Dynamics of the Titanium Ground State Atoms and Ions in HiPIMS Discharge***, **Jaroslav Hnilica (hnilica@mail.muni.cz)**, P. Klein, P. Vasina,* Masaryk University, Brno, Czech Republic*; R. Snyders, N. Britun,* University of Mons, Belgium

High power impulse magnetron sputtering (HiPIMS) is a very attractive physical vapor deposition technique, which has been of great interest over the last two decades. Continuous development of the HiPIMS-based sputtering discharges is tightly related to the more profound understanding of the undergoing physical processes, a crucial factor for the optimization of thin-film growth as well as for further development of sputtering technology in general.

In our study, we combined various optical diagnostic methods for in-situ characterization of HiPIMS discharges. Special attention was dedicated to the visualization of the ground state titanium neutrals and ions in the discharge volume as their direct imaging above the magnetron target is a straightforward way to obtain information about their number density. Two-dimensional time-resolved density mapping of the sputtered particles in a HiPIMS discharge was performed by laser-induced fluorescence (LIF) technique. Atomic absorption spectroscopy (AAS) measurements were utilized in parallel to LIF to follow the number density evolution of sputtered species. Above mentioned methods were used to study effects such as plasma-on time, plasma-off time, gas pressure, pulse energy, or oxygen addition on density evolution of sputtered particles.

As a result of discharge characterization, the number densities, as well as temporal propagation of the neutral and ionized sputtered titanium atoms were determined. The result shows that atoms always remain in the discharge volume, the plasma-off time duration mainly alters the amount of background sputtered atom densities at which the successive pulse starts. At the same time, the plasma pulse duration together with the pulse energy, significantly affect ionization degree of the sputtered titanium above the magnetron cathode, especially shortly after the HiPIMS pulse. On the other hand, the observed titanium atom and ion density dynamics are weakly sensitive to the plasma pulse duration which implies that the initial stages of HiPIMS pulse have a stronger influence on the sputtering process evolution.

The results obtained in this study can be utilized to control the ionization degree, sputtering rate, as well as the other discharge parameters in industrial deposition processes involving HiPIMS discharges.

2:40pm **B8-2-TuA4 Self-Organization of Plasma in RF and DC Magnetron Sputtering Discharges***, **Matjaz Panjan (matjaz.panjan@ijs.si)**,* Jozef Stefan Institute, Slovenia

Investigations of magnetron discharges over the last years showed that plasma in HiPIMS and DCMS is organized in dense and often periodic structures called spokes or ionization zones [1,2]. In the talk, we will show that periodic plasma structures also form in RF magnetron sputtering and are present over a wide range of discharge conditions [3]. The existence of spokes in continuous, pulsed and oscillatory regimes demonstrates that plasma self-organization is fundamental process in magnetron discharges and therefore important for understanding the physics of magnetron sputtering. To obtain better insight into plasma self-organization in different magnetron regimes, we studied spokes in RFMS and DCMS at similar discharge conditions using an ICCD camera and electrical probes. In both regimes, the spokes were observed for a wide range of discharge powers (50-150 W) and pressures (0.25-2 Pa). The number of spokes in the RFMS was always larger than in the DCMS when operating the discharge at the same pressure and discharge power. The number of spokes increased with the increasing gas pressure for both magnetron operations. The influence of discharge power on the number of spokes was less pronounced in both regimes. These observations suggest that the plasma self-organization in RFMS and DCMS is mainly related to the electron energy dissipation due to collisions with the gas. For this reason, we examined the inelastic collisions between electrons and argon atoms. Furthermore, we simulated the dissipation of electron energy in the drift direction and compared the calculations to the length and number of spokes for particular discharge conditions. Overall, the simulations agree well with the observed length and number of spokes for both regimes.

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3:00pm **B8-2-TuA5 Understanding and Influencing the Energy Delivered to the Film in Bipolar HiPIMS***, **Tomas Kozak (kozakt@ntis.zcu.cz)**, A.D. Pajdarova, J. Capek,* University of West Bohemia, Czech Republic*; M. Cada, Z. Hubicka,* Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic*; P. Mares,* HVM Plasma, s.r.o., Czech Republic

Benefiting from high degree of ionization of process gas and, especially, target material atoms, the high-power impulse magnetron sputtering (HiPIMS) technique provides increased energy delivered to the film resulting in hard, dense and defect-free coatings [1]. Asymmetric bipolar pulsed magnetron sputtering is one of the major techniques used for deposition of dielectric films allowing the neutralization of charge on the target during a positive voltage pulse on the magnetron. Moreover, the positive magnetron voltage causes an increase of plasma potential leading to enhanced energies of ions incident on the growing film [2]. Using the positive pulse in a HiPIMS discharge, where the degree of ionization is much higher, can result in substantial increase of energy delivered to the film and improvement of film properties [3]. Additionally, this technique might be more suitable for the industry than using separate substrate bias source.

This paper presents a systematic study of ion energy spectra in a bipolar HiPIMS discharge employing a rectangular positive voltage pulse (with controllable amplitude, delay after the main negative pulse and pulse length). The time-averaged spectra of ions measured at the substrate position exhibit a prominent high-energy peak corresponding to the ions accelerated by the increased plasma potential during the positive pulse. The position of the peak can be varied by positive pulse amplitude, its size scales with the pulse length and its width can be slightly influenced by the delay of the positive pulse. Moreover, time-resolved mass spectroscopy has been used to analyze the time of arrival of ions at various energies. Features of the energy spectra related to the magnetron voltage transients were identified. They indicate changes of the plasma potential in front of the substrate. To fully understand the ion energy spectra, the mass spectroscopy results are supported by Langmuir probe measurements of plasma and floating potential, and also electron density and temperature, at several positions in the discharge.

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4:00pm **B8-2-TuA8 The Use of HiPIMS with Positive Pulses to Tailor Film Ion Assistance and the Resulting Microstructural Properties***, **Ivan Fernandez (ivan.fernandez@nano4energy.eu)**, J.A. Santiago, A. Wennberg, A. Mendez,* Nano4Energy SL, Spain*; F. Papa,* GP Plasma, USA

Recently, it has been demonstrated that the addition of a positive voltage pulse adjacent to the negative HIPIMS sputtering pulse allows the increase of film ion assistance and thus, the improvement of coating properties on both biased and insulating substrates. Also, the energy of the incoming ions is proportional to the amplitude of the positive voltage. Some examples of experiments carried out in industrial coating machines will be presented in this study, such as the improvement on film density, mechanical properties and deposition rate in an industrial batch coater for metal nitrides, or the increased barrier performance of films deposited on PET in an industrial scale (330 mm wide web) web coater.

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4:20pm **B8-2-TuA9 Reversed Voltage as Deposition Rate Buster***, **Wojciech Gajewski (Wojciech.Gajewski@trumpf.com)**, A.W. Oniszczuk, P. Różański,* TRUMPF Huettinger sp. z o.o., Poland*; R. Mroczyński,* Warsaw University of Technology, Poland*; M. Puźniak, M. Żelechowski,* TRUMPF Huettinger sp. z o.o., Poland

Application of the so called positive or reversed pulse voltage is widely used in the DC processes. It has been shown that positive pulses applied after the cathode discharge reduces arcing rate. This results in stable processes which is very important to obtain coatings with designed stoichiometry and quality. Moreover, the appearance of the positive voltage enhances the metal ions flux towards the substrate increasing the deposition rate. Nowadays the reversed pulse feature is also accessible for the HIPIMS technology, providing new possibilities for coatings deposition.

In this work the technological aspects of the HIPIMS pulse formation with reversed voltage pulse will be introduced. Next, the optimization of the morphology and optical parameters of thin TiN coating deposited by means of the HIPIMS discharge with and without reversed pulse will be discussed. Furthermore, the applicability of the Design of Experiments - Taguchi method for power supply-related parameters influence on the coating properties will be analyzed in details. It will be shown that the Taguchi method allows to reduce the number of test runs necessary to identify the influence of critical HIPIMS parameter setting and combination on coating properties. Finally, the influence of the HIPIMS reversed voltage pulse on the TiN deposition rate as well as the coating properties will be discussed.

4:40pm **B8-2-TuA10 Evolution of Ionization Fraction of Sputtered Species in Standard, Multi-pulse and Reactive HiPIMS***, M. Fekete, K. Bernatova, P. Klein, J. Hnilica, **Petr Vasina (vasina@physics.muni.cz)**,* Masaryk University, Brno, Czech Republic **INVITED**

High power impulse magnetron sputtering (HiPIMS) technology attracts the interest of the industry as the coatings deposited by HiPIMS exhibit enhanced properties compared to conventional dc magnetron sputtered (dcMS) coatings. This is because HiPIMS generates very dense plasma, which results in a large fraction of ionized sputtered particles. However, a significant drawback of HiPIMS is a lower deposition rate compared to dcMS, which can be mitigated by operation of HiPIMS in multi-pulse mode (m-HiPIMS). M-HiPIMS further changes the coating structure and resulting properties due to the enhanced ion flux to the substrate because of the interaction of the preceding and the subsequent pulse. The evolution of the sputtered species ionization fraction is studied using a recently developed effective branching fraction method. This non-invasive method utilizes the optical emission signal to quantify the absolute ground state number densities of the sputtered titanium species. Influence of the preceding pulse on the subsequent pulse in the non-reactive m-HiPIMS process is examined as a function of delay between two successive pulses.

The sputtered species ionization fraction plays an important role also in reactive processes. In reactive HiPIMS process, the hysteresis curve is generally reduced in width and shifted towards lower reactive gas supplies compared to reactive dcMS. We report on the evolutions of the sputtered species ionization fraction in reactive HiPIMS discharges in oxygen, nitrogen and acetylene gases for a constant mean power and pulse duration, when varying the repetition frequency. The ionization fraction of the sputtered species increases with the partial pressure of the reactive gas, which was attributed to a combination of different effects taking place in HiPIMS plasma. Further, the hysteresis curve shape changes with the change of the repetition frequency. Larger ionization fraction of the sputtered species leads to larger difference in the hysteresis curve shape. The hysteresis behavior of reactive HiPIMS is modelled utilizing a modified Berg model. The back-attraction of the sputtered species to the target is incorporated into the modified Berg model. The results from simulations prove that the back-attraction of sputtered metal ions is the main effect causing the hysteresis curve reduction and shift in reactive HiPIMS compared to reactive dcMS.

Coatings for Biomedical and Healthcare Applications
Room Royal Palm 1-3 - Session D3-TuA

Biointerfaces: Improving the Cell Adhesion and Avoiding Bacteria. What Kinds of Coatings/Surfaces Should be Used?

Moderators: Vincent Fridrici, Ecole Centrale de Lyon, LTDS - Université de Lyon, France, Sandra E. Rodil, Universidad Nacional Autónoma de México, México, Danieli B.C. Rodrigues, University of Texas at Dallas, USA

1:40pm **D3-TuA1 Transferred Plasma Induced and Generated Inside a Tube by a Flexible Atmospheric Plasma Jet and its Application in Tube Inner Wall Activation***, J.H. Hsieh, **Yi-Jin Wei (yjwei@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan*; C. Li,* National Yang Ming University, Taiwan

Recently, atmospheric plasma technology has been found to have a huge potential and bright future in plasma medicine. In the meantime, tubes are indispensable in our daily life and biomedical fields. However, the practical applications of tubes are sometimes limited by their poor wettability. Furthermore, the flexibility and extendibility of plasma jets are critical in many of the bio-medical applications. In this study, silicone tubes were used to extend the length of the primary plume. Following this, the plasma jet was used to induce transferred plasma formed inside PET and PTFE tubes with varied diameters. A customized atmospheric pressure plasma jet (APPJ) equipped with unipolar pulse power supply was used to generate He plasma and act as the primary plasma jet. Then, the secondary plasma (transferred plasma) was induced by the primary plasma jet. The secondary plumes were analyzed by OES and UV absorption in order to realize the concentrations of formed radicals. In addition, electron temperature and density were calculated as a function of tube length. The effect of tube length on the density of hydroxyl (OH) and single oxygen radicals was also investigated. The results show that the densities of OH and O radicals in the second discharge decreased with the increase of tube diameter. The results of water contact angle measurement show that the tubes can be activated due to the substitution of oxygen atoms. Also, the bactericidal efficiency was influenced.

2:00pm **D3-TuA2 Onion Extract-Mediated Silver Synthesized Coatings on Aluminum with Excellent Antibacterial and Self-Disinfecting Properties**, ***Henry Agbe (henry.agbe@yahoo.co.uk)***, *D. Sarkar, X. Chen,* University of Quebec at Chicoutimi, Canada; *J. Jann, N. Faucheux, G. Soucy,* University of Sherbrooke, Canada; *J. Luc Bernier,* A3 Surfaces, Canada

The design and manufacture of high-touch surfaces with inherent antibacterial and self-disinfecting properties can reduce microbial burden and subsequent nosocomial infections in hygiene critical environment. In the present study, Alluem Cepa (onion extract) has been used as both reducing and stabilizing agent to synthesize Ag-nanocomposites, followed by a simple ultrasonic dip coating process on anodised aluminum (AAO/Al). Morphological features and chemical compositions of the Ag-nanocomposite coatings have been characterized using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction spectroscopy (XRD), UV-Vis absorption spectroscopy and attenuated total reflection-Fourier transform infrared spectroscopy (FTIR).

The as-synthesized Ag-nanocomposites demonstrate excellent antibacterial property, with zone of inhibition (ZOI) values of 25.3 ± 0.8, 20.8 ± 0.5, and 21.3 ± 3.6 mm for *Staphylococcus Aureus* (gram + ve), *Pseudomonas aeruginosa* (gram -ve) and *Escherichia coli* (gram -ve), respectively. The Ag-nanocomposite coatings on AAO/Al coupons exhibit excellent self-disinfecting property, and have potential as high-touch self-disinfecting surface and adjunct to hand hygiene for reducing infections in hygiene critical environment.

2:20pm **D3-TuA3 Advanced Materials for Implant Applications**, ***Laszlo Sajti (Laszlo.Sajti@ait.ac.at)***, *J. Horky, M. Krystian, B. Mingler, M. Bammer,* AIT Austrian Institute of Technology GmbH, Austria **INVITED**

In this talk we address a comprehensive overview of recent developments of various metallic, ceramic and polymeric biomaterials covering a broad range of implant solutions. We emphasize the cross-correlated features of these biomaterials including their surface topography, chemistry, as well as mechanical properties for both permanent and biodegradable applications. We equally address productions methods suitable for industrial processing to achieve optimized biomaterial performance regulating cell adhesion and proliferation, providing a desired antibacterial property as well as short-term and local burst release of antibiotics.

In the field of metallic implants, equal channel angular pressing of biomaterials such as low-alloyed magnesium, titanium and titanium alloys will be presented mainly for trauma, craniomaxillofacial and orthopedic implantology providing optimal mechanical properties. Concerning Mg-based biodegradable implants, we present previously unprecedented ultimate tensile strength values up to 350 MPa opening new possibilities to reconstructive surgical interventions.

We also address the importance of implant-organ and implant-cell interfaces, with the aim of developing tailored implant surfaces that support a high degree of cellular acceptance and biocompatibility. In this context, nanotechnology-enhanced implant materials are presented providing long-term antibacterial and antithrombotic behavior, preventing bacterial adhesion and for bone-anchoring applications an improved osseointegration.

These novel implant materials act as bioactive platforms towards "ideal implants" with combined material properties linking an efficient tissue regeneration with the suitable mechanical characteristics. The nano-additives are based on laser-generated ultra-pure nanoparticles, allowing specific cellular actions with full-embedding into polymeric matrices or used as implant coatings.

Finally, we report on the most important mechanical, corrosive and biological characteristics of these novel materials providing insights into their biophysical performance, durability, and strength relevant for in-vivo applications.

3:00pm **D3-TuA5 Antimicrobial Properties of Ag/Cu Doped Amorphous Carbon Coatings for Application in Aerospace**, *S. Field, G. Sanzone, P. Navabpour,* ***Jinlong Yin (jinlong.yin@teercoatings.co.uk)***, *H. Sun,* Teer Coatings Ltd, UK; *D. Lee,* Birmingham City University, UK; *J. Liu, P. Ju,* Shanghai Aerospace Equipments Manufacturer, China

Manned space station not only creates a suitable environment for astronaut's long-term presence, but also provides favourable conditions for the breeding of micro-organisms. Currently, the microbial control measures are, frequently sampling the space cabin air and surfaces to detect early signs of a rise in microbial contamination, keeping surfaces clean by the use of disinfected clothes, ensuring that all equipment is well maintained in particular the life support systems and regularly vacuuming of the spacecraft to remove dust etc. Before launch, spacecraft are sterilized, and astronauts are quarantined for several days prior to a mission. However, these measures only reduce the microbe populations rather than eliminate them.

Our proposed solution is to coat the key parts/components with antimicrobial thin films using magnetron sputtering technology. The antimicrobial coatings will eliminate or at least slow down the growth of fungi or bacterias on the surfaces. To produce such a coating, Ag, or Cu, or a mix of Ag & Cu can be doped into a matrix of wear-resistant or solid self-lubricant thin films to produce nanocomposite coatings. Many reserch works have been done via similar approach for food and beverage industry[1], and antifouling applications for marine industry.

However for the magnetron sputtered nanocomposite coatings doped with Ag, the mechanism for killing bacteria is still not clear whether it is silver ions or silver nanoparticles that are disrupting the growth of bacteria. A systematic study by T. Hrkac et al [2] demonstrated that the Ag ion concentration required to kill bacteria is higher than the concentration released from magnetron sputtering coatings. It's very likely that the disruption of the cell membrane by silver nanoparticle plays a more important role. If this is the case, it would be interesting to investigate the nanoparticle size influence on the antimicrobial performance.

In this study, we integrated a gas aggregation cluster source into a standard magnetron sputtering system. The Ag nanoparticles are produced in the cluster source, and their size distribution is tightly controlled. Then these size-controlled Ag nanoparticles are embedded into the matrix of an amorphous carbon coating which was produced by the normal magnetron sputtering. The preliminary test results of such nanocomposite coatings will be reported in this presentation, and compared with the results from normal co-deposition samples in which silver nanoparticles are formed by self-segregation.

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4:00pm **D3-TuA8 Targeting Biofilm Superhydrophobic Coating to Reduce Microbial Accumulation on Titanium Surface**, ***Bruna Nagay (bruna.eguminagay@hotmail.com)***, *J.G. Souza, R. Costa, J. Cordeiro,* University of Campinas (UNICAMP), Piracicaba Dental School, Brazil; *M. Bertolini,* University of Connecticut, USA, Brazil; *A. Almeida,* University of Campinas (UNICAMP), Piracicaba Dental School, Brazil; *B. Retamal-Valdes,* University of Guarulhos, Brazil; *F. Nociti-Junior,* University of Campinas (UNICAMP), Piracicaba Dental School, Brazil; *M. Feres,* University of Guarulhos, Brazil; *E. Rangel,* São Paulo State University, Brazil; *V. Barão,* University of Campinas (UNICAMP), Piracicaba Dental School, Brazil

Polymicrobial infections are one of the most common reasons for implanted biomaterials failure. Thus, studies have been proposing the use of superhydrophobic coatings due to its non-fouling properties to reduce microbial adhesion on biomaterials.

Therefore, the aim of the current study was to develop, for the first time, a one-step technique using low-pressure plasma technology to create a biocompatible superhydrophobic coating on titanium (Ti) surface to reduce polymicrobial biofilms formation. Based on this, we developed a superhydrophobic coating on Ti by glow discharge plasma technology using Ar, O_2 and HMDSO gases. Surface topography/morphology, wettability, roughness, film thickness, molecular structure, electrochemical behavior, proteomic profile of proteins adsorbed on surface, and biocompatibility with fibroblast F3T3-cells analyses were performed. Initial in vitro microbial (human saliva as inoculum) and fungal (C. albicans) adhesion (2 h) were tested on the coated and non-coated surfaces. S. mutans adhesion (4 h) was performed to test whether the extracellular polymers synthesized in biofilms could reduce non-fouling property of superhydrophobic surface. Polymicrobial biofilm formation (24 h) on the surfaces was tested with human saliva as inoculum, and biovolume measurements and morphology were performed. To test whether reduced biofilm formation on developed surface could enhance the effect of antimicrobials, 24 h biofilms were exposed to chlorexidine and Amoxicillin antibiotic. Colony-forming units (CFU) counts were performed for all the in vitro microbiological analysis. An in situ test, in which volunteers wore a palatal appliance containing coated and non-coated Ti discs, treated extraorally with 20% sucrose solution (4 times per day), was also conducted. After 3 days, the biofilms were collected for microbiologic analysis by checkerboard DNA-DNA hybridization (for level and proportions of 40 bacterial species).

Data analysis showed that newly developed coating presented: i) increased significantly roughness and hydrophobicity (contact angle over 150°) ($p<0.05$), ii) enhanced corrosion resistance ($p<0.05$), iii) slightly altered protein adsorption composition at proteomic level, iv) reduced microbial (bacterial and fungal) adhesion and biofilm formation in vitro ($p<0.05$), and v) 1.5-fold reduction in growth for the 40 bacterial species evaluated in situ. Furthermore, coated surfaces did not affect fibroblast viability and proliferation. Thus, this new superhydrophobic coating developed by one-step glow discharge plasma technique is a promising biocompatible strategy to reduce microbial adhesion and biofilm formation on Ti surface.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E1-2-TuA

Friction, Wear, Lubrication Effects, and Modeling II

Moderators: Nazlim Bagcivan, Schaeffler AG, Germany, Manel Rodríguez Ripoll, AC2T Research GmbH, Austria

1:40pm **E1-2-TuA1 The Synergistic Effect of Surface Texturing with TMD Coatings for Improving Friction in Lubricated Contacts***, F. Rosa,* Instituto Pedro Nunes, Portugal*; V. Richhariya, F.S. Silva,* University of Minho, Portugal*; P. Amoroso, A. Ramalho,* University of Coimbra, Portugal*; **Albano Cavaleiro (albano.cavaleiro@dem.uc.pt)**,* SEG-CEMMPRE - University of Coimbra, Portugal

Harmful additives are often added to liquid lubricants in order to reduce the contact friction and, ultimately, the wear. However, with more restricted environmental regulations, new approaches should be discussed. In the case of sliding lubricated contacts, surface texturing can be a solution for, overall, reducing the friction and, consequently, the wear. Among the methods available for surface texturing, laser technique has been one of the most used. Moreover, under certain conditions, such as high contact loads and/or low sliding speeds, oil lubrication may prove to be inefficient being surfaces coated with a self-lubricant material, such as those films based on transition metal dichalcogenides (TMD), an excellent option.

In this talk, we will present a research work where the synergetic effect of surface texturing with self-lubricant coatings is explored. Firstly, the influence of laser parameters on the shape, size, pore-aspect-ratio, area-density-ratio will be present and discussed. Different tribological conditions and tests allowed to show the difference in the tribological performance of polished and textured surfaces. Basically, Stribeck curves were determined for the different samples. Best results were found for dimple sizes close to 100 micron and a pore depth/diameter ratio close to 1/10. In the best cases, an improvement of 12% of the average total friction performance was achieved. The highest improvement occurred in conditions of boundary and mixed lubrication regimes. Then, the effect of the TMD coating was studied. For coated samples the improvements were much more significant with values over 35% in the average friction performance, again with best values in mixed and boundary lubrication regimes.

2:00pm **E1-2-TuA2 Tribological Properties of Vanadium-doped Coatings via Reactive Molecular Dynamic Simulations***, **Ilia Ponomarev (ponomili@fel.cvut.cz)**, T. Polcar, P. Nicolini,* Czech Technical University in Prague, Czech Republic

Friction and wear cause a quarter of losses of the global energy production. A well-known practical approach to reduce friction is to introduce another substance, called lubricant, to the contact surfaces. A variety of lubricants, both liquid and solid, are available on the market; the global lubricants market size was estimated at $128.51 billion in 2018.

However, friction reduction in some specific conditions may still be a challenge. Providing lubrication in oxidative environments at high temperatures, which is essential for certain technological applications, such as cutting tools, may serve an example of such a problem. Traditional lubricants, both liquid and solid, are unsuitable for the task due to their lack of oxidation resistance.

A possible solution of the problem – a hard and oxidation-resistant coating (e.g. TiN, Si_3N_4), containing a dopant that would, upon operation, diffuse to the surface of the coating and provide lubrication. Vanadium is a popular choice as such a dopant; in the operation conditions (above 700ºC, humid air) it is known to form oxides on the surface, which in turn melt, providing liquid lubrication. However, the exact mechanisms of oxidation and the effects of conditions on the resulting V_xO_y phases are not entirely clear.

We are studying the process of vanadium oxidation computationally. We use reactive molecular dynamics within Reactive Force Field (ReaxFF) approach. ReaxFF is an empirical potential, that is shown to be capable of performing at the Density Functional Theory (DFT) based methods level of accuracy, while consuming significantly less computational resources. ReaxFF enables nanosecond-long simulations for tens of thousands of atoms at the same computational cost, as hundreds of picoseconds for hundreds of atoms in DFT.

We develop a suitable ReaxFF parameterization and apply it to the oxidation simulations. We find vanadium pentoxide, V_2O_5, to be the predominant outcome of the oxidation. We study the effects of oxygen pressure, load, temperature and humidity on the oxidation rate and reaction outcome.

We further explore tribological properties of the V_xO_y phases yielded by oxidation and find out the mechanism of the vanadium oxide action. Sliding simulations in a wide range of conditions provide the answer to the question, how much V do we need for providing lubrication.

2:20pm **E1-2-TuA3 Influence of Laser Texturing Treatments on the Tribological Performance Of Tmd-C Coatings***, **Ana Manaia (ana.manaia@ipn.pt)**, T. Vuchkov,* Instituto Pedro Nunes, Portugal*; M. Shamshiri,* University of Coimbra, Portugal*; A. Cavaleiro,* SEG-CEMMPRE - University of Coimbra, Portugal

Transition metal dichalcogenides (TMD) coatings have been deposited by magnetron sputtering for applications requiring low friction, due to their layered structure and weak inter-layer bonding. However, such a lower bonding energy induces also very low mechanical strength with the low loading bearing capacity in sliding contact. One of the possible ways to improve mechanically TMD coatings is through the modification of the chemical composition by adding a third element, such as C, maintaining the tribological behavior of TMD coatings due to the occurrence of self-adaption phenomena during sliding process.

For other hand, surface texturing treatments, in particular laser surface texturing has emerged in the last decade as a suitable solution for tribological applications resulting in substantial improvement in load capacity, wear resistance and low friction coefficient mechanical components.

The novel idea behind this study is to treat locally the TMD coatings in order to induce crystallization promoting the formation of a softer easily self-adapted material dispersed in the original potential hard and self-lubrication (TMD+C coating), allowing low-friction even if the conditions for the self-adaption process are not ideal.

The aim of the present study is to improve the self-lubricity of a W-S-C coating using a laser treatment method. For these purposes, W-S -C were deposited by sputtering into steel substrates and treated by UV laser which is a pulsed UV (355 nm) Inngu Laser using different patterning solutions and laser power conditions. X-Ray diffraction on the UV treated areas confirm the existence of an amorphous structure, however the Raman spectra shows a crystallization of WS_2 in the structure which might result in a better tribological behavior. Hardness of the studied samples were evaluated by nanoindentation technique and the treated zones have lower hardness values (3 GPA) compared with untreated zones. The formation of WS_2 tribofilms on the outermost surface can be introduced as a self-lubricating mechanism and the friction of coefficient can decrease from 0,15 (reference sample) until 0,08 fiction coefficient during pin-on-disc testing against steel counter bodies.

2:40pm **E1-2-TuA4 The Thinnest of The Thin: Friction and Adhesion Behavior of Graphene and other Two-Dimensional Materials***, **Robert Carpick (carpick@seas.upenn.edu)**,* University of Pennsylvania, USA **INVITED**

Two-dimensional materials provide a rich playground for exploring new and unexpected physical phenomena at the atomic limit of thickness, and provide opportunities for many applications including demanding tribological systems. This includes protective low friction coatings and additives, functional adhesive layers in flexible electronics, and nanoelectromechanical switches. I will focus on friction and adhesion behavior of nanoscale contacts with 2D materials measured with atomic force microscopy (AFM) and compared with molecular dynamics (MD) simulations. First, nanocontacts with 2-dimensional materials like graphene will be discussed. Friction is far lower than typical bare substrates, but depends on the number of 2D material layers present. An initial model attributing this to out-of-plane puckering [1] is now enhanced by MD showing a strong role of energy barriers due to interfacial pinning [2]. We also observe a large, order-of-magnitude increase in friction when graphene is fluorinated [3]. Using MD, we interpret this in the context of the Prandtl-Tomlinson (PT) model, where the potential energy surface (PES) corrugation controls friction. We also observe a non-monotonic dependence of friction on humidity for graphite. Using MD, this behavior is attributed to adsorbed water molecules that at low coverage act as pinning sites, but at high coverage form a quasi-ordered layer that provides a low friction incommensurate interface [4].

We also discuss 2D transition metal dichalcogenide (TMD) films including MoS_2. TMDs exhibit intrinsically low friction, although not as low as graphene. Like with fluorinated graphene, we attribute this to the (PES) corrugation [5]. To explore the temperature dependence, we use matched AFM and MD to study friction for tips sliding on monolayer and multilayer MoS_2 from cryogenic to elevated temperatures. Friction sometimes decreases dramatically with temperature (thermolubricity). However, the temperature dependence is at times weak, suggesting that atomic details of the contact can matter substantially, which we explore with MD simulations. Finally, new results from nanocontact experiments of 2D materials obtained *in situ* using transmission electron microscopy (TEM) will be presented. We observe nanoscale tip-on-tip contact and sliding behavior for few layer MoS_2, revealing intrinsic contact, adhesion, and friction properties of these ultrathin layers.

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[5] M. R. Vazirisereshk *et al.* **Nano Lett.** 19, 5496 (2019).

4:00pm **E1-2-TuA8 Electrical Tuning of Vibrational Modes in Transition Metal Dichalcogenides***, **Florian Belviso (belviflo@fel.cvut.cz)**, A. Cammarata,* Czech Technical University in Prague, Czech Republic

We investigated the atomic scale tribological properties of transition metal dichalcogenides (TMDs) by using ab-initio techniques. Such compounds are formed by triatomic layers presenting MX2 stoichiometry (M: transition metal cation, X: chalcogen anion) held together by van der Waals forces.

We considered 6 prototypical MX2 TMDs (M=Mo, W; X=S, Se, Te) with hexagonal P63/mmc symmetry, focusing on how specific phonon modes contribute to their intrinsic friction.

Within the DFT framework, we described the exchange-correlation interaction energy by means of the PBE functional, including long range dispersion interactions in the Grimme formulation (DFT-D3 van der Waals).

We identified and disentangled the electro-structural features that determine the intra- and inter-layer motions affecting the intrinsic friction by means of electro-structural descriptors such as orbital polarization, bond covalency and cophonicity.[1]The study of the structural distortion modes allowed us to predict possible paths of exfoliations.

We show how the phonon modes affecting the intrinsic friction can be adjusted by means of an external electrostatic field. In this way, the electric field turns out to be a knob to control the intrinsic friction.

The presented outcomes are a step forward in the development of layer exfoliation and manipulation methods, which are fundamental for the production of TMD-based optoelectronical devices and nanoelectromechanical systems.

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4:20pm **E1-2-TuA9 Improvement of Adhesion of Sputtered Mo-S-N Coatings using a DC Magnetron Sputtering for Low Friction Applications***, **Kaushik Hebbar Kannur (khebbarkannur.ireis@hef.fr)**,* IREIS/HEF Group & University of Coimbra, France*; C. Pupier, C. Heau,* IREIS/HEF Group, France*; A. Cavaleiro,* SEG-CEMMPRE, University of Coimbra, Portugal

Transition-metal dichalcogenide (TMD) coatings tend to undergo mechanical failure due to their lamellar structure and also due to their low adhesion. An innovative technique has been used to improve the adhesion and the mechanical characteristics of the coating when deposited on steel substrate by using an additional plasma source to promote an additional ion flux to the growing film independently of magnetron sputtering.

In this research work, Mo-S-N solid lubricant films are synthesized by DC magnetron sputtering a molybdenum disulphide (MoS_2) target in a reactive atmosphere. An industrial PVD machine equipped with a single target and an independent plasma source facing the substrate was used. Nitrogen was introduced in the chamber as a reactive gas with increasing partial pressures. For high N contents the coatings became amorphous. Using N_2 as a reactive gas, it was possible to incorporate up to 35 atomic percent nitrogen in the coating. Varying the ion energy and flux of energetic species bombarding the growing film, S/metal ratio was changed to enhance mechanical behavior, by preferentially re-sputtering sulphur from the film. Then, the S/metal ratio was progressively increased from 0.3 to 1.8, to make a gradient from an almost metal layer to the required sulfide. Combining the ion bombardment of the growing film with the incorporation of N it was possible to reach hardness of 8 GPa, which is more than 10 times the one of pure MoS_2 coatings. Tribology testing of a Mo-S-N coating against a steel cylinder, using reciprocating mode has shown high wear resistance and low friction, less than 0.03 under vacuum and 0.09 in humid air.

4:40pm **E1-2-TuA10 Use of Digital Tribology to Evaluate the Combined Effect of Surface Texture and DLC Coatings during Ball-on-disk Reciprocating Tests***, **Vanessa Seriacopi (vanessaseriacopi@usp.br)**,* University of São Paulo, Brazil*; E.F. Prados, L.F.G. Ambrosi,* Federal University of ABC, Brazil*; I.F. Machado, R.M. Souza, N.K. Fukumasu,* University of São Paulo, Brazil

Hard ceramic coatings and textured surfaces can improve lubrication and contact conditions, reducing friction and wear. Combined, coatings and textured surfaces can be tailored to improve the lubrication regime and/or increase load carrying capacity. In this work, a tribological numerical-experimental approach was developed, in which the main objective consisted in evaluating the combination of hard carbon-based coatings and surface texturing on the friction and wear of steel surfaces. Ball-on-disk reciprocating tests were carried out under fully floaded boundary lubrication regime using PAO base oil, 20 and 80 N normal loads, 10 Hz frequency and 4 mm stroke length. Balls were made of AISI 52100 bearing steel, while the disks were made of AISI 4340. The following conditions for the disk were considered: (1) as-received; (2) textured; (3) coated with DLC and (4) textured and coated with DLC. The texture was produced by laser processes, generating dimples with 80 µm diameter and 360 µm pitch on the surfaces. DLC coatings were deposited using a PECVD process with low deposition temperature, resulting in a thickness of about 1.6 µm. Surface characteristics after tribological tests were analyzed by nanoindentation, micro-scratch tests, confocal microscopy, SEM/EDS and Raman spectroscopy. The digital tribology platform TriboCODE, based on the Finite Element Method, was applied to investigate stresses and strains arising from the combined effect of the coating and texture on the steel substrate. Results showed that the combination of surface texturing and DLC reduced the friction coefficient and wear of the disk surface, mainly promoted by the high hardness of the coating combined with the enhanced lubrication condition provided by the dimples. Also, surface texture provided a mechanical anchor to the coating, while DLC improved load carrying capacity, maintaining the dimple geometry in the wear track. Numerical results corroborated the experimental findings, since the stress fields were able to predict stress concentration regions (critical), which promoted coating detachment based on the load effect. Finally, damage models were applied to indicate regions susceptible to cracking, delamination, and fracture of the coating on the textured steel substrate.

5:00pm **E1-2-TuA11 Up-scale of the Deposition Process for Self-Lubricating Mo-Se-C Coatings Deposited by Magnetron Sputtering***, **Todor Vuchkov (todor.vuchkov@ipn.pt)**,* Instituto Pedro Nunes, Portugal*; M. Evaristo,* SEG-CEMMPRE - University of Coimbra, Portugal*; T. Bin Yaqub,* Instituto Pedro Nunes, Portugal*; A. Cavaleiro,* SEG-CEMMPRE - University of Coimbra, Portugal

Carbon alloyed transition metal dichalcogenide (TMD) thin films had shown promising tribological performance providing low friction and wear during tribological testing in diverse environments (e.g humid air, dry nitrogen, vacuum, elevated temperatures). Molybdenum diselenide is a TMD compound which is studied to a lesser extent, compared to the molybdenum and tungsten disulphides, which are often subjected to studies in the field of tribology. Some of the advantages of the $MoSe_2$ over the disulphides reported in the literature is the lower sensitivity to humidity, and better stoichiometry of the TMD phase. The studies reported in the literature regarding the synthesis of carbon alloyed $MoSe_2$ coating, to the best of the authors knowledge, were only made in smaller laboratory scale deposition units which can only fit small substrates with simple geometries. With the aim of upscaling the deposition process for Mo-Se-C coatings, deposition of Mo-Se-C coatings was performed by closed-field unbalanced magnetron sputtering in a semi-industrial deposition unit (UDP 650/4, Teer Coatings Ltd.). The deposition unit was equipped with 2 graphite and 1 $MoSe_2$ target. The relationship between the process parameters and properties of the deposited coatings was studied. Some of the process parameters studied were: the target to substrate distance, the power applied to the graphite targets, and the substrate bias. The carbon contents achieved were between 40 and 60 at. %. The Se/Mo ratio was higher for increased deposition distances (between 1.7 and 2). Usage of substrate bias resulted in lower Se/Mo ratio of ~1.5. The cross-sectional micrographs revealed denser columnar morphology compared to the pure $MoSe_2$ coatings. Furthermore, substrate bias usage resulted in a featureless cross-sectional morphology. All the carbon alloyed coatings were X-ray diffraction amorphous. The hardness of the carbon alloyed coatings varied between 4 and 7 GPa, depending on the chemical composition. The pure $MoSe_2$ coatings had a hardness of 0.5-2.5 GPa. The preliminary tribological studies revealed coefficient of friction of 0.08-0.12 and 0.04-0.07 in normal laboratory air and under dry N2 environment, respectively. The wear rates were between 5×10^{-7} and 3×10^{-6} mm^3/Nm.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific Salon 2 - Session G3-TuA

Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

Moderators: Stepan Kyrsta, Oerlikon Balzers Coating, Luxembourg, Christoph Schiffers, CemeCon AG, Germany

1:40pm **G3-TuA1 Characterization of Different AlCrN PVD Coatings Deposited into H13 Steel for Lube-free Aluminum Die Casting Application***,* ***Nelson Delfino de Campos Neto (ndelfino@mymail.mines.edu)****, A.L. Korenyi-Both, S.P. Midson, M.J. Kaufman,* Colorado School of Mines, USA

In the high-pressure die casting process, organic lubricants are sprayed onto the die surface prior to each shot to prevent the liquid aluminum from soldering and sticking to the steel die. The organic-based lubricants act as a parting agent, but also produce several undesirable outcomes including: i) reducing the quality of the castings by increasing the amount of entrapped gasses, ii) increasing production costs, and iii) producing effluents that must be treated and discarded. However, portions of the die that become extremely hot, such as small core pins, are difficult to lubricate, and so PVD coatings are often applied to these areas to assist in minimizing soldering. Ideal PVD coatings for die casting applications must exhibit excellent adhesion to the die substrate, have good mechanical and tribological properties, high oxidation resistance, and exhibit chemical inertness to and/or be non-wetting by liquid aluminum.

Recent research at the Colorado School of Mines examined whether PVD coatings could be used to minimize or eliminate the use of conventional organic lubricants during die casting, and a test was developed to quantitatively measure the adhesion strength of aluminum die casting alloys solidified against PVD coated steel substrates. Three PVD coatings (AlCrN, AlTiN and CrWN) were identified where the aluminum die casting alloy exhibited zero adhesion strength to coated substrates. To evaluate the performance in a commercial die casting environment, an entire H13 steel die was PVD coated with AlCrN, and the testing demonstrated that the PVD coating enabled a reduction in the required amount of conventional lubricant spray by around 85%.

To further reduce or eliminate the use of conventional lubricants, coatings with improved non-wetting behavior need to be identified. In the present study, three different AlCrN-based PVD coatings have been examined, and characterization techniques have been used to determine their structure, mechanical properties, wear resistance and adhesion resistance to molten aluminum alloys. This study has demonstrated that small differences in the AlCrN coating can led to appreciably improved performance.

2:00pm **G3-TuA2 12 µm in PVD with HiPIMS***,* ***Christoph Schiffers (christoph.schiffers@cemecon.de)****, T. Leyendecker, W. Kölker,* CemeCon AG, Germany

Higher coating thickness gives higher wear volume. Today's standard in tool coatings is 3-4 µm. More than 6 µm is for traditional coating technologies not a viable option due to excessive intrinsic stress. No real improvement are the usual work arounds such as bond coats and multilayers with soft intermediate layers. The process gets slower and more prone to failures. A dense morphology with low compressive stress is needed.

HiPIMS is a good candidate since it is known for a dense structure without any droplets resulting in toughness and hardness at the same time. The real innovative leap is stress management by synchronising the HiPIMS pulses on the cathodes with the substrate bias. This paper will introduce the concept of selective ion biasing. Plasma analytics reveal that the flux arriving at the substrate per HiPIMS pulse is composed of the wanted metal ions coming from the target and other ion portions which highly influence the intrinsic stress of the growing film. Selective ion biasing is a fully new tool and allows to precisely select certain ion portions out of the pulse while suppressing unwanted species. Now the coating developer can actively tune the intrinsic stress of the film by setting the synchronisation parameters.

Full control on the process and the growing film – that's the quantum leap of selective ion biasing. And this for different HiPIMS frequencies and pulse data for each and every cathode – tailored for the respective target material.

A case study of FerroCon®Quadro as a 12 µm PVD coating illustrates how HiPIMS moves the frontiers of the possible in tool coatings. Applications such as the milling of crank shafts, railway tracks and heavy duty turning show the enormous performance benefit of very thick PVD coatings for cutting tools. 12 µm PVD work, in HiPIMS.

2:20pm **G3-TuA3 Smart PVD Hard Coatings with Temperature Sensor Function***, K. Bobzin, T. Brögelmann,* ***Nathan Christopher Kruppe (kruppe@iot.rwth-aachen.de)****, J. Janowitz,* Surface Engineering Institute - RWTH Aachen University, Germany

In manufacturing technology, such as machining and primary forming, the performance of the tools have to conform to increasingly higher standards. Aditionally, recording process data during production is becoming more and more important in the Industrie 4.0. Thin hard coatings serving as protection from wear and corrosion have been state of the art in many manufacturing applications for years. Integrating additional features into the coatings will help extend the process limits faced by the manufacturing technology. One approach here is to exploit the electrical properties of thin films to design sensors for temperature measurement. The overall objective of this study is therefore the design of new, smart wear and corrosion protective coatings by means of physical vapor deposition (PVD) on the example of aluminum die casting. These coatings should facilitate an online measurement of the surface temperature in the interface between tool and aluminium alloy melt for temperatures between room temperature and processing temperature of several hundred degrees Celsius. The two presented multilayer coating systems consist of hard coatings. Their temperature sensor function is based on the thermoelectric effect. Electrically insulated by Al_2O_3, the one material pair consists of the monolithic layers TiAlN and CrAlN. The other material pair consists of the monolithic TiAlN and the nanolaminate CrN/AlN. Besides analyzing the coating properties, the focus of the investigations is on the temperature sensor function. In addition to reference measurements using calibrated thermocouples and thermography, the temperatures are determined using the measured electrical potential differences of the sensor coating. While both coating systems have promising mechanical properties and a sufficient adhesion to the steel substrate AISI H11, the sensor coating TiAlN + CrN/AlN is characterized by a significantly better temperature sensor function. This study has proven that measuring of the surface temperature is possible, especially with this multilayer hard coating.

2:40pm **G3-TuA4 Silicon in Cutting Tools***,* ***Albir Layyous (alayyous@netvision.net.il)****,* Layyous Consulting, Israel*; L. Qiu,* Central South University, China **INVITED**

Silicon have been used widely in cutting tools, started as Silicon Nitride base, followed by SiC whiskers reinforcement of Al_2O_3, Silicon alloying of PVD and CVD coatings, has been proved to enhance the machining performance of TiAlN base coatings, furthermore Silicon Carbide thin layers were coated successfully as wear resistance or interlayer for diamond coating. Recently CVD TiSiN and TiSiCN coatings were prepared and investigated successfully in a commercial CVD hot-wall reactor, where hardness and oxidation resistance were increased. Importance of silicon usage in cutting tools was reviewed.

Key Words: Cutting Tool, Silicon Alloying, Physical Vapor Deposition, Chemical Vapor Deposition

4:00pm **G3-TuA8 Cross-sectional Characterization of Microstructural, Phase and Elemental Changes during High-Temperature Oxidation of AlCrSiN Coatings***, **Nikolaus Jäger (nikolaus.jaeger@unileoben.ac.at),*** Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; S. Spor,* voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany*; M. Meindlhumer,* Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Austria*; H. Hruby, F. Nahif,* voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany*; C. Mitterer,* Montanuniversität Leoben, Austria*; J. Keckes,* Erich Schmid Institute for Materials Science, Austrian Academy of Sciences, Leoben, Austria*; R. Daniel,* Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Austria

Increasing demands in machining and forming industry towards advanced applications such as dry cutting or high-speed machining stimulate the development of coatings with enhanced properties to protect the surface of tools and workpieces under extreme conditions. Besides substantial requirements on the mechanical properties, also thermal stability and oxidation resistance play a key role in high-temperature applications.

In this work, the high-temperature oxidation of AlCr(Si)N coatings with 0, 2.5 and 5 at.% Si-content was studied. Differential scanning calorimetry together with thermogravimetric analysis and ex-situ X-ray diffraction revealed a shift of the on-set temperature for oxidation from 1100°C for AlCrN to 1260 °C for both Si-containing coatings and a much slower oxidation progress for the latter due to their nanocomposite microstructure. In addition to these conventional characterization methods, an AlCrSiN coating with 5 at.% Si was partially oxidized at 1400 °C for 1 h and studied along its cross-section to investigate microstructural and elemental changes during high-temperature oxidation.

X–ray nano-diffraction of the sample cross-section revealed the formed phases, residual strain state and structural variations across the coating thickness: (i) A dense oxide layer at the surface comprising mainly of Al2O3 and Cr2O3 protected the coating from further oxidation. (ii) Below this oxide layer, a fine-grained transition zone with incomplete oxidation was found. (iii) The bottom half of the coating was not oxidized and consisted only hexagonal AlN.

A detailed TEM analysis allowed for a better understanding of the microstructural and elemental changes during oxidation and revealed: (i) a separation of the oxide layer into an Al-rich and a Cr-rich part, (ii) a strong outwards diffusion of Cr into the oxide layer and (iii) a pronounced separation of the not oxidized part of the coating into Al-rich and a Si-rich grains.

4:20pm **G3-TuA9 PVD Coated Tools and Surface-structured Workpieces in Dry Cold Forming of Steel***, K. Bobzin, T. Brögelmann, N.C. Kruppe,* Surface Engineering Institute - RWTH Aachen University, Germany*; T. Bergs, P. Mattfeld, D. Trauth, R. Hild,* Laboratory for Machine Tools and Production Engineering - RWTH Aachen University, Germany*; **Dennis Christopher Hoffmann (hoffmann@iot.rwth-aachen.de),*** Surface Engineering Institute - RWTH Aachen University, Germany

Cold bulk metal forming, particularly forward extrusion, is used for mass production of steel components. To ensure robust forming processes, the state of the art is phosphating the workpieces and the use of lubricants which is harmful to the environment and health. Therefore, phosphating and lubricants should be substituted by new approaches from an ecological, economic and legislative perspective. To achieve dry, lubricant-free cold forming of steel, two approaches are being pursued here. The tool-sided approach focuses on self-lubricating hard coatings, which are deposited on the forming tools by means of physical vapor deposition (PVD). The developed coating system (Cr,Al)N+Mo:S is synthesized by the hybrid technology direct current magnetron sputtering/high power pulsed magnetron sputtering (dcMS/HPPMS) in an industrial coating unit. It consists of a hard matrix (Cr,Al)N which is modified by Mo and S to provide friction reduction due to the formation of MoS_2 reaction layers under tribological load. The workpiece-sided approach focuses on the surface structuring by shot peening with various peening materials and particle shapes. In order to reproduce the load collective during the extrusion of steel, the developed coating system (Cr,Al)N+Mo:S was tested in a pin-on-cylinder (PoC) tribometer against four structured counter parts which simulates an open tribological system. Here, a coated pin of AISI D2 is pressed with F_N = 2,600 N and a defined feed onto a rotating cylinder of AISI 5115. Furthermore, a heating device was integrated which heats the pin up to T = 250 °C. Subsequently, the pins were analyzed by confocal laser scanning microscopy (CLSM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The self-lubricating coating system leads to a significant friction reduction of up to 40 % compared to the tested uncoated pins. Wear analysis reveal that the coated specimens exhibit less adhesive and abrasive wear. Furthermore, an influence of the particle shape on the adhesive wear could be observed. Based on these tests, the performance of the coating system in interaction with different workpiece topographies was tested in forming trials using an industrial press. For this purpose, forming dies with an aspect ratio of 2.5 were successfully coated throughout the inner geometry. The subsequent analyses show that the coated dies have led to a significant reduction of the necessary punch forces and occurring wear. Hence, the developed coating system (Cr,Al)N+Mo:S exhibits great potential to conduct dry, lubricant-free cold bulk metal forming processes at industrial scale.

4:40pm **G3-TuA10 Coating Design for Components for Extreme Applications***, **Ricardo Alexandre (ricardo@teandm.pt),*** TeandM - Technology, Engineering and Materials, S.A., Portugal **INVITED**

Coating design plays a paramount role in coating performance enabling performance increases in industrial components and tools.

Thru the decades, coating design development has evolved from simple single layer coatings to more and more complex designs, starting from bilayers to current advanced nanostructures.

When we look at extreme applications are these coatings able to protect and functionalize the surface successfully? At what extend production processes can be impacted? What about complying with demanding and restrictive product specifications?

The application, at industrial scale, of sophisticated coating designs poses limitations? What kind?

These are questions challenging, not only, coating developers, but also job coaters in direct contact with the market applications, where clients bring about complex and demanding surface treatment challenges driven by productivity focused production processes and sophisticated products.

In order to bring some light into these questions four case studies will be presented. These case studies combine extreme working conditions (wear, corrosion, temperature, etc.) with product/process demanding specifications. Coating designs, its performance impact and industrial scale coating challenges and limitations will be discussed.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific Salon 6-7 - Session H3-TuA

Characterization of Coatings and Small Volumes in Harsh Environments I

Moderators: Thomas Edwards, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, James Gibson, RWTH Aachen University, Germany, Peter Hosemann, University of Californa at Berkeley, USA

1:40pm **H3-TuA1 Investigating Plasticity Effects on Failure and Fracture at the Microscale***, **Nathan Mara (mara@umn.edu),** K. Schmalbach,* University of Minnesota, USA*; R. Ramachandramoorthy, J. Michler,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; W. Gerberich,* University of Minnesota, USA **INVITED**

Due to pronounced effects of sample size on the measured mechanical response, a major challenge persists in correlating microscale measurements to macroscale measurements, especially for ductility and fracture. For brittle materials with small plastic zone size relative to the sample size (e.g., Si), micro cantilever and 3-point bending have shown promising results. However, for semi-brittle (e.g., W) materials, the plastic zone size becomes comparable to the sample dimension and thus the conventional analysis methods based on linear-elastic and elastic-plastic fracture mechanics prove difficult or impossible to apply. We intend to address the challenges of diminished sample size inherent to evaluating fracture behavior at the microscale through investigation of the Ductile-to-Brittle Transition (DBT) in materials such as Si, SiC, and W. By using the DBT as our benchmark to bulk fracture behavior, we present an investigation of the interplay of sample size with the onset of increasing plasticity with temperature on fracture behavior. Trends in activation parameters will be discussed in terms of changes in dislocation-based mechanisms as a function of test temperature, strain rate, and loading state, and used to predict fracture behavior based on an analytical model.

2:20pm **H3-TuA3 High Strain-Rate Mechanical Characterization of Small Volumes and Coatings by Nanoindentation***, **Benoit Merle (benoit.merle@fau.de)**,* Materials Science & Engineering 1, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Constant strain rate nanoindentation is a popular method for accessing the local strength of complex materials. However, with currently available testing systems using continuous stiffness measurement (CSM), nanoindentation is so far limited to strain rates of ~0.1 s-1, which precludes it from high strain rate applications.

Here, we show that the current limitation derives primarily from a plasticity issue related to the continuous stiffness measurements. Using a "sweet spot" frequency one order of magnitude higher than the standard harmonic oscillation, we show that valid hardness measurements are possible up to ~1 s-1.

In order to access even higher deformation rates, the Oliver-Pharr evaluation method was modified, so as to avoid the need for a measurement of the contact stiffness. With this improvement, the experimental upper strain rate limit is mostly determined by the time constants of the hardware components and lies around 100 s-1 with most current commercial systems.

2:40pm **H3-TuA4 Local Deformation Mechanisms under Ambient and Non-ambient Conditions Tested via Advanced Nanoindentation***, **Verena Maier-Kiener (verena.maier-kiener@unileoben.ac.at)**,* Montanuniversität Leoben, Austria **INVITED**

Nanoindentation over the recent years established itself as a versatile tool for probing local mechanical properties beyond hardness and modulus. By adapting and improving standard nanoindentation testing methods, reliable protocols capable of probing thermally activated deformation processes can be accomplished. Abrupt strain-rate changes within individual indentations allow determining the strain-rate dependency of hardness at various indentation depths. For probing lower strain-rates and excluding thermal drift influences, long-term creep experiments can be performed by using the dynamic contact stiffness for determining the true contact area. From both procedures hardness and strain-rate, and consequently quantities such as strain-rate sensitivity, activation volume and activation energy can be reliably deducted within individual indentation tests, permitting information on the locally operating thermally activated deformation mechanism.

This presentation will first discuss various testing protocols including possible challenges and improvements, with particular emphasis towards testing at higher temperatures and under hydrogen atmosphere. Second, it will showcase different examples highlighting the direct influence exerted by microstructure and environmental conditions on the underlying deformation behavior in pure and highly alloyed material systems.

4:00pm **H3-TuA8 W-based Nanocrystalline Binary Alloys: Thermal Stability at High Temperatures***, **Tomáš Polcar (t.polcar@soton.ac.uk)**, T.H. Huminiuc, A. Alasqalani,* University of Southampton, UK

The reduction of grain size is a well-known route to improve the mechanical properties of alloys. Pure nanocrystalline metals show remarkably high strength, arising in connection with reduced dimensionality and small grain size. Yet, the use of such materials is severely limited, in particular due to a microstructural instability that significantly reduces strength over time [1]. Such instability is inextricably linked to the small crystalline grains and the consequently large grain boundary area. Indeed, the associated high interfacial energy finally induces the coarsening of the microstructure, which in turn results in the softening of the material. The addition of solutes to nc-metals can slow coarsening to a significant extent, yet it does not eliminate the tendency of the microstructure to coarsen. A thermodynamic approach exhibits greater promise. The thermodynamic analysis of nc-metal alloys indicates that minority species tend to segregate at grain boundaries, which allows a decrease of the grain boundary (GB) energy, and thus a reduction of the grain boundary mobility. Under such conditions, nc-metal alloys with a positive enthalpy of grain boundary segregation minimize the Gibbs free energy at a certain grain size, and attain a thermodynamically stable nanostructure.

We deposited four W-X alloys (X = Ti, Ta, Ag, Al) by magnetron sputtering and analyzed their structure before and after annealing (up to 1600 K) by transmission electron microscopy including in situ observation at high temperature. In particular, we focus on the segregation of solute elements and the growth (or absence of) of the grain size. The experimental results have been complemented by thermodynamic and ab initio simulations. Nanoindentation was employed to analyze the effect of annealing on mechanical properties. Finally, sputtered alloys are compared by those prepared by ball milling/sintering methods.

4:20pm **H3-TuA9 High Temperature Erosion Performance Evaluation of Advanced Materials***, **Debdutt Patro (debdutt.p@ducom.com)**, S. Josyula, H. Prasanna,* Ducom Instruments, India*; F. Alemano, D. Veeregowda,* Ducom Instruments, Europe

High temperature erosion testing at temperatures exceeding 600°C involves simultaneous erosion-oxidation interactions that can affect the interpretation of the erosion rates reported from such experiments. Ducom high temperature air jet erosion tester was used to conduct erosion tests at 1000°C on both alumina ceramic and Inconel 600 superalloy using alumina as an erodent. Erosion tests were conducted on as-received samples as well as pre-conditioned samples. Gravimetric and profilometric analysis was conducted after the test to obtain erosion rates and volumetric loss and SEM was conducted on the scar to identify the damage mechanisms. The magnitude of oxidative weight gain was found to be comparable to erosion related weight loss. Observed erosion rates were different for as-received and pre-conditioned samples with the pre-conditioned samples showing better repeatability. The high temperature erosion rates of IN 600 vs. alumina tested at different angles and SEM images indicate characteristic ductile and brittle erosion behavior respectively. The study highlights the importance of pre-conditioning of samples on (a) accurate erosion performance assessment of materials and (b) repeatability during high temperature erosion testing of materials.

Topical Symposia
Room Pacific Salon 3 - Session TS2-2-TuA

New Horizons in Boron-Containing Coatings: Modeling, Synthesis and Applications II

Moderators: Marcus Hans, RWTH Aachen University, Germany, Helmut Riedl, TU Wien, CDL-SEC, Austria, Johanna Rosen, Linköping University, Sweden

1:40pm **TS2-2-TuA1 Superior High-temperature Behavior of Amorphous Coatings from Quinary Hf-B-Si-C-N System***, **Petr Zeman (zemanp@kfy.zcu.cz)**, S. Zuzjakova, R. Cerstvy,* University of West Bohemia, Czech Republic*; E.I. Meletis,* University of Texas at Arlington, USA*; J. Vlcek,* University of West Bohemia, Czech Republic

Multielement ceramic coatings are appropriate candidates for high-temperature applications due to their excellent behavior at temperatures exceeding 1000°C. When the excellent oxidation resistance is combined with the thermal stability of a high optical transparency, they can be applied for high-temperature passive protection of optical and optoelectronical devices. On the other hand, a combination of the high oxidation resistance and the thermal stability of the electrical conductivity makes them suitable for capacitive pressure, vibration or tip clearance sensors in a severe oxidation environments.

The present work focuses on systematic investigation of high-temperature behavior of two amorphous Hf-B-Si-C-N coatings with different electrical and optical properties. The coatings were prepared by reactive pulsed dc magnetron co-sputtering of a B_4C-15%Hf-20%Si target in two Ar+N_2 mixtures (15% and 20% N_2 fractions). Particular attention is paid to thermogravimetric analysis and differential scanning calorimetry of the coatings in air and Ar, and to the evolution of the film structure, microstructure and elemental composition with increasing annealing temperature from 1100°C to 1700°C.

The coating prepared at the 15% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{22}C_6N_{40}$ and is electrically conductive, while the coating prepared at the 20% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{17}C_4N_{45}$ and is optically transparent. Both coatings are sufficiently hard (≈ 20 GPa) and exhibit a superior oxidation resistance up to 1600°C due to the formation of a nanocomposite diffusion barrier surface layer consisting of HfO_2 nanocrystallites surrounded by a borosilicate amorphous matrix. A small difference in the composition results, however, in a different thermal stability of the amorphous structure of the coatings above 1400°C. While the $Hf_7B_{23}Si_{17}C_4N_{45}$ coating underneath the oxide layer retains its amorphous structure, the $Hf_7B_{23}Si_{22}C_6N_{40}$ coating crystallizes into different phases (Si_3N_4, B(C)N, HfCN, HfB_2) with a unique self-organized structures [1,2].

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[2] *"Microstructure evolution in amorphous Hf–B–Si–C–N high temperature resistant coatings after annealing to 1500 °C in air"*, Y. Shen, J. C. Jiang, P. Zeman, V. Simova, J. Vlcek, E. I. Meletis, Sci. Rep. **9**, 3603 (2019).

2:00pm **TS2-2-TuA2 Mechanical Property Evaluation of VNbMoTaWCrB Refractory High-entropy Alloy Thin Films by Micropillar Compression and Nanoindentation**, ***Yen-Yu Chen (cyy15@ulive.pccu.edu.tw)***, Chinese Culture University, Taiwan*; S.-Y. Chang Chang,* National Tsing Hua University, Taiwan*; S.-B Hung Hung, C.-J. Wang Wang,* National Taiwan University of Science and Technology, Taiwan*; J.-G Duh Duh,* National Tsing Hua University, Taiwan*; J.-W. Lee Lee,* Ming Chi University of Technology, Taiwan

Refractory high-entropy alloys (HEAs) show outstanding mechanical and thermal properties than traditional alloys. Recently, the application of HEA thin films as functional and protective coatings has been widely investigated. Following our previous studies on VNbMoTaW based refractory HEA thin films, the mechanical properties of the thin films were further investigated by micropillar compression and nanoindentation methods in this study. A series of VNbMoTaWCrB thin films were fabricated by a pulse direct current magnetron sputtering method. The hardness and elastic modulus of thin films were evaluated by nanoindentation. The yield strength of each HEA micropillar under uniaxial compression was analyzed. The elastic and plastic deformation behaviors and the fracture toughness of these HEA thin films were studied. The effect of Cr and B concentrations on the hardness, elastic modulus, and fracture toughness of VNbMoTaWCrB HEA thin films were also discussed in this work.

2:20pm **TS2-2-TuA3 Thick Nitrogen-Doped Boron Carbide Coatings on Planar and Spherical Substrates by Magnetron Sputtering**, ***Paul Mirkarimi (Mirkarimi1@llnl.gov)****, A. Engwall, L. Bayu Aji, J. Bae, S. Shin, M Bagge-Hanson, C Walters, A Nikroo, S. Kucheyev,* Lawrence Livermore National Laboratory, USA, United States of America

Boron carbide is an attractive inertial confinement fusion (ICF) ablator and a unique ultra-hard material with numerous current and potential applications. However, the fabrication of thick, adherent, high-quality boron carbide coatings has proven to be very challenging, particularly in the case of deposition onto curved substrates. Here, we study the deposition of thick (> 10 microns) films of boron carbide on both planar and spherical substrates by magnetron sputtering. We focus on how film properties can be controlled via nitrogen doping and thermally-activated and radiation-induced stress-relaxation. Particular emphasis is on understanding the effects of nitrogen incorporation, substrate temperature, and the angle of incidence of the depositing species on film nucleation and growth. This work was performed under the auspices of the US DOE by LLNL under contract DE-AC52-07NA27344.

2:40pm **TS2-2-TuA4 Boron-containing Metallic-glass Coating: Unique Properties and Various Applications**, ***Jinn P. Chu (jpchu@mail.ntust.edu.tw)***, National Taiwan University of Science and Technology (NTUST), Taiwan **INVITED**

A group of thin film metallic glasses have been reported to exhibit properties different from conventional crystalline metal films, though their bulk forms are already well-known for properties such as high strength because of their amorphous structure. Boron is one of the widely-used constituents for forming metallic glasses. Amorphous FeB-based alloys are excellent examples for this case, which have been developed for widely use as the energy efficient transformer core material. In this presentation, I will give a review of unique properties of this type of coating, followed by the first-ever metallic glass nanotube (MGNT) arrays on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter, with wall thicknesses of ~103 nm. Two examples are presented based on modifications of this scheme. First, the MGNT array is prepared on a heating device on Si wafers and, with an applied electric voltage to the heating device underneath, the array surface is functioned as biomimetic artificial suckers for thermally adhesion response in biological systems. Second, after modification of biotin, the MGNT array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin. The detection limit of the MGNT arrays for streptavidin is estimated to be 25 nM. Thus, the MGNT arrays may be used as a versatile platform for high-sensitive label-free optical biosensing.

4:00pm **TS2-2-TuA8 Boron Carbide Thin Films for State-of-the-Art Neutron Detectors at the ESS**, ***Jens Birch (jens.birch@liu.se)***, Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

The European Spallation Source (ESS), currently being built in Sweden, will be capable of delivering neutron beams more than an order of magnitude brighter or more intense than existing neutron sources, which will enable faster neutron scattering experiments on new materials using new techniques. For best utilization of the brightness and intensity, novel thin film based neutron-optical components, such as mirrors and larger area detectors, are being developed.

Combining expertise in neutron/detector science at the detector groups of ESS and Institut Laue-Languevin (ILL) in Grenoble with thin film materials science at the Thin Film Physics division at Linköping University, we have successfully developed affordable ^{10}B -based thin film neutron converter coatings, that allows for eliminating the present unsustainable use of the rare isotope ^{3}He in state-of-the-art neutron detectors.

The primary material choice is magnetron sputter deposited B_4C, enriched in the neutron absorbing isotope ^{10}B. As opposed to pure ^{10}B coatings, $^{10}B_4C$ thin films can be grown with properties that fulfill the requirements of being mechanically and chemically stable as well as being radiation hard, while maintaining a high volume density of ^{10}B. These properties are essential for implementation in complicated detectors at large scale infrastructures such as the ESS. Despite the known tendency of B_4C to generate high compressive stresses during thin film growth, we show that well adherent 1µm thick films with residual stress as low as 0.09 GPa can be grown by DC magnetron sputtering at a substrate temperature of 400°C. By employing HiPIMS it is possible to lower the substrate temperature to ~100°C which is useful for sensitive substrates such as PCBs.

The implementation of $^{10}B_4C$ thin film neutron converters in large area detector designs have been tested in prototypes and demonstrators at ILL, ISIS (UK) and SNS (Oakridge USA) which have shown that the performance of $^{10}B_4C$-based large area detectors for scattering, reflectometry, as well as time-of-flight inelastic spectroscopy performs on par or better than the ^{3}He-based counterparts. Thus, ESS is now aiming for equipping a majority of its foreseen detector area with $^{10}B_4C$ thin film-based technology, this will require more than 6000 m^2 of $^{10}B_4C$ coatings.

The line-of-sight nature of the sputter deposition process for $^{10}B_4C$ film growth poses limitations on the production as well as design of the detectors. An outlook where employing conformal coverage deposition methods will be presented, allowing future $^{10}B_4C$ neutron detectors to be solid state devices with sensor pixels in the range of 10x10 μm^2 (rather than the present ~cm^2).

4:40pm **TS2-2-TuA10 Effects of Thermal Annealing on Structure and Mechanical Properties of $MgAlB_{14}$ Thin Films Deposited by DC Magnetron Sputtering**, ***Sathish Kumar Shanmugham (sathish.kumar.shanmugham@liu.se)***, Linköping University, IFM, Thin Film Physics Division, Sweden*; A. Petruhins, J. Rosen, P. Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

The influence of deposition and post-deposition annealing temperature on the micro-structure, morphology and mechanical properties of $MgAlB_{14}$ thin films prepared by DC magnetron sputtering technique was investigated. The $MgAlB_{14}$ films were deposited on Si(100) substrates at two different substrate temperatures (25 °C and 350 °C). The as-deposited films were annealed ex-situ in argon atmosphere at 350 °C, 500 °C, 700 °C and 1000 °C for 2 hours. The effects of thermal annealing on structure, morphology and mechanical properties were investigated by X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and nanoindentation. The as-deposited films were amorphous at both 25 °C and 350 °C substrate temperatures. The results indicate that the structure, morphology and mechanical properties of the films did not significantly change at lower annealing temperature up to 500 °C. At higher temperatures above 500 °C the annealing caused increase in crystallinity with the formation of polycrystalline orthorhombic $AlMgB_{14}$ phase at 1000 °C. The film surface examined by the atomic force microscopy revealed that the root mean square (rms) roughness increased from 3 nm to 32 nm with increasing annealing temperature. Significant increase in nanoindentation hardness and Young's modulus with increasing annealing temperature were observed, as compared with as-deposited films. A maximum hardness of 26 GPa with the corresponding modulus of 242 GPa was exhibited by the $MgAlB_{14}$ thin films annealed at 1000 °C.

5:00pm **TS2-2-TuA11 Recent Process Development of Magnetron Sputtering Deposited Boron Carbide Thin Films for Neutron Detection at the European Spallation Source**,
***Chung-Chuan Lai (chung-chuan.lai@esss.se)**, C. Höglund, P.-O. Svensson,* Detector Group, European Spallation Source ERIC, Sweden*; L. Robinson,* Detector Group, European Spallation Source ERIC,Sweden, Sweden*; J. Birch, L. Hultman,* Thin Film Physics Division, IFM, Linköping University, Sweden*; R. Hall-Wilton,* Detector Group, European Spallation Source ERIC, Sweden

The construction of European Spallation Source (ESS) is aimed to build the brightest large neutron spallation source for research in material science. Since the decision made in 2009 to site ESS in Lund, Sweden, the staff in ESS has pushed forward the development in all fields to fulfill the goal of a world leading research facility. In line with increasing needs and costs for helium-3 (^{3}He), design and development of neutron detectors using boron-10 (^{10}B) gain practical value as a promising alternative for large area neutron detectors in ESS. Amorphous boron carbide (a-B_4C) is a common chemical form of choice for the detectors mainly due to its 80 at.% of B stoichiometry, chemical stability, and non-toxicity. In ESS Detector Group, a reliable and reproduceable direct-current magnetron sputtering deposition process for amorphous boron carbide (a-B_4C) coatings has been developed by ESS Detector Coatings Workshop in Linköping, Sweden, in collaboration with Linköping University. The process produces coatings with good adhesion to Al and Ti substrates, low H and O content, ~85 % mass density of bulk B_4C, and good radiation hardness. On top of this, the Coatings Workshop are continuously developing new processes of depositing a-B_4C coatings on a wider range of substrate materials or dimensions for the needs of various detector designs, e.g., PCB materials (G-10 and FR-4), other metals (Cu and Au), glass, Al foils with a thickness down to 18 mm, and removable substrates for stand-alone B_4C films. Characterization of the coatings helps to determine the influence of changing deposition parameters, such as substrate temperature, working pressure, and substrate materials, as well as a possible tradeoff of desired properties, such as low O content. We have also observed changes in the microstructure related to the difference in surface material and smoothness, which can further affect the physical properties or adhesion of the deposition films. Development of the coating processes has allowed the Coatings Workshop to be the go-to facility for institutes to search for a new generation of neutron detectors using $^{10}B_4C$ films, which is the core technology for more than half of the instruments in ESS.

5:20pm **TS2-2-TuA12 Fe-based Thin Film Metallic Glass Coated on Porous Substrates as an Alternative Photocatalysts for Decolorization of Dye in Industrial Wastewater**,
***Bryan Hubert (bryan_hubert_alim@yahoo.com)**,* National Taiwan University of Science and Technology,Taiwan, Taiwan*; J.P. Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan*; P.M. Yiu,* National Taiwan University of Science and Technology, Taiwan

Two different kinds of Fe-based thin film metallic glasses (TFMGs) with atomic composition of $Fe_{65}Ti_{13}Co_8Ni_7B_6Nb_1$ and $Fe_{41}Cr_{15}Co_7Mo_{14}C_{15}B_6Y_2$ were fabricated by magnetron sputtering deposition on various porous substrates to act as a catalyst for dye decolorization. This method showed high potential for effectively coated TFMGs with lower heat required and low-cost process, while Fe-based TFMGs coated on various kind of porous substrates i.e. filter paper exhibited higher color removal efficiency and faster dye decolorization performance compared to the bare filter paper. This result was occurred due to Fe-based TFMGs was a zero-valent iron which had an amorphous atomic packing structure to activate sulfate radical as an reactive species to decompose organic material in dye solution become non toxic substance and its surface contact area enhancement.

The synthesized TFMGs were first characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) to check its morphology, deposition quality, and chemical composition, followed by X-Ray Diffraction (XRD) to confirm its amorphous structure. Photocatalytic activity of TFMGs that involved peroxymonosulfate (PMS) activation on the degradation of typical industrial dye in wastewater, i.e. Naphthol Green B (NGB) were investigated under combination of various parameters, such as LED irradiation, dye concentration, PMS concentration, film thickness, and catalyst amount. The reusability of TFMGs as a catalyst were also studied in this experiment by repeating the degradation process for multiple times. The result was further discussed in this study by the related authors.

Special Interest Talks
Room Town & Country - Session SIT2-TuSIT

Special Interest Session
Moderator: Grzegorz (Greg) Greczynski, Linköping University, Sweden

7:00pm **SIT2-TuSIT1 Design, Metallurgy and Manufacturing Technologies of Targets for Hard Coating and Tribological Applications***, Peter Polcik (peter.polcik@plansee.com),* Plansee Composite Materials GmbH, Germany **INVITED**

Today, major share of tools and components is coated with hard coatings utilizing physical vapor deposition methods. The continuous improvement of coatings takes place by introducing new architectures and by implementation of new compositions in thin films designed for special applications. Furthermore, the coating suppliers work on cost and quality optimization for mass product implementation. The results of these efforts are for instance larger coating chambers and shorter process times leading to new target dimensions and shapes as well as the increase in power density applied to the targets.

The targets used for hard coating applications are produced either by powder or by melting metallurgy processes. Targets manufactured by powder metallurgy are characterized by several advantageous properties such as uniform microstructure, high density, as well as homogeneity concerning distribution of chemical elements. The quality of such targets depends on the manufacturing process and for the most part on the quality of the powder ingredients used.

Different ongoing developments of hard coatings are focused on beneficial effects by alloying with selected elements to control the composition of the coating. The big challenge is to apply a suitable technology for production of targets containing all these elements on the one side and to consider the impact of the purity of the targets on the whole production chain and the performance of the final product on the other side. In order to support the efforts of equipment manufacturers and coating designers, new technologies must be applied to produce targets in appropriate shape and dimensions.

The application driven demand on no reactive driven PVD processes requires ceramic based targets consisting of carbides, nitrides, borides or even mixtures of such phases. The challenge is to provide such targets not only suitable for lab scale coating equipment but also for large scale industrial PVD coaters. Further examples of target materials developed recently, utilizing sophisticated manufacturing technologies, are metal doped graphite as well as composite materials doped with elements increasing coating deposition rates.

To deliver cost-optimized targets for mass applications the whole process chain, including powder quality and standardization of raw materials, must be considered. The mentioned efforts, comprising the increase of target utilization, are also strongly related to the increase in power density applied to the targets. Therefore, the development of materials with high heat conductivity and thermal shock resistance are included in the challenges for target suppliers.

Coatings for Use at High Temperatures
Room Pacific Salon 1 - Session A2-2-WeM

Thermal and Environmental Barrier Coatings II

Moderators: Sabine Faulhaber, University of California, San Diego, USA, Kang N. Lee, NASA Glenn Research Center, USA, Pantcho Stoyanov, Pratt & Whitney, USA

8:00am **A2-2-WeM1 Advances in the Development of Highly Crystalline EBCs by Advanced Plasma Spray Processes***, **Molly Gentleman O'Connor (Molly_Gentleman@praxair.com)**,* Praxair Surface Technologies Inc., USA*; M. Sweet,* Praxair Surface Technologies, Inc., USA **INVITED**

The development of robust environmental barrier coatings by plasma spray has been limited by the propensity of environmental barriers to retain significant volume fractions of amorphous phase in the as sprayed state. This material upon crystallization experiences a change in volume that can crack the coating decreasing the environmental protectivity. As a result, conventional processing routes require the use of significant post-deposition heat treatments to crystallize the coating slowly to minimize the effects of volume change induced cracking in the coating. In this review, the use of cascaded torch technology combined with highly crystalline phase pure powders will be discussed as a possible path to expand the processing capability window of EBC coatings. Praxair Surface Technologies' Inc. proprietary coating deposition process will be discussed and examples of highly crystalline EBC coating in the as sprayed condition will be presented. Characterization and performance data will be discussed.

8:40am **A2-2-WeM3 Characterization and Performance Testing of Highly Crystalline as-sprayed EBCs***, **Kenneth Kane (kaneka@ornl.gov)**,* Oak Ridge National Laboratory, USA*; M.L. Sweet,* Praxair Surface Technologies Inc., USA*; M. O'Connor,* Praxair Surface Technologies, Inc., USA*; B.A. Pint,* Oak Ridge National Laboratory, USA

Next generation gas turbines will rely heavily on ceramic matrix composite components to achieve increased operating temperatures and higher efficiencies. To protect those components from severe oxidation and subsequent volatilization, improved durability environmental barrier coatings (EBCs) must be designed. One major challenge to achieving this goal is the propensity of rare earth (RE) silicate EBCs produced by atmospheric plasma spray (APS) to have significant volume fractions of vitreous and metastable phases present in the as-sprayed condition. To address this, post-deposition heat treatments to obtain the stable crystal structure are often employed. Recently a method was developed for depositing crystalline EBCs without a post-deposition heat treatment or auxiliary heating during deposition. Furnace cycle testing in air+90%H2O has been conducted on conventional and crystalline-deposited EBCs to determine the advantages of improved crystallinity on coating performance. Oxidation kinetics, silica scale structure and morphology, and coating cyclic life performance will be compared. This work was sponsored by the U. S. Department of Energy, Office of Fossil Energy, Advanced Turbine Program and Praxair Surface Technologies Inc. Research and Development.

9:00am **A2-2-WeM4 Thermal-Corrosive Properties of Y_2SiO_5 Environmental Barrier Coatings under Isothermal Heat Treatment***, **Byung-Koog Jang (jang.byungkoog@kyudai.jp)**,* Kyushu University, Japan*; S.W. Kim, Y.S. Oh, S.M. Lee, H.T. Kim,* Korea Institute of Ceramic Engineering and Technology, Republic of Korea

The improvement of the gas turbine inlet temperature is a key factor involved in increasing the fuel efficiency and reducing the carbon emissions of a gas turbine. Due to the high limit point of temperature capability, non-oxide silicon-based ceramics, such as SiC/SiC_f, Si_3N_4 and SiC, have been investigated extensively as potential structural material for hot gas parts for next-generation gas turbines. However, abundant investigations have indicated that the disadvantageous factor of Si_3N_4 and SiC as it applies to gas turbines is that they lose observable weight in the combustion environment.

In the present study, the influence of isothermal heat treatment on thermo-corrosive properties of Y_2SiO_5 EBCs (environmental barrier coatings) on SiC was investigated. The hot corrosion between Y_2SiO_5 coatings and artificial CMAS ($CaO–MgO–Al_2O_3–SiO_2$) was examined by isothermal heating at 1400°C in air during 1~50 hrs. The evaluation of hardness and Young's modulus was performed on the cross-section of Y_2SiO_5 coatings by nano indentation method. The isothermal heat treatment improves the hardness and Young's modulus of Y_2SiO_5 coatings.

9:20am **A2-2-WeM5 Studies on Microstructure and Properties of Thick Mo Coatings obtained via Molten Salt Electrolysis***, **Subir Kumar Ghosh (sghosh@barc.gov.in)**, J. Varshney, C. Srivastava, V. Kain,* Bhabha Atomic Research Centre, India

Refractive metals and their alloy coatings have got tremendous attention in recent years because of their inherent higher temperature oxidation resistance and mechanical properties, corrosion resistance to molten salt and hydrogen permeation barrier applications in ITER and hydrogen storage appliances. In this study, thick metallic Molybdenum (Mo) was electrodeposited on various metallic substrates by molten salt electrolysis from oxide-fluoride based electrolyte. The effect of current density and electrolyte temperature on coating thickness and quality of coating were investigated. Detailed parameter optimization was done to obtain compact, defect free smooth thick Mo-coating. GIXRD of the coatings confirmed about the deposition of bcc Mo metal with strong texture along <110> direction. Cross section FESEM attached with EDS of the coating revealed deposition of nonporous and uniform deposition of Mo coating with good adhesion to Cu and Cu pre-coated stainless steel substrates. It was also observed that even though thick defect-free Mo coating can be directly deposited on SS substrates but the chemical attack on SS by the highly corrosive electrolyte led to formation of weak substrate/coating interface. Adhesion of Mo-coatings on various substrates was measured quantitatively using adhesion tester and the results were analyzed in detail. The measured microhardness of the coatings was correlated with microstructure and composition. In addition to this, the results related to hydrogen permeation across the Mo-coating will also be discussed.

Keywords: Mo coating, Molten salt electrolysis, FESEM, GIXRD

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9:40am **A2-2-WeM6 Development of Hydrogen Barrier Coatings based on Tungsten Alloys***, **Issam Lakdhar (issam.lakdhar@utt.fr)**, A.A. Alhussein,* Université de Technologie de Troyes (UTT), France*; J. Creus,* LASIE, CNRS-Université de La Rochelle, France

Nowadays, hydrogen energy, classified as one of the cleanest energy sources, developed in the industrial countries around the world presents a substitution for oil and other fuels. However, the transport and the storage of the smallest chemical element at ambient conditions still a crucial issue because hydrogen can dissolve, permeate in any metallic material and cause its embrittlement and failure (pipelines, tanks …).

Surface treatment is one of the solutions used to protect metallic structures used in the hydrogen industry. The coating barriers are an effective and practical option to reduce hydrogen permeation. In general, two crucial parameters govern the process of hydrogen permeability: the diffusion coefficient and solubility. Some bulk materials have a low hydrogen permeability in particular W[1],Mo, Ti and ceramics (e.g. SiC[2]and alumina Al2O3).

The goal of this work is to develop hydrogen barriers based on tungsten-alloy thin films (ternary alloys W-C-Si /W-Al-C) and alternative nitride and carbide multilayers (WC/TiN) elaborated with physical vapor deposition technology. According to some specifications, protective coatings must be dense and without defects. The optimization of elaboration parameters was necessary to obtain good films. Many characterizations were carried out (SEM, XRD, Scratch and Nano-indentation,…) to understand the influence of film microstructure, morphology and chemical composition on the hydrogen permeation through the coatings. The coating efficiency was evaluated under hydrogen with doing chemical and electrochemical loadings and the hydrogen quantity absorbed was determined with analytical and experimental methods (Thermal-Desorption Spectroscopy (TDS)).

The mechanical characterizations (tensile and fatigue tests) are performed to evaluated the real behavior of a coated structure under hydrogen. The coating performance as a barrier will be compared with other films reported in the literature and should allow us to continue our development for advanced coatings to increase the life duration of structures under hydrogen.

Keywords: Thin films, Barrier coatings, Hydrogen industry, PVD, electrochemical and mechanical properties.

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11:00am **A2-2-WeM10 Different Additions of Fluoride to the Image of the Wear Behavior of the tc$_4$ Alloy as a Hard and Lubricated Phase at High Temperatures*, Zikun Xie (1102729399@qq.com),*** *X.F. Cui, G. Jin, E. Liu, W. Su,* Harbin Engineering University, China

In this study, TC4-10CaF$_2$ (CaF$_2$ coating) and TC4-10CaF @Ni [mailto:TC4-10CaF2@Ni(10wt.%25)] (CaF$_2$@Ni coating) coatings were successfully fabricated on the TC4 substrate by plasma cladding technology. The formation and evolution of tribo-layer was confirmed by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive X-Ray Spectroscopy (EDS). The maximum microhardness of CaF$_2$ coating and CaF$_2$@Ni coating were 525.5HV and 417.5HV, respectively. Compared with substrate and CaF$_2$ coating, CaF$_2$@Ni coating presented brilliant wear performance from 25 ℃to 600 ℃. The wear loss of CaF$_2$@Ni coating decreased 75.4% compared to substrate at 600 ℃The wear mechanism of tribo-layer transited from abrasive wear to oxide wear and adhesive wear with temperature increased. The excellent wear performance depends on the stable and consecutive oxide layer. No accumulation of fluoride was found. Through the analysis of the wear loss and the SEM images of the wear surface, the tribological behavior of CaF$_2$ coating was subjected by the softening of CaF$_2$. Meanwhile, the soft Ni@CaF$_2$ promoted the formation of dense oxide layers at high temperature.

Keywords: TC4/CaF$_2$ and TC4/CaF$_2$@Ni coatings; Plasma cladding; Friction and wear

Acknowledgements

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11:20am **A2-2-WeM11 Corrosion Resistance and Fatigue Behavior of Bare and Coated Ni-based Superalloys*, Sebastien Dryepondt (dryepondtsn@ornl.gov),*** *R.P. Pillai,* Oak Ridge National Laboratory, USA*; J.M. Kurley,* Oak Ridge National Laboratory, USA, United States of America

Rising temperature in land-based gas turbines has led to an increase of corrosion degradation of turbine blades operating at ~700-750º C. MCrAlY overlay bond coatings with or without a thermal barrier coatings (TBC) can provide some protection against this type 2 low temperature hot corrosion attack, but the coating impact on the blade mechanical performance needs to be evaluated. Hot corrosion testing in O_2+0.1%SO_2 environment with NA_2SO_4 salt deposition at the sample surface was conducted on bare CM247, Rene 80 and IN738 at 700º C for up to 100h. Systematic image analysis of the corroded specimens revealed a deeper metal loss for the IN738 alloy compared to the CM247 and Rene 80 alloys. Coupons of Rene 80 coated with two different types of MCrAlY coatings or MCrAlY + TBC were also exposed. Significant reduction of mass losses was observed for the MCrAlY coated samples, but the coatings were heavily oxidized after 60h of exposure. On the contrary, the MCrAlY + TBC coating was very protective with very limited corrosion attacks. Finally, low cycle oxidation testing was initiated on bare and coated CM247 specimens at 750º C in air and first results with a total deformation of 0.8% showed no impact of the coating on the number of cycles to failure. The next step is to conduct similar fatigue tests in a corrosive environment.

11:40am **A2-2-WeM12 Effects of Mo Interlayer on the Oxidation Behaviour and Degradation Mechanism of Amorphous SiAlN Coating at 1000 °C in Steam Environment*, Zhaohe Gao (zhaohe.gao@manchester.ac.uk),*** The University of Manchester, UK*; J.K. Malecka, P.J. Kelly,* Manchester Metropolitan University, UK*; P. Xiao,* The University of Manchester, UK

Loss-of-Coolant Accident (LOCA) in a Light Water Reactor, such as occurred in the Fukushima Daiichi Power Plant, could be potentially mitigated by applying an oxidation-resistant coating onto the surface of the Zr alloy fuel rod as accident tolerant fuel cladding. In this study, 1.1 µm thick SiAlN amorphous coatings, consisting of AlN nanoparticles dispersed in an amorphous Si_3N_4 matrix, have been deposited on Zr alloys with 300 nm or 750 nm Mo interlayers and studied in a steam environment at 1000°C. The SiAlN coating with a 750 nm Mo exhibits excellent oxidation resistance without observable oxide scale after up to 4 hours at 1000°C, while the coating with a 300 nm Mo forms a thin oxide scale in an identical atmosphere after 1 h. The downward diffusion of Si into underlying Zr alloy, followed by relatively faster outward diffusion of N, generates excessive Si and lean N in the outmost surface of SiAlN, thereby resulting in the oxidation of the amorphous coating. A critical composition content of N below which oxidation can happen is predicted and verified. The sluggish effect of Mo on the downward diffusion of Si has also been discussed and this study provides a new insight into the degradation mechanism of this amorphous coating.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B3-WeM

Deposition Technologies and Applications for Diamond-like Coatings I

Moderators: Chris Engdahl, Crystallume, USA, Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

8:00am **B3-WeM1 Tribological Characterizations of Si-doped Diamond-like carbon (DLC) Deposited by FCVA with TMS Gas Against to AISI 52100 Ball*, Jisoo Kim (kimjs@kims.re.kr),*** *J. Kim, Y.-J. Jang, Y.-J. Kang, J. Kim,* Korea Institute of Materials Science (KIMS), Korea, Republic of Korea

Diamond-like carbon (DLC) is one of the most promising materials for tribological applications having superior surface properties including low friction, high hardness, and wear resistance. In addition to the DLC film itself, many previous researches revealed that additional metallic and organic dopants enhanced tribological properties of DLC films by forming the transfer layer composed of low frictional components. Especially, in case of silicon (Si), the formation of silicon-rich oxide debris critically reduced running-in period and friction coefficient of DLC films. Although the reduction of friction coefficients (FCs) incorporating silicon into the DLC film was widely studied, it is yet to be explored that how Si-doping can affect the structure of DLC film deposited using filtered cathodic vacuum arc with tetramethylsilane (TMS) gaseous media. Furthermore, the type and effect of transfer layer on tribological characteristic during the running-in period is also still unclear.

In this study, Si-doped DLC film was deposited using FCVA with TMS gas in terms of gas flow rates. And the tribological characteristics of them against to AISI 52100 (SUJ2), bearing steel, ball were specified through ball-on-disc wear tests. Although FCVA generally forms tetrahedral amorphous carbon (ta-C) without dopants, additional use of TMS gas increased the working pressure up to 0.4 Pa and induced sp^2 (C-H)-rich carbon structures. The composition of silicon increased up to ~20 at.% by using 12 sccm of TMS gas flow rate. A sudden increase of Si fraction was observed using higher flow rate than 7 sccm because the working pressure became higher than 0.4 Pa when the higher flow rate than 7 sccm was used. The FC and running-in period decreased following the increasing flow rate of TMS gas. At lower Si fraction than ~10 at.%, tribofilm composed of iron oxides increased friction and induced fluctuation of FC with relatively long running-in period. However, with the higher fraction of Si, tribofilm composed of silicon-rich oxides was quickly and stably formed during the tribological interaction with the AISI 52100 ball. This tribofilm could prevent the direct contact of steels with DLC films inhibiting the formation of Fe_2O_3 which can lead critical worn out of steel balls increasing friction coefficient. Thus, it could be concluded that Si-doped DLC film could obtain lower FC than 0.1 with extremely short running-in period by the rapid formation of silicon-rich oxides tribofilm and this could prevent the formation of iron oxides which can critically increase FC and worn-out of the counter material, AISI 52100 bearing steel.

8:20am **B3-WeM2 DLC Coatings Deposited by Novel Doping Strategies with HiPIMS*, José Antonio Santiago Varela (joseantonio.santiago@nano4energy.eu),*** Nano4Energy SL, España*; I. Fernández-Martínez, A. Wennberg,* Nano4Energy SL, Spain*; M.A. Monclús, J.M. Molina-Aldareguia,* IMDEA Materials Institute, Spain*; V. Bellido-Gonzalez,* Gencoa Ltd, UK*; M. Panizo-Laiz,* Universidad Politecnica de Madrid, Spain*; J.C. Sánchez-Lopez, T.C. Rojas,* CSIC, Spain*; S. Goel,* Cranfield University, UK*; J.L. Endrino,* IKERBASQUE, Spain

Diamond-like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its many properties, DLC stands out for a good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear. Nevertheless, a factor limiting the widespread application of DLC coatings is their thermal stability. DLC is very temperature-sensitive since its sp^3-sp^2 structure undergoes a graphitization process at high temperatures that deteriorates both hardness and coefficient of friction. In order to overcome this limitation, new ways to modify DLC coatings for acceptable high temperature performance have been explored. In this work, we investigated a novel deposition technique of hard DLC coatings doped with various elements (e.g. W, Cr, Ti, Si) using HiPIMS by incorporation of positive pulses. Highly ionized plasma discharges were obtained during HiPIMS deposition. The high ion energy bombardment resulted in a higher sp^3 to sp^2 bond ratio. EELS and Raman spectroscopy were used to characterize the sp^3 and sp^2 structures in the deposited films. Nanoindentation tests revealed improved mechanical properties (hardness up to 35 GPa) for doped DLC coatings. Additional high temperature nanoindentation tests performed in the range of 27 ºC to 450 ºC showed that the mechanical properties at high temperature are dependent on the sp^3 content. Pin-on-disk tests were carried out in order to assess the tribological performance of the coatings both at room and high temperature. The increased toughness and reduced compressive stress that doping provides to the carbon matrix together with a high sp^3 bonding structure obtained with HiPIMS deposition improves the stability of DLC coatings for high temperature tribological applications. Finally, micromilling trials were carried out to assess the performance of these doped DLC coatings in micromachining of Ti6Al4V samples and compared to an uncoated tool, an increased tool performance was obtained.

8:40am **B3-WeM3 Lab Grown Diamond and Its Applications***, Bohr-Ran Huang (huangbr@mail.ntust.edu.tw),* National Taiwan University of Science and Technology, Taiwan **INVITED**

Diamond is well known as one of the most valuable gems and possesses many excellent properties, such as an extremely high degree of hardness, high thermal conductivity, high electrical resistivity, chemical inertness, and good optical transparency. When properly doped with impurities, diamond also has potential as a useful semiconducting material. and it has been demonstrated as promising candidate for several applications. Since 1950, scientists had been trying to synthesize diamond(lab grown diamond) by many kinds of chemical vapor deposition techniques. Syntheses and applications of diamond, diamond-like, polycrystalline diamond and nano-diamond are reviewed. Especially, nano-diamond based microelectronic devices are highly reliable and efficient in multifunctional applications.

The key properties of the nanodiamond materials with excellent electrical and optical properties certainly encourage several progressive pioneering technologies by tailored developments. Markedly, the nanodiamond materials comprise of ultra-nano sized grains, which is less than 100nm in size with significant grain boundaries, revealing superior electrical conductivity than diamond films with micron sized grains these makes it a highly stable material. Moreover, the emerging technologies makes nano-diamond a cost-effective materials. The applications of nanodiamond are not used only in bio-electronics and vacuum applications, but also in photodetectors, gas sensors, microplasma devices, VOC sensors and electro-chemical sensors.

9:20am **B3-WeM5 Effects of Target Poisoning on the Microstructure and Mechanical Properties of WC_x Coatings Fabricated by Superimposed HiPIMS and MF System***, **Igamcha Moirangthem**, J.-W. Lee (jefflee@mail.mcut.edu.tw),* Ming Chi University of Technology, Taiwan

The high power impulse magnetron sputtering (HiPIMS) technology leads into a new era in the thin film fabrication, which draws lots of attention from researchers and industries. To improve the low deposition rate of HiPIMS, the superimposition concept by introducing middle frequency (MF) pulses during off-time of HiPIMS pulsing was adopted for fabrication of transition metal nitride hard coatings. Tungsten carbide and tungsten doped diamond-like carbon coatings (DLC) are characterized by their excellent chemical and tribological properties, high hardness, low friction and high wear resistance. In this study, WC_x coatings including tungsten carbide and tungsten doped DLCs were fabricated at different tungsten target poisoning ratios using a superimposed HiPIMS and MF power system. The microstructure and phase of WC_x coatings were investigated by a field emission scanning electron microscope and X-ray diffractometer. Surface morphology and roughness were examined by an atomic force microscope. The hardness and adhesion of the coatings were characterized by nanoindentation and scratch tester. The friction coefficients of the coatings were measured by a pin-on-disk tribometer. Effects of target poisoning on the phase, microstructure, deposition rate and mechanical properties of WC_x coatings were explored in this work.

9:40am **B3-WeM6 Preparation of Hybrid ta-C/MoS_2-Films by using Laser Arc Technology***, **Frank Kaulfuss (frank.kaulfuss@iws.fraunhofer.de)**, F. Hofmann, Y. Han, F. Schaller,* Fraunhofer IWS, Germany*; T. Kruelle,* Fraunhofer IWS,Germany, Germany*; S. Makowski, V. Weihnacht, A. Leson, L. Lorenz, M. Zawischa,* Fraunhofer IWS, Germany

Hydrogen-free ta-C coatings are already used to reduce friction in lubricated environments. The application under minimum quantity lubricated and non-lubricated boundary conditions remains a great challenge. The addition of the dry lubricant MoS_2 is intended to improve the performance characteristics of the ta-C in this case. For the production of ta-C coatings, the Laser Arc process is particularly suitable, with which very hard and low-defect coatings can be produced. MoS_2 targets can be combined and alternately evaporated using the same technique.

By adapting the discharge conditions, ta-C/MoS_2 layers could be produced in different variants. In addition to ta-C with simple MoS_2 top layer, multilayers with alternating deposition were also produced with single layer thicknesses in the nanometer range. The plasma states of the components, which have a large influence on the layer formation, were investigated as well as the cathode spot behaviour at the different materials (graphite, MoS_2). The investigations also concentrated on the mechanical properties of the layers, which were determined by SEM, TEM, X-ray diffraction, nanoindentation and scratch testing. In addition, tribological tests provide information on the influence of the layer structure in different applications.

11:00am **B3-WeM10 Effect of Mechanical and Thermochemical Steel Substrate Pre-treatment on DLC Coating Durability***, D. Tobola,* Institute of Advanced Manufacturing Technology*; **Tomasz Liskiewicz (t.Liskiewicz@mmu.ac.uk)**,* Manchester Metropolitan University, UK*; L. Yang,* Leeds University, UK

DLC coatings are becoming well established across many industrial sectors including aerospace, automotive, oil and gas, and cold forming tools. While DLC coatings exhibit good mechanical properties and low coefficient of friction for themselves, DLC coating–substrate systems may suffer from insufficient wear resistance. This is typically due to mismatch in mechanical properties of the DLC coating and the substrate material, as the coating design is often done in isolation from the coating-system design [1]. This paper describes the wear mechanisms and reports characteristics of the DLC coating-steel substrate system behaviour after mechanical and thermochemical steel substrate pre-treatments.

We have investigated two tool steel substrates, Sverker 21 (AISI D2) and advanced powder metallurgy alloyed steel Vanadis 8. Initially, the substrates were heat treated in vacuum furnace and gas quenched resulting in hardness of 59±1 and 64±1 HRC respectively. Subsequently the samples were subjected to mechanical turning and burnishing with 130N and 160N forces, using diamond composite tools with ceramic bonding phase [2]. Afterwards, a nitriding process was carried out in two different ways: in a vacuum furnace with subsequent polishing, and in a PVD chamber as a plasma nitriding pre-treatment for subsequent DLC coating deposition.

Two different DLC types were deposited for comparison including WC doped and undoped coatings [3]. Coated samples were subjected to a series of ball-on-disc wear tests against Al_2O_3 and Si_3N_4 counterparts. X-ray diffraction (XRD), instrumented indentation, scanning electron microscopy (SEM), and laser confocal microscopy were employed to examine the phase composition, nano-hardness, Young's modulus, surface microstructure, elemental distribution and 3D surface topographies of the wear scars. Selected variable factors including the type of steel, the burnishing force, type of counter-body material and applied coating system were subjected to statistical analysis. The effect of sequential processes used as pre-treatment on DLC coating durability was demonstrated and the results are discussed in light of improving the cold forming tolls tribological performance.

11:20am **B3-WeM11 Effect of Long Carbon Bombardment Step on the Adhesion of Thick H-free DLC Coating Deposited by Cathodic Arc Evaporation***, **Felipe Mazuco (felipesmazuco@gmail.com)**,* University of Sao Paulo, Brazil*; J.A. Araujo,* MAHLE Metal Leve - Tech Center, Brazil*; R.M. de Souza,* University of Sao Paulo, Brazil

The tribological behavior of H-Free DLC coatings result in important industrial applications in automotive components and machinery parts. In these applications, demands for thicker coatings (up to 30 um) have recently grown. The main restriction in the application of thick hydrogen-free DLC coatings is the adherence to the substrate, since the high compressive stresses tend to delaminate the coating when a certain thickness is reached. Many studies were conducted in the last two decades to enhance the adherence of DLC by interfacial modifications. The most promising strategies are related to the use of a metal intermediate layer and to the use of a graded interface between the substrate and the DLC layer. In the present work, an H-free DLC film was deposited by unfiltered cathodic arc over a gas nitrided stainless steel substrate with metallic Cr as bond layer. It was included an additional step where carbon ions were accelerated by high bias potential before the deposition of functional DLC, to produce a carbon transition layer to act as a buffer layer. Different thicknesses of this transition layer were produced, including a sample without this step, for reference purposes. The coating adherence was evaluated by scratch test. In addition, the microstructure of the interface was analyzed by scanning transmission electron microscopy (STEM) and the sp-type bonds were quantified by electron energy loss spectroscopy (EELS). The other deposition parameters of the functional DLC were kept the same and no remarkable difference was observed between samples. The DLC thickness was approximately 23 um. The critical loads determined by scratch test were 87 N and 75 N for the samples with thin and thick carbon transition layer, respectively. In addition, a critical load of 7 N was obtained for the sample prepared without the high bias step. The analysis of the microstructure close to the interface with Cr bond layer revealed a mixing layer of Cr and C of about 5 to 10 nm. Furthermore, it was observed the formation of the transition layer characterized by a homogeneous carbon layer with high sp2 content (81 – 83%) when compared to functional DLC. The thicknesses of the transition carbon layer were 40 nm and 110 nm for the samples prepared with high bias step. Results indicate a significant enhancement in adhesion in the DLC samples prepared with the high bias step, which can be correlated to the presence of the mixing layer and the carbon transition layer. Moreover, a decrease in adherence was observed for an increase in the thickness of the transition layer, which can be attributed to the lower shear strength of this sp2 rich layer.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B7-WeM

Plasma Surface Interactions, Diagnostics and Growth Processes

Moderator: Yolanda Aranda Gonzalvo, University of Minnesota, USA

8:00am **B7-WeM1 Energy and Momentum Fluxes at Plasma Processing of Materials***, **Holger Kersten (kersten@physik.uni-kiel.de)**, T. Trottenberg, M. Klette, LH. Hansen, A. Spethmann, F. Schlichting,* IEAP, U Kiel, Germany **INVITED**

For an optimization of plasma-based processes as thin film deposition or surface modification, respectively, suitable diagnostics are required. In addition to well-established plasma diagnostic methods (e.g. optical emission spectroscopy, mass spectrometry, Langmuir probes, etc.) we perform examples of “non-conventional” low-cost diagnostics, which are applicable in technological plasma processes. Examples are the determination of energy fluxes by calorimetric probes and measurement of momentum transfer due to sputtered particles by force probes. In particular, energy and momentum transfer transport through the plasma sheath combined with the possibility to measure the effect of charge carriers as well as energetic neutrals are of interest and become possible by these diagnostics.

Total energy fluxes from plasma to substrate have been measured by special calorimetric sensors. A typical method is the passive thermal probe (PTP) based on the determination of the temporal slope of the substrate surface temperature (heating, cooling) in the course of the plasma process. By knowing the calibrated heat capacity of the sensor, the difference of the time derivatives yields the integral energy influx to the surface. Simultaneously, the electrical current to the substrate can be obtained and by variation of bias voltage the energetic contributions of charge carriers can be determined. By comparison with model assumptions on the involved plasma-surface mechanisms the different energetic contributions to the total energy influx can be separated.

Furthermore, for thin film deposition by sputtering it is essential to determine the sputtering yield as well as the angular distribution of sputtered atoms. In addition to simulations (TRIM, TRIDYN etc.) an experimental determination of the related quantities is highly demanded. For this purpose, we developed a suitable interferometric force probe. The sensitive probe bends a few µm due to momentum transfer by the bombarding and released particles, i.e. sputtered target atoms and recoiled ions. By knowing the material properties of the cantilever and by measuring its deflection, the transferred momentum, e.g. the force in µN range, can be determined experimentally. In the present study, measurements are compared with TRIM simulations for different experimental discharge conditions.

8:40am **B7-WeM3 Utilizing Visible Spectroscopy to Determine Ionization Behavior of Tungsten Atoms Sputtered by Argon Ions***, **Anton Neff (neffal@ornl.gov)**,* Oak Ridge Institiute for Science and Education, USA*; E.A. Unterberg, M. Zach,* Oak Ridge National Laboratory, USA

Deposition of thin metallic films through the method of physical sputtering, also known as physical vapor deposition, has expanded the scope of thin film coatings. The efficiency of the film deposition and the stability of the deposited film are dependent on numerous conditions. Some of these include: compatibility of substrate and thin film material, surface stresses induced by the deposition method, substrate surface condition (roughness, contamination, etc.), and ion concentration in the sputtered volume [1]. We have developed an ion beam sputtering system to perform precise spatial deposition to minimize loss of sputtered material. We want to optimize the deposition efficiency by analyzing the charge state distribution of the sputtered atoms. In this first study, we are investigating tungsten (W) atoms sputtered by argon (Ar) ions. The system consists of a cubic vacuum chamber with a Kaufman ion source installed at a 45 degree angle to the target, a linearly adjustable target stage, and linearly adjustable substrate stage. The sputter plume is examined with collection optics connected to a high resolution spectrometer and a filterscope [2] system via fiber optic cables. The spectrometer was designed to measure in a wavelength window that includes the 400.88 nm WI line. The filterscope will have narrow bandpass filters for the same WI line as well as a WII line at 364.1 nm. Additionally, the ArI line at 413.2 nm will be monitored by the filterscope to help clarify the analysis of the WI peak because of the background presence of Ar ions. For the WI filter, there will be a secondary filter with a wider band pass (~2.5 ang. wider on each side) to allow for subtraction of the continuum background [3]. This background value will be subtracted from both WI and WII signals, which isolates the low-intensity W lines from the continuum. The filterscope can accommodate 3 slight lines permitting spatial evaluation of the optical emission based on the viewing spot of the collection optics. The filterscope is calibrated to produce a photon flux which can be converted to a particle flux using S/XB calculations, where S in the ionization rate, X is the excitation rate, and B is the branching ratio of an atom interacting with the Ar plasma. The spatial distribution of the particle flux of the sputtered W will be presented.

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9:00am **B7-WeM4 Erosion and Cathodic Arc Plasma of Nb–Al Cathodes: Composite vs. Intermetallic***, S. Zöhrer, M. Golizadeh,* Montanuniversität Leoben, Austria*; N. Koutná,* TU Wien, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany*; **Robert Franz (robert.franz@unileoben.ac.at)**,* Montanuniversität Leoben, Austria

Cathodic arc deposition has been established as one of the standard techniques for the physical vapour deposition of thin films and coatings as it allows the synthesis of a wide variety of materials including metallic films, but also nitrides, carbides and oxides if a reactive background gas is used. In addition, the highly ionised plasma and the achievable high deposition rates allow a variety of control mechanisms to influence the film growth while the manufacturing costs remain rather low due to the short deposition times. With the advent of multifunctional thin films and coatings, the use of multi-element cathodes providing the non-gaseous elements during the synthesis has become an industrial standard. However, a detailed understanding of the discharge properties is vital for the further optimisation of the deposition processes to enable synthesising thin films or coatings with improved properties.

In the case of single-element cathodes, many properties of cathodic arcs show a correlation to the cohesive energy of the cathode material including the burning voltage, the erosion rate, or, to a lesser extent, plasma properties like electron temperatures or average ion energy and charge states. For multi-element cathodes, various phases with different cohesive energies can initially be present in the cathode, or form due to arc exposure, complicating the evaluation of such correlations. To test the influence of morphology and phase composition of multi-element cathodes on cathodic arc properties, we used a Nb–Al cathode model system that includes: pure Nb and Al cathodes; intermetallic Nb_3Al, Nb_2Al and $NbAl_3$ cathodes; and 3 composite Nb–Al cathodes with atomic ratios corresponding to the stoichiometric ratios of the intermetallic phases. Pulsed cathodic arc plasmas from these cathodes were examined using a mass-per-charge and energy-per-charge analyser, showing that charge-state-resolved ion energy distributions of plasmas from the intermetallic and corresponding composite cathodes are nearly identical. An examination of converted layers of eroded cathodes using x-ray diffraction and scanning electron microscopy indicates the formation of a surface layer with similar phase composition for intermetallic and their corresponding composite cathode types. The average arc voltages do not follow the trend of cohesive energies of Nb, Al and intermetallic Nb–Al phases, which have been calculated using density functional theory. Possible reasons for this effect will be discussed based on the current knowledge of multi-element arc cathodes and their arc plasma available in literature.

9:20am **B7-WeM5 A Force Probe as a Tool to obtain Directionally Resolved Momentum Characteristics during Sputter Processes**, ***Mathis Klette (klette@physik.uni-kiel.de)****, T. Trottenberg, M. Maas, H. Kersten,* Kiel University, Kiel, Germany

Ion beam sputter deposition is a well-established technique for producing high quality thin film coatings. The optimization of the coating process requires an understanding of the physical phenomena. Process parameters like the deposition rate can be determined by quartz crystal microbalances, while charged particles in the sputter plume can be characterized by Faraday cups or retarding field analyzers.

However, the majority of the sputter plume consists of neutral particles. Characterizing these requires much more complex diagnostics, such as optical emission, laser-induced fluorescence [1], or mass spectrometry [2].

In contrast, interferometric force probes offer a more direct measurement of all particles including neutrals by measuring the force the sputter plume exerts onto the probe surface. In previous works, these probes have been used to determine the thrust of electric space propulsion engines, forces exerted by a low-temperature plasma onto a solid boundary [3], or the recoil of reflected and sputtered particles at a sputter target [4].

In this work, a sputter plume is generated by an ion beam directed onto a rotatable copper or silver target, respectively. In order to obtain a directionally resolved momentum profile, a force probe is circling the target at a fixed distance, measuring the current and momentum transferred to the probe surface. The obtained momentum profiles are then compared with numerical simulations using SRIM [5]. Both, measurements and simulations, are carried out for different angles of incidence, ion energies, gases, target materials, and working pressures.

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9:40am **B7-WeM6 The Plasma Effect on Electrical Performance of Stannic Oxide P-type Thin Film Transistors**, ***Yu-Chuan Chiu (w4204ww@gmail.com)****, P.-T. Liu, D.-B. Ruan, K.-J. Gan, C.-C. Hsu, S.M. Sze,* National Chiao Tung University, Taiwan

Recently, a perfect native p-type oxide semiconductor, stannous oxide (SnO), has been drawn back into attention, due to the exile choice in development of high-quality p-type materials. Unlike the significant progress in n-type transparent amorphous metal oxide thin film transistor (TFT), p-type TFT often suffer a limited channel mobility and a low on-off current ratio. On the other hand, it was reported that the combination of different plasma treatment may enhance the device performance, significantly. However, the study of plasma effect on p-type TFT is still lacking and unclear. In this work, the p-type SnO TFT with nitrogen-based plasma treatment may exhibit a high on-off current ratio, a high field-effect mobility, and a good subthreshold swing. Besides, the detailed results of material analysis also support those electrical performance improvements.

11:00am **B7-WeM10 Improved Electrical Characteristics of Ge nMOSFET with Post Interfacial Layer Plasma Treatment**, ***Fu-Yang Chu (xxmoon666@gapp.nthu.edu.tw)****, K.- S. Chang-Liao, D.-B. Ruan, H.-I. Yeh, S.-H. Yi, Y. -H. Chien,* National Tsing Hua University, Taiwan

In this work, the effects about an additional post interfacial layer (IL) plasma treatment for germanium (Ge) n-type metal oxide semiconductor field effect transistor (nMOSFET) has been discussed in detail. It is founded that the electrical performance could be further improved by an additional plasma treatment after the traditional germanium dioxide IL formation. The Ge nMOSFET with NH3 plasma treatment exhibits higher on-off current ratio, lower subthreshold swing and higher Gm value, while the equivalent oxide thickness or gate dielectric quality might be kept.

11:20am **B7-WeM11 Optical Emission Spectroscopy of Glow Discharged Plasma Pulsed Nitriding of Pure Iron**, *F. Santiago,* ***Joaquín Oseguera (joseguer@tec.mx)****,* ITESM Estado de México, Mexico

Glow-discharge emissions of pulsed plasma nitriding samples were characterized by optical emission spectroscopy technique. The formation of the compound layer of iron nitrides (ε - $Fe_{2-3}N_{1\pm x}$ + γ' - Fe_4N_y) depends on the temperature and the atmosphere (N_2-H_2-Ar) during the plasma nitriding process of pure iron AMCOR samples. Before the plasma-nitriding processes take place, samples were cleaned by sputtering with an argon plasma. Analysis of spectra emissions of plasma nitriding finds the second positive system, and the first negative system, of the molecular nitrogen system, and argon lines within a range of 200-800 nm. The ionized molecule of nitrogen (0,0), at 391.4 nm, was found as an important emission to correlate the formation of the compound layer of nitrides. The expected microstructure (ε+γ') of nitrided samples were identified by XRD analysis. Cross-sectional views of nitrided samples were analyzed by optical microscopy.

11:40am **B7-WeM12 Variation of Deposition Rate and Plasma Parameters vs Positions in DC Magnetron Sputtering System**, *G. Sabavath,* CMR Engineering College, India*; A.B. Panda,* C.V. Raman College of Engineering, India*; I. Banerjee,* Central University of Gujarat, India*; J. Singh,* Akal University, India*; K.V. Reddy,* CMR Engineering College, India*;* ***Santosh Kumar Mahapatra (skmahapatra741973@gmail.com)****,* Central University of Punjab, India

We demonstrate plasma parameters and their contribution in deposition rate at different axial and radial positions inside the DC magnetron sputtering system. Multi Langmuir probes are used for the estimation of plasma parameters such as electron temperature (T_e) and electron density (n_e) using electron flux (EF) and electron energy distribution function (EEDF) methods. It is observed that deviation in both $n_e$and T_e obtained from EF and EEDF methods is due to the fact that EF is suitable for non-Maxwellian distribution, whereas; EEDF is suitable for Maxwellian distribution. It is observed that both T_e and n_e get decreased with axial and radial distance from the center of the magnetron. The electron density distribution is simulated using the real magnetic field through particle in cell Monte Carlo collisions and its dependency is found on the formation of grain size, which is confirmed from surface morphology. The dependency of deposition rate, thickness and grain size on plasma parameters are studied and corroborated with the simulated results.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 1-3 - Session C3-WeM

Thin Films for Energy Applications: Solar, Thermal, and Photochemical

Moderators: Tushar Shimpi, Colorado State University, USA, Clio Azina, Linköping Univ., IFM, Thin Film Physics Div., Sweden

8:20am **C3-WeM2 Transparent Thermoelectric TiO_2:Nb Thin Films**, *J.M. Ribeiro, F.C. Correia,* ***Carlos Jose Tavares (ctavares@fisica.uminho.pt)****,* University of Minho, Portugal

The design of a transparent conducting oxide (TCO) material with thermoelectric properties is a promising technology for touch–screen displays and solar cell applications. In this work, TiO_2 doped with Nb thin films were deposited by d.c. magnetron sputtering. Several process parameters were adjusted, such as reactive gas (oxygen) partial pressure and deposition time and temperature, which affect the morphology and crystalline structure of the thin films. Hence, by modifying the optical, electric, thermal and thermoelectric properties of the produced TiO_2:Nb thin films, enables their suitability for thermal energy harvesters in devices in order to render them more sustainable. For optimized deposition conditions, TiO_2:Nb thin films with an optical transmittance up to 85 %, a relatively low electrical resistivity (>10 Ω·cm), low thermal conductivity (<2 $W·m^{-1}·K^{-1}$), and a high absolute Seebeck coefficient (>200 $μV·K^{-1}$) corresponding to a power factor of 125 μW·K ·m and ZT figure of merit close to 0.1 were attained, as seen in Figure 1. Both anatase and rutile crystalline phases were discerned in the X-ray diffractograms. Scanning electron microscopy observations provided evidence of a dense microstructure and a smooth film surface with an average thickness of 120 nm. From Figure 2, X-ray photoelectron spectroscopy experiments confirms that Nb^{5+} ions substitute Ti^{4+} in the TiO_2 lattice, providing a charge unbalance to the matrix. Furthermore, due to larger ionic radii, Nb^{5+} scatter phonons more efficiently and reduce the thermal conductivity, which is essential for enhancing the thermoelectric property.

8:40am **C3-WeM3 Thermoelectric Study of ZnO-based Thin Films: The Effect of Bi Dopant Content***, Filipe Correia (f.correia.profissional@gmail.com),* *J.M. Ribeiro,* University of Minho, Portugal*; A.M.M. Mendes,* LEPABE, University of Porto, Portugal*; J.S. Reparaz, L.A. Pérez, A.R. Goñi,* Instituto de Ciencia de Materiales de Barcelona,Consejo Superior de Investigaciones, Spain*; C.J. Tavares,* University of Minho, Portugal

This work reports on the optimization of the thermoelectric properties of ZnO-based thin films for applications that envisage coatings as transparent thermoelectric electrodes in devices [1]. As several reports indicate, point defects are very effective in controlling the thermal conductivity on oxide-based thermoelectrics [2]. The approach consists in introducing Bi ions, a higher mass element, into the ZnO metal-oxide matrix, in order to hinder phonon mediated heat conduction, whilst maintaining the Seebeck coefficient and high electrical conductivity. Hence, in this work, the effect of Bi dopants on ZnO-based thin films was investigated for three distinct Bi concentrations, two thickness (500 nm and 250 nm) and for three types of films: ZnO; ZnO:Al and ZnO:Ga, all produced by a custom-built d.c. magnetron sputtering setup in confocal geometry. The films were characterized concerning their: structural properties by X-ray diffraction and atomic probe tomography in order to verify the existence of secondary phases or Bi atoms segregation at the grain boundaries. Transport properties were studied, namely, electrical conductivity using a Hall effect equipment, by determining resistivity, carrier concentration and mobility. Furthermore, the thermal conductivity was assessed by frequency domain thermo reflectance and the Seebeck coefficient determined using a custom-made equipment operating in vacuum. The optical properties, transmittance and reflectance, were measured in order to understand the Bi doping effect. From the simulation of these experimental curves, the mobility and carrier concentration of the optically active carriers was calculated and compared to the electrical measurements, in particular to study the role of grain boundaries. A comparison between undoped and doped ZnO and ZnO:Al/Ga films is made regarding their thermoelectric properties. Preliminary results show that undoped ZnO has an almost zero Seebeck coefficient, which is substantially enhanced for ZnO:Al,Bi (-44 $\mu V \cdot K^{-1}$) and ZnO:Ga,Bi (-45 $\mu V \cdot K^{-1}$) for optimized conditions. It was observed that the Seebeck coefficient decreases with film thickness. In the best-case scenario, a thermoelectric figure of merit of ~0.01 was attained at room temperature.

1) K. Ellmer, A. Bikowski, Intrinsic and extrinsic doping of ZnO and ZnO alloys, J. Phys. D. Appl. Phys. 49 (2016) 413002–413002. doi:10.1088/0022-3727/49/41/413002.

2) G.K. Ren, et al., Contribution of point defects and nano-grains to thermal transport behaviours of oxide-based thermoelectrics, Npj Comput. Mater. 2 (2016) 1–9. doi:10.1038/npjcompumats.2016.23.

9:00am **C3-WeM4 Hydrothermal Fabrication, Characterization and Piezoelectrically Enhanced Photocatalysis of BiFeO3 Thin Films on FTO Substrate***, Nghi Nhan Nguyen Thi (nghinhan2410@gmail.com),* National Cheng Kung University, Taiwan

This novel work presents a promising application to use $BiFeO_3$ (BFO) thin film as a catalyst for photodegradation of organic pollutions, in which BFO with a small bandgap can absorb the sunlight and generated electron - holes pairs. This photogenerated electron and holes will go to the surface of the photocatalyst and initiate the oxidative/ reductive process. Piezoelectric materials BFO can generate an internal electric field under strain, so the combination of the piezoelectric materials with visible light photocatalysts can create a localized electric field directly on a photocatalyst's surface for the enhancement of photocatalytic activity. With the advantages of the hydrothermal method such as low temperature, easy to control the purity, composition and crystal shape of the nanomaterial structures. The purpose of the research is to successfully fabricate BFO thin films with various morphology, good adhesion, and high-density films. In this study, high-density BFO nanosheets (BFO NSs) and nanoplates (BFO NPs) arrays are grown on the FTO substrate via hydrothermal method at 200^oC in 6 hours. Under piezo-catalysis, both nanosheets and nanoplates exhibited higher reaction rates in comparison with photocatalytic degradation. The better and enhanced photocatalytic efficiency of the $BiFeO_3$ structure was ascribed to the high charge separation efficiency. Under both solar light and mechanical vibrations were used simultaneously, the BFO films exhibited high degradation rates with the BFO NPs degrading approximate 80% of methylene blue (MB) in 80 minutes. This work revealed that thin film such as BFO NPs arrays structure has better photocatalytic efficiency than BFO NSs. Coupling the piezoelectric properties and photocatalytic performance, BFO is a good candidate for photoelectrochemical devices.

9:20am **C3-WeM5 Mo-SnO_2 /rGO Composite by Chemical Reduction as Anode Material for Lithium Ion Batteries***, Yong-Cun Huang (kk2516292@gmail.com), S.B. Brahma,* National Cheng Kung University (NCKU), Taiwan*; C.C. Chang,* National University of Tainan, Taiwan*; J.L. Huang,* National Cheng Kung University (NCKU), Taiwan

The Molybdenum-SnO2/reduced graphene oxide (Mo-SnO_2/rGO) composite has been facilely synthesized through a simple chemical reduction method. It is shown that the Mo-SnO2 nanoparticles are homogeneously anchored onto rGO sheets. Mo adding can enhance the interfacial interaction between Mo-SnO2 nanocrystals and rGO sheets, and improve the electrical conductivity of the composite, which lead to the excellent electrochemical performance of Mo-SnO2/rGO composite. Moreover, Mo adding can facilitate the conversion reaction between Li_2O and SnO_2 during cycling, leading to the higher capacity than the theoretical capacity. Via electrochemical tests, the results show that 5%Mo-SnO2/rGO composite has the best electrochemical performance corresponding to high charge capacity of 1117 mAh g^{-1} and a discharge capacity of 483 mAh g^{-1} at the first cycle, good cycling stability about 72% retention (347.9 mAh/g after 100 cycles).

9:40am **C3-WeM6 Rh-Mo_2C-RGO and Mo_2C-RGO as an Electrocatalyst by Wet Chemical Method for Hydrogen Evolution Reaction***, Yu-Hsuan Lee (vince85302@gmail.com), P.C. Huang, S.B. Brahma,* National Cheng Kung University (NCKU), Taiwan*; S.C. Wang,* Southern Taiwan University of Science and Technology, Taiwan*; J.L. Huang,* National Cheng Kung University (NCKU), Taiwan

Hydrogen has been considered as one of the most promising renewable energy for production and storage to replace petroleum-based energy. In this study, a transition metal carbide was used to replace the platinum electrode. We used two-step method to synthesis Mo_2C-RGO and Rh-Mo_2C-RGO. In the first stage, In the first stage, Oleylamine (OLA) was used as a solvent to disperse the molybdenum source on graphene oxide (GO).The second stage is high-temperature carbonization treatment. The molybdenum precursor is crystallized at a high temperature to form molybdenum carbide, and the graphene oxide is reduced at a high temperature to form reduced graphene oxide (RGO). The results show that the Mo_2C power was dispersed in the composite material of RGO. The electrochemical results show that the onset potential of Mo_2C-RGO is about -0.13V and the Tafel slope is 136mV dec^{-1}.

Keyword: Hydrogen Evolution Reaction, electrocatalysis, transition metal carbide

11:00am **C3-WeM10 Synthesis of Si/rGO Composite as Anode Material by Chemical Method***, Hung Ying Chang (bbs60076@gmail.com),* National Cheng Kung University, Taiwan*; S.B. Brahma,* National Cheng Kung University (NCKU), Taiwan*; C.C. Chang,* National University of Tainan, Taiwan*; J.L. Huang,* National Cheng Kung University (NCKU), Taiwan

Si has been considered as one of the most attractive anode materials for Li-ion batteries(LIB) because of its low discharge voltage and high theoretical capacity(3580mAh/g). The formation of stable Si anode remains a challenge, due to the significant volume changes that occur during lithiation and delithiation., which causes a fast capacity fading. In this paper, we propose a novel method for synthesis silicon nanoparticles with a simple one-step procedure using (3-aminopropyl) trimethoxysilane (APTES) and ascorbate sodium (As). Then, the combination of Si nanoparticles and carbon materials, graphene, and graphite has proved to be a promising strategy to enhance the stability of Si-based LIB anode, mainly due to the excellent electrical conductivity and flexible mechanical properties of carbon materials. Furthermore, there is a synergistic effect that growth of Si nanoparticles onto graphene sheets can minimize the restacking effect. Also, the layer structure of graphene can relieve the volume change of alloying materials resulting in improvement of the capacity/cyclic stability of the anode materials. Finally, we successfully synthesis Si/RGO composite by simple chemical reduction method with low cost and low toxicity, and it allows the battery to combine high capacity with stable cycle life performance.

11:20am **C3-WeM11 $LiPO_2F_2$ as an Additive to Improve SEI Performance of Graphite Electrodes in Lithium Ion Batteries**, ***Yu Ju Liao (joyce7511042@gmail.com)***, *S.B. Brahma,* National Cheng Kung University (NCKU), Taiwan; *C.C. Chang,* National University of Tainan, Taiwan; *J.L. Huang,* National Cheng Kung University (NCKU), Taiwan

Components and stability of solid electrolyte interphase have the crucial impact on lithium ion batteries. In this work, using lithium difluorophosphate ($LiPO_2F_2$) as an electrolyte additive to modify SEI performance, and the effect on SEI film formation was demonstrated by electrochemical and microscopy techniques, such as scanning electron microscope (SEM), transmission electron microscope (TEM). Moreover, via electrochemical impedance spectra (EIS) and temperature-dependence of charge-transfer resistances,

kinetics on the interface between electrolyte and electrode is evaluated. From all the results, lithium difluorophosphate indeed improve solid electrolyte interphase performance.

Keywords: lithium difluorophosphate, solid electrolyte interphase, lithium-ion batteries.

11:40am **C3-WeM12 Advanced Nanomaterials for Energy-Related Applications**, ***Eva Schubert (evaschub@engr.unl.edu)***, *C. Briley, U. Kilic, M. Hilfiker,* University of Nebraska-Lincoln, USA; *D. Sekora,* Honeywell Inc.; *M. Schubert,* University of Nebraska-Lincoln, USA **INVITED**

Advancements in nanomaterial fabrication impact and revolutionize pathways to control properties and functionality of devices by using building-block approaches to tailor the material structure during synthesis. With more precision during fabrication processes modern nanotechnology opens up new venues for energy-efficient, low power-consumption and environmentally resourceful applications in diverse industries. Oblique angle deposition is a sophisticated method for bottom-up fabrication of single and multilayer slanted columnar and chiral nanomaterials. The arrangement of nanostructures across a substrate form highly porous thin films with enhanced surface area and large void fractions, which allow interactions with gaseous, liquid or other solid materials in hybrid systems.

We report on utilizing oblique angle deposition to tweak material properties on the nanoscale by arranging building blocks of transition metals (Ti, Co, Pt, Cr etc.), permalloy or silicon to form single and multilayer nanowires and nanospirals. The shape of the nanostructures is determined by anisotropic atomic shadowing and control of surface diffusion during material growth utilizing an oblique angle of incidence for the particle flux. Based on chemical composition and shape of the nanomaterials we discuss unique biaxial anisotropy in their magnetic, photonic and optical behaviors in the context of energy related applications. Special emphasis will be given to applications for energy storage on the example of Li-ion based batteries using large surface nanowire electrodes from silicon and ferromagnetic Co/Py heterostructure nanowires which exhibit high magnetic energy products.

Reversable Li-ion intercalation is achieved by cyclic voltammetry from electrochemical half-cells. During intercalation the electrode material experiences dramatic structural changes which are studied in-situ by means of spectroscopic ellipsometry. The reversible change of the chemical composition and volume expansion are thereby monitored by a change in the optical response and quantified in the context of the inserted and extracted amounts of Li-ions.

Ferromagnetic multilayer nanowires are grown with one or two periods of Co/Py and coated by thin alumina barriers to prevent oxidation. An octupol vector magnet spectroscopic ellipsometry system is used to measure the anisotropic magneto-optical response, and magnetic hysteresis is extracted from line-shape regression optical models accounting for the magnetic order in the materials. We demonstrate that periodicity of the multilayers can be used to optimize the stored magnetic energy given by the energy product from flux density B and field strength H.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room San Diego - Session E1-3-WeM

Friction, Wear, Lubrication Effects, and Modeling III

Moderators: Nazlim Bagcivan, Schaeffler AG, Germany, Tomáš Polcar, University of Southampton, UK, Manel Rodriguez Ripoll, AC2T Research GmbH, Austria

8:00am **E1-3-WeM1 PVD Coatings Interaction with the Environment and Influence of Substrate on Coating Performance**, ***Bojan Podgornik (bojan.podgornik@imt.si)***, Institute of Metals and Technologies, Slovenia **INVITED**

In the past, the development of tools, engines and transmissions would have been impossible without improved steel performance, advanced lubricant additive chemistry and proper lubricant formulation. In order to meet demanding durability and performance requirements forming, engine and transmission oils contain a wide range of additives. Especially anti-wear and extreme-pressure additives are crucial in minimizing friction and wear and protecting contact surfaces under severe contact conditions. The mechanism by which AW and EP additives reduce friction and wear of metallic surfaces under boundary lubrication is well known and described in detail. It is due to formation of tribofilms, activated by tribochemical reactions between additive molecules and metallic surface.

By improving tribological properties hard coatings provide great opportunity for further improving performance, durability and efficiency of forming tools and components, which can no longer be achieved only by steel and lubricant design. However, although DLC and CrN coatings show low friction and wear under dry sliding conditions the majority of automotive components and forming tools will remain lubricated, at least for the near future. Therefore, for successful application of coated components aimed for further performance enhancement in forming and automotive industry (lower friction and energy consumption, higher load bearing capacity,...) coatings will have to perform adequately also under oil-lubricated conditions. Investigations so far indicate that in certain cases even coated surfaces may show improved tribological properties when lubricated by additivated oil. However, the mechanism responsible is not yet fully understood, especially when it comes to the influence of additive type, contact conditions and environment in general. Another important parameter when considering coated components is the substrate. Without proper support even the most superior coatings will fail.

With the aim to add some further understanding to this important area and to be able to fulfil future requirements in automotive and forming industry, the talk will focus on the influence of substrate preparation on the tribological performance of PVD coatings as well as on the reactions between lubricants and typical PVD coatings. Results from investigations on common coatings found in forming and automotive applications will be presented. Furthermore the influence of substrate properties including roughness, hardness and toughness, additive type, additive concentration and contact conditions, including load, sliding speed and temperature on the tribological behaviour of PVD coatings will be discussed.

8:40am **E1-3-WeM3 Tribologically Enhanced Self-healing of Niobium Oxide Surfaces**, ***Samir Aouadi (samir.aouadi@unt.edu)***, *A. Shirani, J.J. Gu, B. Wei, D. Berman,* University of North Texas, USA

Activating a self-healing process is a viable approach for preventing the failure of ceramics experiencing mechanically-induced crack propagation. Previously, it was demonstrated that niobium oxide (Nb_2O_5) exhibits self-healing properties activated by the formation of Nb-Ag-O ternary oxide when heated above 945 °C in presence of silver. In this study, we explore the mechanism of lowering the high-temperature healing requirement by assisting the process of crack repair with a normal load and shear stresses. Specifically, we propose to use tribologically-induced local heating as a mechanism to enhance the self-healing ability of Nb_2O_5. During a pin-on-disk test, whereby a niobium oxide flat was sliding against a silver-coated ball, a sudden lowering of the coefficient of friction was observed at elevated temperatures (~600 °C). The better performance of the coating was associated with a surface reconstruction process initiated inside the wear track. Extensive characterization analysis of the wear track using energy-dispersive x-ray spectroscopy, Raman spectroscopy, and x-ray diffraction confirmed the presence of an Nb-Ag-O ternary oxide phase inside the wear track formed at elevated temperature. The formation of an Nb-Ag-O ternary oxide at a much lower than thermodynamically-required temperature suggests that the self-healing process can be initiated directly during mechanically induced stresses. Such a process is a new recipe for improving wear and crack resistance characteristics of ceramic components and maybe tuned to provide the desired frictional response.

9:00am **E1-3-WeM4 Ni-based Self-Lubricating Laser Claddings for Hot Forming and High Temperature Vacuum Applications***, H. Torres,* AC2T Research GmbH, Austria*; B. Prakash,* Lulea University of Technology, Sweden*; **Manel Rodriguez Ripoll (Manel.Rodriguez.Ripoll@ac2t.at)**,* AC2T Research GmbH, Austria

This work proposes a novel self-lubricating Ni-based laser cladding able to control friction at high temperatures while maintaining a superb wear resistance. The cladding microstructure consists of nickel dendrites surrounded by borides and homogeneously scattered pure silver pockets encapsulated within molybdenum and chromium sulfides that arise from the thermal decomposition of MoS_2 during deposition. This resulting microstructure is able to control friction from room temperature to 600 °C in ambient air and at least until 300 °C in vacuum. In ambient air, the friction reduction mechanism is determined by the silver and chromium sulfide pockets. Atomic force microscope investigations show that chromium sulfides have a high hardness and a low intrinsic friction. They additionally support further friction reduction by silver smearing due to their high hardness. At higher temperatures, the contribution of silver diminishes due to oxidation so that the contribution of chromium sulfides to self-lubrication is dominant.

The self-lubricating cladding shows decreased friction against Al-Si-coated 22MnB5 steel under hot stamping conditions. The presence of silver leads to a noticeable decrease in friction down to 0.3 during Al-Si coating break-up on the counter body, due to smearing next to the affected region. In the case of hot stamping against AA6082 aluminium alloy, the self-lubricating claddings in synergy with solid lubricants decrease friction and counter body wear at high temperatures compared to grade 1.2367 hot work tool steel commonly used in hot forming. These findings illustrate that the implementation of Ni-based self-lubricating laser claddings can lead to decreased costs while at the same time ensuring the quality of the hot stamped components.

In the case of high temperature vacuum performance, the presented self-lubricating cladding is able to effectively control and reduce friction down to a value of 0.25 against 440C martensitic stainless steel at room temperature and 300 °C by the smearing of silver over the chromium sulfides. This friction reduction mechanism is enhanced by the thermal softening of the pure silver phase at elevated temperatures, contrary to air atmosphere, where smearing is hampered by oxidation. This overall tribological performance makes the presented cladding also as potential candidate for space applications.

9:20am **E1-3-WeM5 Silver as the Component of Tribological Nanocomposite Coatings: Benefits, Drawbacks, and Principles***, **Andrey Bondarev (bondaan2@fel.cvut.cz)**,* Czech Technical University in Prague, Czech Republic*; D.V. Shtansky,* National University of Science and Technology "MISiS", Russia*; T. Polcar,* Czech Technical University in Prague, Czech Republic

One of the major challenges facing lubricant related research is the development of materials capable of maintaining both low coefficient of friction (CoF) and low wear rate in a wide temperature range. Nanocomposite coatings can combine advantages of hard and self lubricating phases and therefore are good candidates for various tribological applications. Design of new deposition methods and compositions of hard self-lubricating nanocomposite coatings is of great fundamental and applied importance for fields of industry. In the present study, metallic Ag and Ag-consisted phases were considered as solid lubricants. Various multicomponent nanocomposite materials were studied: MoCN-(Ag) and VCN-(Ag), as well as TiNbCN–(Ag) and Si-Ta-C-N-(Ag) coatings . In case of VCN-Ag and MoCN-Ag coatings it was supposed silver play a role of active component which reacts with hard matrix components at elevated temperatures and forms lubricious phases. Contrariwise in case of TiNbCN–Ag and Si-Ta-C-N-Ag coatings silver phase does not interact with matrix phases. It was shown that a significant reduction of CoF values can be achieved either by the formation of lubricious V_2O_5, MoO_3, Ag_xMo_yO Ag_xV_yO phases during high-temperature tribological tests. Melting of silver molybdates and vanadates was triboactivated at high temperatures that promoted CoF 0.18 at 700 °C. In case of TiNbCN–Ag coatings it was shown that a relatively high amount of Ag (15 at.%) is required to provide lubrication and self-healing ability in the temperature range of 25-700 °C.Also TiNbCN-Ag coatings also provided an active oxidation protection and self-healing functionality due to the segregation of Ag metallic particles at the sites of coating's cracking or oxidation. The Si-Ta-C-N coatings is the special case, the coatings demonstrated extremely high oxidation resistance because of formation of dense $TaSiO_x$ amorphous oxide layer. This 100nm thick $TaSiO_x$ oxide layer demonstrated lubricious behavior itself (CoF = 0.28 at 800 °C) due to triboactivated formation of oxide fibers in the tribological contact zone. When Ag was added into Si-Ta-C-N coatings, $TaSiO_x$ oxide layer blocked its diffusion to the surface at high temperatures and negate the effectiveness of Ag as the solid lubricant.

9:40am **E1-3-WeM6 Tribological Properties of Duplex PEO/Chameleon Coating on Aluminum Alloys***, **Andrey Voevodin (andrey.voevodin@unt.edu)**, J. Shittu, A. Shirani,* University of North Texas, USA*; A. Yerokhin,* University of Manchester*; A. Korenyi-Both,* Colorado School of Mines, USA*; J.-E. Mogonye,* Army Research Laboratories, USA*; D. Berman, S.M. Aouadi,* University of North Texas, USA

In this study, plasma electrolytic oxidation (PEO) was used to create a porous oxide structure on AA 6082 aluminum alloys. This surface treatment resulted in the formation of a graded hard ceramic coating with a porous outer region. The porous regions were burnished with solid lubricants to create a hard/solid lubricant duplex multifunctional structure with an adaptive tribological response. The tribological proprieties of the duplex system was investigated by carrying out pin-on-disk and reciprocating wear tests in humid air using a range of temperatures, loads, and sliding speeds. A low friction coefficient was maintained for all test conditions, suggesting the self-adaptive nature of the selected solid lubricant mixture. High temperature pin-on-disk tests were carried at 400 ° C with an apparatus equipped with an *in situ*Raman system to monitor real time chemistry changes in the wear track. *In situ*Raman spectroscopy provided new insights into the tribochemical processes that occur at elevated temperatures for different loads and sliding speeds.

11:00am **E1-3-WeM10 Development of Wear Maps on Borided AISI 316L Stainless Steel Under Ball-On-Flat Dry Sliding Conditions***, **Ricardo García-León (ragarcial@ufpso.edu.co)**, J. Martinez-Trinidad, I.E. Campos-Silva,* Instituto Politécnico Nacional, Grupo Ingeniería de Superficies, Mexico*; U. Figueroa-López,* Tecnologico de Monterrey, Campus Estado de México, Mexico, México*; H. Martínez-Gutiérrez,* Instituto Politécnico Nacional, Mexico

In the present work, wear maps on the borided and non-borided AISI 316L stainless steel (reference material) were obtained in 3D and 2D to provide a global visualization about the material loss under different dry sliding conditions. A FeB-Fe_2B layer was developed at the surface of the AISI 316L steel using the powder-pack boriding process (PPBP) at 1223 K with 6 h of exposure, obtaining a layer thickness of ~39 microns. Firstly, depth-sensing Berkovich nanoindentation test was conducted along the cross-section of the boride layer/substrate system to estimate the distribution of hardness, Young's modulus, and residual stresses.

The sliding wear tests were performed on the borided AISI 316L steel and reference material according to ASTM G133-05 standard procedure. A linear reciprocating sliding tribometer with a ball-on-flat configuration and a counterpart of Al_2O_3 (ball of Ø=6 mm) were used for this purpose. The test conditions at room temperature, for both materials, were: sliding distance 100 m, a constant applied load of 5, 10 and 20 N and sliding velocities of 5, 10, 20 and 30 mm/s. The failure mechanisms on the wear tracks were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) techniques.

The 3D maps showed the wear behavior, of both materials, as a function of the load and sliding speed. In the case of the boride layer, the wear resistance reached a maximum value of 8.90 mm^3/Nm for the condition of 20 N and 30 mm/s, whereas for the reference material the wear resistance was about of 447.40 mm^3/Nm for the condition of 5 N and 5 mm/s.

On the other hand, the 2D maps presented the different failure modes along the regions of wear identified as severe, medium and mild. On the wear tracks developed on the borided AISI 316L stainless steel and reference material, the dominant wear mechanisms were plowing, oxidation, smearing and plastic deformation. Finally, the results showed that the presence of the FeB-Fe_2B layer at the surface of the AISI 316L stainless steel increased the wear resistance around 49 times compared to the reference material.

11:20am **E1-3-WeM11 DC vs RF Sputtered C based $MoSe_2$ Lubricant Coatings - Routes for Optimization of Stoichiometry, Microstructure and Hardness**,
***Talha bin Yaqub (talha.yaqub@gmail.com)**, T. Vuchkov, P. Sanguino,* University of Coimbra, Portugal*; T. Polcar,* Czech Technical University in Prague, Czech Republic*; A. Cavaleiro,* SEG-CEMMPRE - University of Coimbra, Portugal

Carbon based Transition Metal Dichalcogenides (TMD-C) is a highly developed class of solid lubricant coatings. Excessive lab-scale research has been published on W-S-C and Mo-S-C coatings but potential industrial applicability is still a question mark. The issues like low film stoichiometry, low hardness, low crystallinity of TMD phase and huge discrepancies between literature on microstructure, makes it difficult to have a solid guideline on the properties of TMD-C coatings. The present work aims at the optimization of C based RF and DC magnetron sputtered $MoSe_2$ solid lubricant coatings by resolving these issues. The depositions were carried out using confocal plasma sputtering i.e. targets were tilted at an angle to the substrate normal. This approach enhanced the deposition rate and homogenity in the coatings. C content was varied from 18 - 25 at. %. Se/Mo Stoichiometry of 2 was achieved for DC sputtered $MoSe_2$ while it was less (1.87) for RF coatings. DC and RF sputtered pure $MoSe_2$ coatings had different morphology in scanning electron microscope micrographs. With C additions, the achieved morphologies for DC and RF coatings were similar and highly compact. Despite low C content, the high compactness and dense morpholgy is related to the confocal top-down sputtering. X.ray diffraction displayed (002) basal planes peaks with preferential orientations. These planes play vital role in easy shear properties of TMDs but have never been observed in XRD of TMD-C coatings, in literature. Presence of $MoSe_2$ nanocrystals was also evident from transmission electron microscope and Raman spectroscopy analysis. Hardness values achieved in this work were higher than the literature. The authors used C content much less than the one recommended (50 at. %) in the literature. This low C content coupled with the deposition approach used, gave much improved results here. Moreover, the presence of nanocrystals of $MoSe_2$, high stoichiomtery and high hardness gives optimum sliding results. Preliminary unidirectional pin on disk tribological results (in humid atmosphere) displayed COF values around 0.04 versus >0.1 of the literature. So, the issues related to stoichiometry, microstructure, crystallinity and hardness have been resolved. Besides, a guideline has been provided for optimization of Mo-Se-C coatings, by either DC or RF power supplies.

11:40am **E1-3-WeM12 Doping Effect on the Running-in Behaviour of the DLC Coatings**,
***Kosta Simonovic (kosta.simonovic@fel.cvut.cz)**, T. Vitu,* Czech Technical University in Prague, Czech Republic*; M. Danek,* Advamat Ltd., Czech Republic*; J. Jankovec, T. Polcar,* Czech Technical University in Prague, Czech Republic

The running-in period (Fig. 1) is defined as the time needed for the stable friction coefficient to be reached [1]. During the running-in, a surface suffers the highest stresses and, consequently, it has the highest probability of failure. Furthermore, during the running-in asperities on the contacting surfaces wear off, thereby altering contact geometry, which improves aligning of the load-bearing surfaces. Simultaneously to the asperities wear-off process, chemical changes at the surface responsible for the generation of the tribofilm begin to occur. Joined, these two processes define the running-in and the performance of the sliding pair.

Contemporary research is focused on the evaluation of the final coating performance and tribological mechanism of a coating based on the results of the sliding experiments. Undoubtedly, these efforts have been crucial for the understanding of the tribological mechanism of DLC, namely graphitisation process which is responsible for low friction of the DLC coatings [2]. Surprisingly, less attention has been devoted to the running-in process [3], although processes occurring during the running-in are considered as the key to the overall tribological processes of the coating. Overmore, different dopants are added to the DLC coatings to improve their tribological properties. Namely, metallic elements are added to improve the adhesion, friction and wear while non-metallic elements are added for modification of thermal stability, surface energy, etc. Although the effect of dopants on final tribological properties is known, less is known about their effect on the running-in [4].

To understand the effect of dopants on the running-in of the DLC coatings, we have employed newly developed reciprocating tribometer integrated with the 3D surface optical profilometer. The integrated system provides us with the possibility to record the progression of the running-in, generation of the wear-track and improve the understanding of the mechanisms that lead to the steady-state sliding and therefore the effect of dopants on the running-in behaviour of the DLC coatings.

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Surface Engineering - Applied Research and Industrial Applications
Room Pacific Salon 2 - Session G5-WeM

Hybrid Systems, Processes and Coatings

Moderators: Hana Barankova, Uppsala University, Angstrom Laboratory, Sweden, SangYul Lee, Korea Aerospace University, Republic of Korea

8:00am **G5-WeM1 Characterization of the Combination of Microwave and Laser Ablation Plasmas**,
***Enrique Camps (enrique.camps@inin.gob.mx)**, E. Campos-Gonzalez,* Instituto Nacional de Investigaciones Nucleares, Mexico

The main aim of the present work is to report on the study of the combination of continuous plasma, formed by a microwave electron cyclotron resonance (ECR) discharge and pulsed plasma of laser ablation which allow studying the formation of materials in the form of thin films making use of the relatively high densities of the microwave discharge and the wide range of ion energies produced in the pulsed laser ablation plasmas. With this arrangement it is possible to deposit thin films of materials that in the usual microwave discharge require the use of pollutant and corrosive substances, as the required element is obtained from a pure solid target. Moreover, as the laser ablation process is carried out in plasma as the background gas, instead of a neutral gas, the presence of contaminants, such as oxygen can be significantly reduced. For the purpose of the present paper a nitrogen microwave ECR discharge was combined with the plasma created during the ablation of an aluminum target, in order to deposit AlN thin films. Plasma parameters were measured by a Langmuir probe, and the chemical species contained in the plasma were analyzed by optical emission spectroscopy (OES).

8:20am **G5-WeM2 Low Temperature Deposition of SiO_2 and Si_3N_4 using PEALD**,
***Birol Kuyel (b.kuyel@nanomaster.com)**, A. Alphonse, J. Marshall, K. Hong,* Nano-Master, Inc., USA

This Continuous Flow Process* is used to deposit PEALD of GaN, Al_2O_3, and AlN films on Si substrates. It is shown that with this process ultra-smooth and uniform films with thickness linearly proportional to the number of cycles are deposited. It is then applied to low-temperature PEALD deposition of SiO_2 and Si_3N_4 films on Si wafers. SiO_2 and Si_3N_4 film thickness, uniformity, index, roughness and surface composition are studied. However, oxidation Si_3N_4 films has been observed after sitting 54 Days at room temperatures .

*US Patent # 9,972,501 B1 May 15, 2018

8:40am **G5-WeM3 Frontiers of Surface Engineering for Ultra-low Friction and Wear**,
***Ali Erdemir (erdemir@anl.gov)**,* Argonne National Laboratory, USA **INVITED**

In recent years, great strides have been made in the design and synthesis of new materials and coatings (such as atomically thin graphene, MoS_2, HBN, etc. and diamondlike carbons) affording friction coefficients as low as 0.001. When considering the fact that friction and wear related energy losses account for nearly a quarter of the global energy output at these days, the further development and uses of such materials will help in achieving a sustainable energy future that is also environmentally sensible. In this presentation, a comprehensive overview of what makes and breaks super-low friction in such materials is provided in relation to the many intrinsic and extrinsic factors acting on them and on sliding interfaces. In light of the recent analytical, experimental, and computational advances, an attempt will also be made to elucidate those underlying mechanisms that are most responsible for such ultra-low friction and wear behaviors. Several case studies involving monolithic and hybrid coating systems providing super-low friction and wear are also presented as the most exciting developments in tribological field. Overall, these and other novel approaches are leading the way for the design and production of next generation tribological systems that can dramatically increase efficiency, reduce carbon emission, as well as improve reliability in future moving mechanical systems.

9:20am **G5-WeM5 Hybrid Technologies for Multifunctional Coatings Properties***, Dr. Pierre Collignon (pierre.collignon@pd2i.com),* PD2i SAS

Reducing friction and wear of the mechanical components is the big challenge to improve efficiency in many industries. DLC coatings is already used to reduce friction and wear on large scaled on automotive components which help to decrease the consumption and CO2 emission. To overcome some limitation in DLC coatings properties and to achieve a wide multifunctional property we have developed a new hybrid technology by combining plasma nitriding and PVD/PeCVD in the unique process.To increase productivity and reduced manufacturing cost, we have developed a one- unique hybrid technology equipment in which duplex surface treatment in thermotical treatment and thin film coating are associated .The plasma nitriding increase the mechanical and thermal fatigue resistance on precision components, and the DLC coating reduce the friction and improve wear resistance, find that this Duplex DLC offer a higher corrosion resistance in which process are made separately in 2 steps with two equipment's. few types of applications showing already achievement, and the potential of such innovations will be discussed furthermore.

9:40am **G5-WeM6 From *On-line* Sensor Validation to *in-situ* Monitoring of Layer Growth: Coatings around Fiber-Bragg-Gratings***, **Uwe Beck (uwe.beck@bam.de)**, A. Mitzkus, M. Sahre, T. Lange, M. Weise, M. Bartholmai, V. Schukar, F. Basedau, D. Hofmann, E. Köppe,* BAM Berlin, Germany

The lack of *on-line* validation procedures for structure-embedded fiber-optical strain sensors, in particular fiber-Bragg-gratings (FBG), resulted in limited applications in structural health monitoring (SHM). Degradation under service conditions and ageing as a result of climatic influences or delamination under load were unsolved validation issues. This could be overcome by means of an auto-diagnosis procedure based on FBG-sensors coated by electrochemical deposition (ECD) with a magnetostrictive NiFe-coating on top of an adhesive Cu/Cr adhesive layer deposited by physical vapour deposition (PVD) around the FBG strain sensor. This allows at any time under service a validation of sensor functionality, stability, and reliability. For this purpose, a magnetic strain-proportional reference field is introduced. The optical read-out is realized by the measurement of the Bragg-wavelength shift. The ratio of resulting strain and exciting magnetic reference field should be constant given that the sensor is in proper function [1, 2, 3].

In principle, the magnetostrictive coating around the FBG should also work as *on-line* magnetic field sensor and other applications in material science. One of these applications is the *in-situ* monitoring of ECD processes as the deposition of the ECD NiFe-layer on the FBG revealed. Challenges are the monitoring of temperature, deposition stages/thickness, and resulting mechanical stress under given plating conditions. Monitoring problems can be solved by applying a pre-coated FBG to the electrolytic process as the shift of the Bragg wavelength is affected by both the temperature of the electrolyte near the substrate and the stress formation in the growing layer. The experimental FBG set-up and the quantitative determination of temperature- and stress-related strain are described for a nickel-iron electrolyte. The in-situ measurement of Bragg wavelength shifts of a pre-coated FBG during electrochemical deposition allows a detailed analysis of stress states due to changes in the growth morphology of the layer. The separation of mechanical and thermal contributions to this shift provides information on the individual deposition processes in terms of a process fingerprint [4].

[1, 2, 3] DFG projects SCHU 2707/2-1, BA 5015/1-1, BE 3206/2-1.

[4] A. Mitzkus, M. Sahre, F. Basedau, D. Hofmann, and U. Beck; Journal of The ECS, 166 (6) B312-B315 (2019)

11:00am **G5-WeM10 Stabilization of FCVAS Based Hybrid System for Deposition of Thick Tetrahedral Amorphous Carbon Films and its Applications***, **Jongkuk Kim (kjongk@kims.re.kr)**, Y.-J. Jang,* Korea Institute of Materials Science (KIMS), Korea, Republic of Korea*; D.H. Kim, Y. Kang,* Korea Institute of Materials Science (KIMS), Korea*; J. Kim,* Korea Institute of Materials Science (KIMS), Korea, Republic of Korea **INVITED**

Diamond-like carbon (DLC) is used in various industrial applications such as automobile, mechanical machinery and optical lens, etc. due to their excellent physical, chemical and mechanical properties. In the case of automobile application, the coated films are required to have high thermal stability to prevent the film delamination during actual operating conditions.

However, many kinds of hard coatings (a-C, a-C:H) were very unstable under high temperature. During the operation, coated surface undergoes high mechanical, thermal and chemical stresses. Therefore, the surface quality degrades very quickly to an unacceptable level.

It is known that tetrahedral amorphous carbon (ta-C) is a hydrogen-free carbon coating with 70 ~ 80 % of sp3 phase, which results in smooth surface, good thermal resistance and wear resistance.

In particular, despite the high thermal stability and hardness, ta-C film deposited by vacuum arc method was difficult to be thickened due to high internal stress. Furthermore, it is hard to make thick coated layer as a carbon cathode became unstable when the coating process proceeds long time.

Our Research Group tried to improve the stability of the carbon cathodes for long-time coating process by controlling electric and magnetic fields. We have optimized the discharge stability so that the carbon arc target can be used stably at a discharge current of 160A for up to 24 hours.

The designed hybrid coating system consists of 1) Anode layer ion source (LIS) for the etching process, 2) Unbalanced magnetron sputter (UBM) for the deposition of interlayer, and 3) Filtered cathodic vacuum arc (FCVA) source for the deposition of ta-C film.

To adopt the designed hybrid coating process, the system was established with a single LIS, double UBMs, and eight FCVA with the maximum working area of 900 mm in diameter and 500 mm in height. For 5 µm coating of ta-C, the system can be operated for longer than 20 hours stably.

For the further application, we applied ta-C coating films on non-ferrous cutting tools (0.3 ~ 2 µm), piston rings (5 ~ 7 µm) of automotive engine parts, and semiconductor inspection probes with conductive ta-C (0.2 µm).

11:40am **G5-WeM12 Fabrication of Hf0.5 Zr0.5O2 Ferroelectric Tunnel Junctions by Hybrid Pulsed Laser and RF Magnetron Sputtering Technique***, **Rajesh Katoch (rajesh.katoch@emt.inrs.ca)**, Y. Gonzalez, A. Ruediger,* Institut National De La Recherche Scientifique, Canada*; S. Asadollahi, M. Patterson, A. Sarkissian,* PLASMIONIQUE Inc, Canada

We report on the deposition of high quality thin films for ferroelectric tunnel junctions by using a hybrid system which combines pulsed laser deposition (PLD) and RF magnetron sputtering (MS). The novel technique allows growing films at higher deposition rate, higher density, and smoother surface at lower temperatures [1] making the process suitable for many applications. The performance of this technique is demonstrated through fabrication of CMOS compatible structures, namely Hafnium Zirconium oxide (Hf0.5 Zr0.5O2) ferroelectric tunnel junctions on Si (100) substrates. Hf0.5 Zr0.5O2, is an important lead-free oxide material for its wide range of applications in ferroelectric random-access memories [2], ferroelectric field-effect transistors[3], artificial neural networks [4] among others. In this presentation we will compare and contrast the structures fabricated by conventional PLD, MS systems with the hybrid system, under similar deposition conditions, including deposition temperature and pressure. Optical emission spectroscopy will be used to gain insight on impact of plasma composition on deposited film structure.

References:

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[3] T. Ali, P. Polakowski, S. Riedel, T. Büttner, T. Kämpfe, M. Rudolph, B. Pätzold, K. Seidel, D. Löhr, R. Hoffmann, M. Czernohorsky, K. Kühnel, X. Thrun, N. Hanisch, P. Steinke, J. Calvo, J. Müller, Appl. Phys. Lett. 2018, DOI 10.1063/1.5029324.

[4] B. Mittermeier, A. Dörfler, A. Horoschenkoff, R. Katoch, C. Schindler, A. Ruediger, G. Kolhatkar, Adv. Intell. Syst. 2019, DOI 10.1002/aisy.201900034.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific Salon 6-7 - Session H2-2-WeM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes II

Moderators: Olivier Pierron, Georgia Institute of Technology, USA, Timothy Rupert, University of California, Irvine, USA

8:00am **H2-2-WeM1 Micromechanical Behavior of (C, N, O)-enriched Body-centered Cubic VNbTaMoW Alloy***, H. Zaid, J.W. Stermfel, A. Aleman, K. Tanaka, M.E. Liao, M.S. Goorsky, J.-M. Yang,* ***Suneel Kodambaka (kodambaka@ucla.edu)****,* University of California Los Angeles, USA

We determined the crystallinity, composition, and micromechanical responses of a compositionally-enriched VNbTaMoW alloy using a combination of X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy, nano- and micro-indentation, and *in situ* scanning electron microscopy based microcompression tests. We find that the alloy is a single-phase, body-centered cubic polycrystal that is nearly equiatomic, $V_{0.20}Nb_{0.20}Ta_{0.20}Mo_{0.22}W_{0.18}$, with a lattice constant of 0.319 ± 0.001 nm and spatially homogeneous (heterogeneous) elemental composition at millimeter (micrometer) length scales. We measure high (~ 10 at.%) concentrations of C, N, and O that decrease with increasing depth from the surface. Both elastic moduli and indentation hardnesses decrease with increasing indentation depth, which we attribute to changes in C and N concentrations across the bulk. [1] Uniaxial compression of cylindrical pillars revealed that they deform plastically with size-dependent increases in yield strengths (from 3.4 GPa to 7.3 GPa) and displacement bursts and decrease in strain hardening with decreasing diameter (from 1.08 µm to 0.24 µm). We suggest that the increase in yield strengths with decreasing diameter is likely due to a change in dislocation density while the size-dependence in strain hardening is due to dislocation generation and pile-up at grain boundaries. [2]

[1] H. Zaid, J.W. Stremfel, K. Tanaka, M.E. Liao, M.S. Goorsky, J.-M. Yang, S. Kodambaka, Effect of composition on mechanical properties of body-centered cubic VNbTaMoW alloy, *submitted*.

[2] H. Zaid, A. Aleman, S. Kodambaka, Size-dependent yielding and strain-hardening of compositionally-enriched body-centered cubic VNbTaMoW alloy, Scr. Mater., 178 (2020) 518-521.

8:20am **H2-2-WeM2 Improving the High Temperature Hardness of Nanocrystalline Copper through Tungsten Nanoparticles***,* ***Nadia Rohbeck (nadia.rohbeck@empa.ch)****, T.E.J. Edwards, E. Huszár, L. Pethö, X. Maeder, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

The hardness of copper (Cu) can be greatly improved by a refined microstructure consisting of nano-sized grains. So far the application of such nano-grained Cu has been inhibited by its inability to withstand elevated temperatures and even at room temperature spontaneous abnormal grain growth has been observed.

Here, we show that the hardness of nano-grained Cu can be retained by incorporating about 1 vol% of tungsten (W) nanoparticles. Therefore, thin film Cu was synthesised by physical vapour deposition (PVD) inside a custom-built deposition chamber that had been modified to allow for concurrent co-deposition of W nanoparticles. *In situ* high temperature indentation measurements were performed up to a maximum of 400°C.

By comparing the hardness evolution with temperature of the Cu film containing W nanoparticles with the pure Cu sample, differences in the deformation mechanism become apparent. In the as deposited state both samples exhibited an identical hardness of 3.2 GPa and when the temperature increased the hardness decreased by equal amounts in both films. From 200°C onwards, however, the drop in hardness was notably sharper in the pure Cu film. After cool down, the hardness was found to be reduced by 50% in the pure Cu, whereas the Cu-W nanoparticle sample had retained more than 90% of its initial hardness value.

Subsequent TEM imaging showed that the W nanoparticles with a diameter of 4 nm were randomly distributed within the Cu matrix at an average spacing of 9 nm. The microstructure consisting of columnar grains with a high density of nanotwins was not changed after the thermal exposure. The pure copper films showed larger grains and exhibited a completely changed texture. Here we could prove that by incorporating as little as 1 vol% of second phase particles in nanocrystalline copper, the microstructure can be stabilised even at high temperatures leading to an improved hardness.

8:40am **H2-2-WeM3 Toward Novel Stretchable Electronics with Nanostructured Metallic Glass Films***,* ***Matteo Ghidelli (m.ghidelli@mpie.de)****,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; H. Idrissi,* Université Catholique de Louvain, Belgium*; A. Orekhov,* University of Antwerp, Belgium*; J.P. Raskin,* Université catholique de Louvain, Belgium*; J.U. Park,* Yonsei University, Republic of Korea*; A. Li Bassi,* Politecnico di Milano, Italy*; T. Pardoen,* Université catholique de Louvain, Belgium

Thin film metallic glasses (TFMGs) are emerging materials characterized by outstanding combination of mechanical/electrical properties involving a yield strength close to the theoretical limit, large ductility (> 10%) [1] and metallic-like conductivity [2]. Nevertheless, the synthesis of advanced TFMGs with engineered microstructure and the understanding of their mechanical/electrical properties is barely tackled, requiring the development of novel synthesis strategies and cutting-edge techniques for submicrometer scale characterization.

Here, we report the use of Pulsed Laser Deposition (PLD) as a novel technique to synthetize nanostructured $Zr_{50}Cu_{50}$ (%at.) TFMGs. We show how the control of PLD process parameters (background gas pressure and laser fluence) enables to synthetize different film microstructures involving atom-by-atom or cluster-assembled growth, resulting in a variety of film structures including compact fully amorphous, amorphous nano-porous with large free volume interfaces, and amorphous embedded with nanocrystals. High-resolution TEM reveals a nano-laminated atomic structure characterized by alternated layers with different chemical enrichment and local atomic order.

This self-assembled nanoarchitecture is at the basis of unique mechanical properties including large elastic modulus (145 GPa) and hardness (10 GPa). Quantitative *in-situ* TEM tensile tests reveal that films have an outstanding yield strength (3 GPa) and ductility (> 9%) product which is significantly dependent on the microstructure with large/low plasticity and low/high yield strength obtained for nanogranular/compact metallic glass films. Finally, we developed a stretchable transparent electrode based on nanogranular TFMGs nanotrough network showing excellent stretchability (70%) and low sheet resistance (~3 Ω/sq) which is then integrated in wirelessly rechargeable transparent heater, demonstrating the potential of these films for novel stretchable electronic devices.

[1] M. Ghidelli, H. Idrissi, S. Gravier, J.-J. Blandin, J.-P. Raskin, D. Schryvers, T. Pardoen, Acta Mater. 2017, 131, 246-259.

[2] B. Wan An, E.-J. Gwak, K. Kim, Y.-C. Kim, J. Jang, J.-Y. Kim, J.-U. Park, Nano Lett. 2016, 16, 1, 471-478.

9:00am **H2-2-WeM4 An Innovative Metal/Insulator/Metal Structure for Application of Damping Oscillator within One-Selector-One-Resistance***,* ***Chih-Yang Lin (hubery820919@gmail.com)****, T.C. Chang,* National Sun Yat-Sen University, Taiwan*; P.H. Chen,* Chinese Naval Academy, Taiwan

This paper presents a comprehensive study of oxide-based selector characteristics with a universal model for interface-type threshold switching (TS) phenomena. The thermal-induced TS transition and electrical-induced TS transition at interface have been confirmed by versatile material and structure systems. The physical understanding of evolution in energy barrier and MIT metallic state modulation have been studied with the proposed innovative vanadium electrode. The selector with vanadium electrode owns better characteristic, after series to a resistance, it shows the damping characteristic which can be applied to be a promising oscillator.

9:20am **H2-2-WeM5 X-Ray Photoelectron Spectroscopy Analysis of Electronic Band Structure for MIM Capacitor Interfaces***,* ***Son Hoang (son.hoang@emdgroup.com)****,* Intermolecular Inc., a subsidiary of Merck KGaA, Darmstadt, Germany, USA*; T. Ngo, E. Januar, M.E. McBriarty, A. Lee, C. Clavero,* Intermolecular Inc., a subsidiary of Merck KGaA, Darmstadt, Germany

Metal-Insulator-Metal (MIM) capacitors play a crucial role in many applications including dynamic random access memories (DRAM), radiofrequency and analog circuits, and high power microprocessor units. For the DRAM applications, the understanding of the electronic band structure of the interface between the high-k dielectric and metal is crucial to design an effective strategy to control the leakage current. Future DRAM MIM capacitors aim at an increasingly thinner oxide layer with equivalent oxide thicknesses below 0.5 nm [1], posing challenges in probing interfacial properties using conventional metrology methods.

In this work, we report an entirely XPS-based workflow to determine the interfacial band structure of TiN/ZrO_2/TiN stacks. The TiN/ZrO /TiN stacks were deposited on Si substrates by magnetron sputtering of TiN and atomic layer deposition of ZrO_2. XPS is a surface-sensitive technique, probing only the top 6-10 nm of the material being analyzed. Conventionally, XPS is used to analyze the composition, chemical states, and valence band structures of materials. In our case, we also employ XPS to determine the work function of TiN via cut-off energy measurement and the bandgap of the ultrathin ZrO_2 layer via examining the onset of energy loss in O1s core-level spectra [2]. An electronic band model of the interface is proposed based on the combined analyses, allowing us to determine barrier height and providing insight into the potential leakage of the stack.

[1] S. Y. Lee et al., Appl. Phys. Lett. 105 (2014) 201603

[2] M. T. Nichols et al., J. Appl. Phys. 115 (2014) 094105

Topical Symposia
Room Pacific Salon 3 - Session TS2-3-WeM

New Horizons in Boron-Containing Coatings: Modeling, Synthesis and Applications III

Moderators: Marcus Hans, RWTH Aachen University, Germany, Helmut Riedl, TU Wien, CDL-SEC, Austria, Johanna Rosen, Linköping University, Sweden

8:00am **TS2-3-WeM1 Thermo-physical Properties of CVD Ti(B,N) Coatings***, **Christina Kainz (christina.kainz@unileoben.ac.at)**, N. Schalk, M. Tkadletz, C. Saringer,* Montanuniversität Leoben, Austria*; M. Winkler,* Fraunhofer Institute for Physical Measurement Techniques IPM, Germany*; A. Stark, N. Schell,* Helmholtz-Zentrum Geesthacht, Germany*; J. Julin,* Helmholtz-Zentrum Dresden-Rossendorf, Germany*; C. Czettl,* CERATIZIT Austria GmbH, Austria

Hard protective coatings are commonly subjected to temperatures up to 1000 °C, which has a significant influence on their thermo–physical properties and the associated performance in application. Within the present work, temperature dependent physical properties of chemical vapor deposited (CVD) coatings within the Ti(B,N) system were correlated with their chemical composition. High–energy X-ray diffraction experiments in inert atmosphere proved that CVD TiN, TiB_2 and ternary TiB_xN_y coatings with varying B contents are thermally stable up to 1000 °C. With increasing B content, the TiB_2 fraction in the coating increased gradually, whereas the grain size decreased. First order tensile strains of TiN and ternary TiB_xN_y coatings with different compositions decrease during heating. Contrary, TiB_2 exhibits compressive strain enhancement up to the deposition temperature, followed by strain relaxation thereafter up to 1000 °C. Nanocrystalline TiB_2 exhibits more pronounced grain growth during annealing compared to coarse grained columnar TiN. The mean thermal expansion coefficient decreases as the B content increases from 9.18×10^{-6} K^{-1} in TiN to 7.95×10^{-6} K^{-1} in TiB_2. The thermal conductivity decreases from 45 W/mK in TiN to 14 W/mK in TiB_2 and correlates with the grain size of the coatings. Annealing of TiB_2 resulted in an increment of the thermal conductivity (38 W/mK), which is ascribed to the less pronounced phonon scattering with increasing grain size and lower defect density. In summary, the present work provides a comprehensive overview of the thermo-physical properties of CVD coatings in the Ti(B,N) system filling a gap in the existing literature.

8:20am **TS2-3-WeM2 Effect of MB_2 (M = Zr, Ta, Nb, Hf, Ti, V, Cr) and W_2B_5 Target Composition on Plasma Properties and Thin-Film Stoichiometry During Magnetron Sputtering***, **Igor Zhirkov (igor.zhirkov@liu.se)**,* Linköping University, IFM, Thin Film Physics Division, Sweden*; F.F. Klimashin,* Linköping University, Sweden, Austria, Sweden*; G. Greczynski,* Linköping University, Sweden*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J.E. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan, USA*; I. Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J. Rosen,* Linköping University, Sweden

DC magnetron sputtering (DCMS) is a widely used technique for the deposition of decorative, protective, and wear-resistive coatings. However, high power impulse magnetron sputtering (HiPIMS), due to the pulsed nature and higher peak current/power, is able to provide a much higher degree of sputtered atom ionization. This allows for a better control of the material flux, and a pathway for tuning of thin-film stoichiometry and microstructure. The physical vapor deposition synthesis of metal diborides (MB_2) is an expanding area of research and is primarily carried out by sputtering from a compound target. For both HiPIMS and DCMS, the material flux from the target goes through three primary stages – sputter ejection, plasma transport, and film deposition. The target composition is rarely preserved in the resulting film stoichiometry. In the present work, we have performed a systematic study of HiPIMS and DCMS plasmas generated from circular 5 cm diameter ZrB_2, TaB_2, NbB_2, HfB_2, TiB_2, VB_2, W_2B_5, and CrB_2 targets at Ar pressures of 3 and 20 mTorr. For all depositions, the average power is kept constant at 50 W, with HiPIMS being operated at a repetition rate of 100 Hz and a pulse length of 100 µs. Plasma characterization, including plasma chemistry and time- and charge-resolved ion energy distributions, is performed with a spectrometer-to-target distance of 15 cm. Corresponding films were deposited using the same geometry, for compositional characterization and a comparison to the plasma and target composition. The obtained results are discussed as a function of the material properties of the metal diboride targets, and in view of the differences in mass of the metal component. The study is aimed at developing an understanding of the synthesis of stoichiometric MB_2 using sputtering techniques.

8:40am **TS2-3-WeM3 Influence of Sputtering-Parameters on Stoichiometry and Mechanical Properties of Selected Binary and Ternary Transition Metal Diborides***, **Vincent Moraes (vincent.moraes@tuwien.ac.at)**, H. Riedl, P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

In the last couple of years, borides or diborides in particular, have drawn great attention in the development of protective coatings with exceptional properties. Their high melting points and excellent hardness are promising attributes to outperform nitride-based materials in various fields of applications.

Transition metal diborides tend to crystallize in two related but slightly different hexagonal structures. Whereas early TMB_2s have their stable configuration in the AlB_2-prototype (α-type, SG-191), late TMB_2s energetically prefer the W_2B_{5-x} prototype (ω-type, SG-194) showing a difference in the crystallographic ordering. Recent investigations on WB_2 have shown that in the case of thin films, the material crystallizes in the α-type, though its energetically preferred structure is the ω-type. Moreover, the thin films show a rather boron deficient chemical composition compared to measurements of bulk materials. On the contrary, HfB_2 clearly crystallizes in the α-type (bulk as well as thin films) with a tendency to an increased boron content.

In this study, we investigate the theoretical and experimental possible influences on stoichiometry, microstructure and the preferred structure type of various transition metal diborides. Therefore, we used Density Functional Theory calculations to study phase stabilities and the impact of point defects in combination with experimental variations on binary and ternary diboride systems such as HfB_2, CrB_2, $V(W)B_2$, or $W(Ta)B_2$.

9:00am **TS2-3-WeM4 Challenges in Determining the Composition of TiB_x Thin Films***, **Niklas Hellgren (nhellgren@messiah.edu)**,* Messiah College, USA*; M.A. Sortica,* Linköping University, Sweden*; J. Rosen,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; V. Vishnyakov,* Institute for Materials Research, University of Huddersfield, UK

We report on compositional analysis of several titanium boride thin films using various analytical techniques; RBS, ERDA, EDX, WDX and XPS. While each technique offer certain advantages, they also suffer drawbacks, which are assessed in this comparative study. ERDA in combination with RBS provide the most reliable absolute quantification, since no calibration standard is required. Using this data as a reference, it was determined that the composition of our films, grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target in Ar discharge, varied over the range .

EDX is readily available in almost all electron microscopes. With a proper understanding of the EDX technique itself, the instrument manufacturer quantification routes and utilizing composition standards it is possible to obtain relatively reliable and accurate data. It is advisable to use Ti L lines as this possibly reduces some systematic errors. WDX spectra have much better energy resolution and allow to avoid some EDX spectra artifacts albeit the technique cost and relative complexity.

XPS is surface sensitive and is routinely performed after sputter cleaning. However, preferential atom sputtering can alter the calculated compositions. We show that this is further complicated by the fact that the degree of preferential sputtering can vary depending on film density and structure. We explore ways to mitigate these uncertainties by careful spectra deconvolution.

It is concluded that all used techniques can fundamentally produce accurate boron quantification if applied with care.

9:20am **TS2-3-WeM5 Metal Diborides Everywhere: Conformal Coating, Infilling, and Alloying by Low Temperature CVD***, John R. Abelson (abelson@illinois.edu),* University of Illinois at Urbana-Champaign, USA **INVITED**

Using low-temperature (< 300°C) CVD, it is possible to deposit refractory metal diborides in an extremely conformal fashion on complex and re-entrant substrate shapes. Kinetically, this is due to the properties of CVD precursor molecules based on borohydride ligands; for example, $Hf(BH_4)_4$ has a (huge) vapor pressure of 15 *Torr* at room temperature and decomposes above 150°C. Under these conditions, growth involves a competition on the film surface: the rate of precursor adsorption is large with respect to the rate of desorption of precursor or products, hence, the surface is dynamically covered with reaction intermediates. The reactivity to impinging precursor is then very low, while in parallel, the adsorbed intermediates react continuously to afford metal diboride film. The result is the growth of extremely conformal layers at useful rates [1] on complex morphologies [2].

We demonstrate the growth of HfB_2 films with > 90 % conformality on deep trenches for microelectronics and on carbon nanotube (CNT) forests 400 µm tall. The HfB_2-coated CNT is a new refractory hybrid material in which the density, modulus, and failure strength can be controllably varied over orders of magnitude via the HfB_2 film thickness.

The metal diboride growth kinetics can be further modified by adding an *inhibitor* molecule that adsorbs on the growth surface, but which does not decompose and ultimately desorbs from the surface without incorporation. We demonstrate three unique results using different inhibitors. First, an inhibitor can be used to convert a 'non-conformal' precursor such as $Ti(BH_4)_3$dme into one that affords conformal coatings [3]. Second, an inhibitor that sticks differentially to film vs. substrate can be used to alter the dynamics of nucleation; for example, the use of NH_3 as an inhibitor produces an extremely uniform density of HfB_2 nuclei on SiO_2, such that the fully coalesced film has a roughness < 1 nm [4]. Third, a highly reactive inhibitor such as atomic H, generated by a remote H_2 plasma, can be used to reduce the growth rate near to the opening of a deep feature but not at depth; the result is superconformal growth (faster at the bottom) by CrB_2.

Finally, we describe the use of alloying elements, such as N, C, or Al, to afford CVD coatings that have various combinations of low-friction and wear [5], or oxidation resistance at temperatures > 800°C.

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11:00am **TS2-3-WeM10 Insights in the Structure, Defects and Stability of Mo_2BC Thin Films by Advanced Characterization Methods***, S. Gleich, R. Soler, B. Breitbach,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; H. Bolvardi, J.O. Achenbach, J.M. Schneider,* RWTH Aachen University, Germany*; G. Scheu,* ***Christina Scheu (scheu@mpie.de),*** Max-Planck-Institut für Eisenforschung GmbH, Germany **INVITED**

Mo_2BC thin films find application as protection layers for cutting tools due to their high strength and ductility. These properties are governed by the microstructure, which can be controlled by the growth temperature or by post-processing annealing. In the present work, the structure and defects of thin Mo_2BC thin films deposited on (100) Si substrates by bipolar pulsed direct current magnetron sputtering were studied in-depth by various (scanning) transmission electron microscopy (S)TEM techniques. The substrate temperatures T_s ranged from 380 °C to 630 °C [1]. Post-processing experiments were performed on the film deposited at 380 °C, which was heated up to 900 °C [2].

The film grown at 630 °C has a columnar structure and is fully crystalline [1]. The grains with a size of around 10 nm possess several defects such as stacking faults as observed in atomic column resolved STEM images, which are related to the slight deviation from the nominal stoichiometry. A different microstructure was found for the films deposited at lower T_s. They consist of an amorphous matrix in which ~1,9 to 1.2 nm sized nanocrystals are embedded [1]. The amount of amorphous matrix is increasing with decreasing T_s while the size of the nanocrystals is decreasing. STEM imaging together with electron energy-loss spectroscopy revealed that all films contain Ar-rich clusters originating from the deposition process. The size of the clusters is similar for all films but their volume content is strongly increasing with decreasing T_s. The observed difference in microstructure can explain the mechanical properties with the highest hardness and Young's modulus value found for the coating deposited at 630 °C.

The microstructural changes of the film deposited at 380 °C induced by annealing were studied by ex-situ and in-situ X-ray diffraction and TEM experiments. The as-deposited, mainly amorphous film transformed to a fully crystalline one. Elongated crystals with a lengths of up to 1 µm were found at elevated temperatures [2]. Furthermore, at temperatures above 840 °C delamination from the Si substrate took place. Nevertheless, the results revealed that an annealing treatment below this temperature is a possible approach to improve the crystallinity and thus the mechanical properties [2].

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11:40am **TS2-3-WeM12 Microstructure and Materials Properties of Understoichiometric TiB_x Thin Films Grown by HiPIMS***, **Jimmy Thörnberg (jimmy.thornberg@liu.se),*** Thin Film Physics Division, IFM, Linköping University, Sweden*; N. Hellgren,* Messiah College, USA*; N. Ghafoor, J. Palisaitis, I. Zhirkov, C. Azina, P.O.Å. Persson,* Thin Film Physics Division, IFM, Linköping University, Sweden*; I. Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J.E. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan, USA*; J. Rosen,* Thin Film Physics Division, IFM, Linköping University, Sweden

High-power impulse magnetron sputtering (HiPIMS) has paved the way toward improved control of the stoichiometry of TiB_x thin films. Whereas conventional direct-current magnetron sputtering (DCMS) yields TiB_x films with excess B, HiPIMS allows for the synthesis of thin film compositions ranging from very understoichiometric to very overstoichiometric TiB_x [1]. Here, we present results on the synthesis and characterization of TiB_x thin films with a B/Ti ratio ranging from 1.4 to 2.7, as determined by elastic recoil detection analysis. The films are grown with both HiPIMS and DCMS, the latter for reference, on biased Al_2O_3 substrates at a distance of 6.5 cm from the target surface, using a substrate temperature of 500 °C, a base pressure of $7x10^{-8}$ Torr, and Ar pressures of 5 and 20 mTorr. In previous work, excess B in overstoichiometric TiB_x thin films is reported to form a tissue phase between grains of stoichiometric TiB_2, resulting in an increased hardness [2]. In the present study, we show a hardness of understoichiometric TiB_x thin films from HiPIMS of ≥45 GPa, with values matching the overstoichiometric counterpart deposited by DCMS. Furthermore, the elastic modulus and thermal conductivity of HiPIMS films with a B/Ti ratio of 1.4-1.5, is 700 GPa and 5.1 W/(m.K), respectively, as compared to corresponding values for DCMS samples of 600 GPa and 3.0 W/(m.K). Based on X-ray diffraction and high-resolution transmission electron microscopy, this work increases the understanding of the effect of composition on the resulting microstructure and materials properties of TiB_x films.

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12:00pm **TS2-3-WeM13 On Hardening Mechanisms in Quasi-Binary Diboride Thin Films***, **Fedor F. Klimashin (fedor.klimashin@liu.se)**,* Linköping University, Sweden*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J.E. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan, USA*; I. Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J. Rosén,* Linköping University, Sweden

Properties of the diborides based on group IV-VI transition metals, such as high hardness, high melting points, and high thermal and electrical conductivities, have sparked the interest of both academia and industry. The number of publications devoted to transition metal diborides is increasing exponentially, and a big effort has already been made to understand their properties on the atomic and subatomic scales. However, the interest in multicomponent diborides is just gaining momentum.

Here, we have used theoretical predictions for guidance and for selecting and producing multicomponent phases with desired properties. We have investigated quasi-binary diboride thin films in the *Me*–Cr–B (*Me* = Ti, Hf, Zr) systems, for a metal fraction of Cr, x = Cr/(*Me*+Cr), up to 0.5. Non-reactive co-sputtering of the confocal MeB_2 and CrB_2 targets resulted in the formation of AlB_2-type (*P*6/*mmm*) quasi-binary diborides. For *x* up to 0.4, no softening could be observed in the *Me*–Cr–B films, even though CrB_2 films of a hardness of 15 GPa are approximately 50 % softer than *Me*B_2. In particular, the Hf–Cr–B films stand out from other *Me*–Cr–B films by showing superhardness (> 40 GPa) for *x* up to 0.45. To provide insights into the hardening mechanisms, we approach the matter from the perspectives of varying strengthening mechanisms, microstructural characteristics, alterations in the stoichiometry, etc. Our results demonstrate a pathway to boost the performance of transition metal diboride thin films, under conditions indicating a high industrial potential.

Special Interest Talks
Room Town & Country - Session SIT3-WeSIT

Special Interest Session
Moderator: Grzegorz (Greg) Greczynski, Linköping University, Sweden

1:00pm **SIT3-WeSIT1 Materials Discoveries at Extreme Conditions: A Path Towards New Advanced Materials*, Igor Abrikosov (igor.abrikosov@liu.se)*,** Linköping Univ., IFM, Theoretical Physics Div., Sweden **INVITED**

More than 100 years ago Gibbs [1] formulated his theory that still serves as a foundation for understanding of materials stability. Predictive power of the theory is well established for materials in the equilibrium state, the state with the lowest energy called the ground state. However, deep insights into mechanisms leading to the formation of metastable phases with energies above the ground state energy are missing, despite their wide appearance in nature and the broad use in technology. The luck of a consistent theory in this field limits our ability to discover and design novel materials.

In this talk we demonstrate that broadly varying external parameters, pressure, temperature and composition, as well as combining theoretical simulations with experiment, one discovers new materials with properties attractive for applications. Moreover, the studies of the behavior of matter at extreme conditions challenge the accepted concepts within materials science. In particular, the crystal structures two newly discovered high-pressure silica phases, coesite-IV and coesite-V contain SiO_6 octahedra, which, at odds with 3rd Pauling's rule, are connected through common faces [2]. We further illustrate intriguing features of recently discovered transition metal nitrides [3]. Finally, we report the synthesis of metallic, ultraincompressible and very hard rhenium nitride pernitride $Re_2(N_2)(N)_2$. Unlike known transition metals pernitrides, it contains both pernitride $(N_2)^{4-}$ and discrete N^{3-} anions, which explains its exceptional properties. Importantly, $Re_2(N_2)(N)_2$, which was discovered via a reaction between rhenium and nitrogen in a diamond anvil cell at pressures from 40 to 90 GPa has been recovered at ambient conditions, and a route to scale up its synthesis has been developed. Thus, the fundamental understanding of the physical principles behind the formation of the metastable structures generated in our studies is essential for the accelerated knowledge-based design of novel materials.

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Coatings for Use at High Temperatures
Room Pacific Salon 1 - Session A3-WeA

Materials and Coatings for Solar Power Concentration Plants

Moderators: Gustavo García Martín, REP-Energy Solutions, Spain, Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Germany

2:00pm **A3-WeA1 The Essential Role of STE/CSP Plants in the Energy Transition. Challenges on Materials to Enhance Competitiveness***, **Luis Crespo (luiscrespo@protermosolar.com)**,* Protermosolar, Spain **INVITED**

High penetration of cheap but non dispatchable renewable generation technologies, like Wind and PV, along with the progressive decommissioning of conventional power plants arise fundamental concerns on policy makers and electrical system operators. The main issue is whether the fleet of generation units will be able to respond to the demand needs, particularly at the times of peak demand. In addition, generation fleet consisting mostly of variable renewables will create other important concerns in terms of grid stability and affordable ramps for the backup plants. STE/CSP is the cheapest renewable technology to provide electricity after sun sets every day. Therefore, the future deployment of STE plants should be mostly done complementing the hourly dispatch profile of PV plants in sunny countries. In addition, STE plants could respond to the request of the system operator at full nominal power at any given time, independently on whether the request is made in a sunny day or after a long row of cloudy days, just by keeping a part of the storage capacity available for this service.

In the paper the specific features and operational flexibility of STE plants will be described. In addition, the current status of the technology along with the deployment plans and potential around the world will be presented.

Innovation in materials, in both working fluids and specific equipment's – receivers, storage tanks, heat exchangers, rotating joints, etc. – is key to improve cost and reliability figures.

2:40pm **A3-WeA3 High-Temperature Protective Coatings against Molten Nitrate Salts for CSP Technology***, **Gustavo García Martín (gustavo.garcia@rep-energysolutions.com)**,* REP-Energy Solutions, Spain*; V Encinas Sánchez, I Lasanta Carrasco, T De Miguel Gamo, F Pérez Trujillo,* Universidad Complutense de Madrid, Spain

The high demand for energy and its production through the burning of fossil fuel is one of the factors responsible for the impact of climate change on the Planet. This has revealed the need to develop and optimize renewable technologies.

Commercial concentrated solar power plants along with thermal energy storage systems, such as "parabolic trough", are more attractive than other renewable energies because of their thermal storage capacity, and are used when the resource (sun) is not available

Molten nitrate salts are currently considered ideal candidates for heat transfer and storage applications because of their properties. However, these salts are known for their high corrosiveness, increasing the associated O&M costs and making this technology still expensive compared to other renewable sources. This situation leads to propose solutions for reducing costs in terms of materials for the thermal storage systems (tanks, pipes, valves and heat-exchangers). One of these solutions is the development of high-temperature corrosion-resistant coatings, since they would avoid using expensive alloys (such as Ni-based alloys). The use of high-temperature protective coatings would be a very suitable option for reducing costs in CSP technology, even more if they enable the widespread use of low-cost steels, such as ferritic-martensitic ones. Thus, this solution would allow not only overcoming the corrosion problems, but also reducing the Levelized Cost of Energy, which would have a significant impact on the CSP technology. In this respect, ZrO_2-based sol-gel coatings appear as suitable option both from a technological and economical point of view.

Thus, in this work, sol-gel zirconia-based coatings were deposited on ferritic-martensitic steels and tested in contact with Solar Salt at 500°C, results being compared with the uncoated substrate. Results were also compared to other steels of interest in CSP industry, such as austenitic stainless steels. The study was developed up to 2000 h under static conditions. Samples were characterized via gravimetric, SEM-EDX, and XRD.

Results showed the good behavior of the coated substrates, with very little weight variations after 2000 h of test in comparison with the uncoated ones, which exhibited significant weight gain and spallation. The good behavior of the proposed coatings was also observed by SEM-EDX and XRD, showing a protective diffusion layer of about 5 mm. Furthermore, results also showed the promising behavior when comparing with steels currently used in CSP industry.

3:00pm **A3-WeA4 Corrosion Monitoring of Protective Sol-Gel Coatings in Contact with Molten Carbonates for the Next Generation of Concentrated Solar Power Plants***, **Francisco Javier Pérez Trujillo (fjperez@ucm.es)**, G García Martín, V Encinas Sánchez, I Lasanta Carrasco, T De Miguel Gamo,* Universidad Complutense de Madrid, Spain

In the last few years the interest in renewable energies has suffered a significant increase, representing the Concentrated Solar Power (CSP) technology the present and the future of the electric energy obtained from the sun in large scale. Commercial CSP plants usually use molten salt mixtures as thermal energy storage medium. The currently used industrial compound is an alkali-nitrate mixture composed of 60 wt.% $NaNO_3$/40 wt.% KNO_3. However, the development of new molten salt mixtures with higher thermal stabilities that allow increasing the working temperature has received great interest in the last few years. In this respect, many authors have recently proposed the replacement of molten nitrate salts by molten carbonate salts, making possible an increase in the operational temperature beyond 700 °C. However, one of the main drawbacks of this medium consists in the severe corrosion problems to which its composition and high temperature lead. Thus, the development of protective coatings for steels could be an interesting alternative, both from a technological and economical point of view, for increasing the lifetime of pipes and tanks in contact with molten carbonates. In both cases, the Levelized Cost Of Electricity would suffer a substantial reduction, which is one of the major objectives currently set in CSP technology.

Additionally, a further improvement in this technology would be the installation of a corrosion monitoring system that allows a continuous recording of corrosion rates. The use of conventional methods for assessing the corrosion in molten salt environments is not adequate when monitoring corrosion process at real-time. Therefore, the monitoring system would lead to a better understanding of the corrosion processes taking place. In this regard the electrochemical impedance spectroscopy (EIS) appears as a powerful technique for monitoring corrosion processes that take place in steels under molten salt environments.

Thus, this work aimed at developing sol-gel protective coatings on stainless steels and monitoring the protective behavior in contact with a eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3 salt by employing EIS technique. To this end, electrochemical sensors were employed. Corrosion tests were performed at 700°C up to 1000 h and EIS results were supported by gravimetric and microstructural characterizations. All results were compared to the uncoated steels.

Results showed the promising behavior of the coated substrates. Corrosion monitoring system showed the protective behavior of the coatings, these improving the behavior of the uncoated samples, where detachments and high weight variations were observed.

3:20pm **A3-WeA5 Magnetron Sputter-deposited TiC-W Multilayered Solar Selective Coatings***, **Yi-Hui Zhuo (e54016324@gmail.com)**,* National Cheng Kung University, Taiwan

Exploring a high performance spectrally selective solar absorber is one of the great challenges for the succes of Concentrating Solar Power (CSP). This work is aimed at the development of solar selective coating. A multi-layered structures of SS/W/TiC-W/HfO_2 is investigated. Tungsten(W) serve as the IR-reflector, cermet made of titanium carbide (TiC) and tungsten (W) serve as the absorber and hafnium oxide (HfO_2) on the surface serve as anti-reflection layer. In the fabrication process, the magnetron sputtering is used to deposit all the layers on the stainless steel (SUS-316L) substrate.The cermet absorber is first optimized by fine tuning the metal volume factor. The thickness of each layers is then adjusted. Good thermal stability is shown after anneal process under 600°C and 800°C. The relationship between material characteristics and optical performance is addressed in this work. Effect of high temperature is studied. Excellent solar selectivity under high temperature is demonstrated.

Keywords: TiC,HfO_2, solar absorber, multilayer absorber, magnetron sputtering

3:40pm **A3-WeA6 Biodegradable Polyurethane Antifouling Coating***, **Mohammad Mizanur Rahman (mohammadmizanur@gmail.com)**,* King Fahd University of Petroleum and Minerals, Saudi Arabia

Controlled biocide leaching is one of the vital criteria's to consider any polymer as an antifouling coating. Besides the pollution of marine environments using excess toxic biocides is a huge concern worldwide. Almost all of the current commercial antifouling coatings contain toxic biocide. Thus, it is important to use a coating, which can control biocide leaching. Biopolymer can be a good choice in this regard as the biodegradable coating can be degraded easily with proper environment. Unfortunately little research has been done in this respect. Most of the research has been done mainly polycaprolactone based polyol. Xanthangum (Xn) might be a good choice. In this study biopolymer xanthan-poly(N-vinyl imidazole) (Xn-VI)was synthesized. The polymer was used in polyurethane (PU) coating to make a water erodible coating to improve the antifouling properties. Coating hydrophilicity, adhesive strength and erosionall varied with the Xn-VI contents. A good antifouling property for longer time was found in the PU-Xn-VI coating using biocide in the field test.

4:00pm **A3-WeA7 Aluminide Coating for Inconel 625 Prepared by Additive Manufacturing: Investigation of the Surface Reactivity of the Substrate***, N. Ramenatte, L. Portebois, S. Mathieu, L. Aranda,* ***Michel Vilasi (michel.vilasi@univ-lorraine.fr)****,* University of Lorraine, France

The project FAIR intends to develop innovative microreactor-exchanger (MR-E) based on 3D printing manufacture in order to intensify the H2 synthesis process. The Ni-based Inco 625 was selected as substrate due to its satisfying high temperature properties. Notably, it can resist against Metal Dusting corrosion provided it is protected by an aluminum reach overlay. The present study made it possible to characterize the coating processes as well as the oxidation behavior of the as-obtained coated substrate in connection with the physicochemical properties of 3D printed alloys (SLM) and in comparison with the conventional melted alloys (CMA).

A. Synthesis of Inco 625 via SLM

This process was conducting using the following main (non-confidential) parameters: alloy powder with a 10µm diameter grain size, melting under Ar atmosphere (P=1bar) and cooling at 10^7 K/s.

The as-obtained substrates are constituted of supersaturated γ grain having the nominal composition of Inco 625 and a textured microstructure showing a grain elongation parallel to the direction of growth.

As expected, the superficial roughness is huge due to the occurrence of fine spherical particles just sealed on the surface.

The wanted mechanical properties are then recovered by applying a heat treatment performed in the conventional conditions.

B. Coating depositions by CVD and slurry processes

Aluminum surface enrichments were performed using two techniques: i) the pack-cementation as CVD technique which is well known and described in the literature and ii) the slurry process also widely implemented for pieces having complex geometry, such as pieces comprising internal small channels. For both techniques, the rate limiting step is the solid state diffusion of metallic elements.

The coating elaborations were carried out on crude SLM and CMA substrates by applying a two steps heat treatment:

- the first one allows the aluminum enrichments through an annealing i) at 640°C during 4h for the packcementation process and ii) at 640°C and then at 700°C during respectively 4h and 1h, for the slurry process.

- The second step allows the NiAl formation by interdiffusion of metallic species which was activated by a high temperature treatment at 980°C during 1h.

Whatever the process, after the first stage of heating treatment, the same coatings were obtained: they are 40 µm thick and are two-phased systems comprising Al3Ni and Al3Ni2. This situation is the consequence of the similar interdiffusion coefficient of metals in SLM and CMA. Moreover, the present experiments evidence obviously that the rate limiting step is effectively the solid state diffusion for both synthesis techniques

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-1-WeA

Properties and Characterization of Hard Coatings and Surfaces I

Moderators: Naureen Ghafoor, Thin Film Physics Division, IFM, Linköping University, Sweden, Marcus Günther, Robert Bosch GmbH, Germany, Fan-Bean Wu, National United University, Taiwan

2:00pm **B4-1-WeA1 Properties of Thin Film Metallic Glass Produced by High Power Impulse Magnetron Sputtering***,* ***Niklas Boenninghoff (d10604812@mail.ntust.edu.tw)****,* National Taiwan University of Science and Technology, Taiwan*; J.P Chu, W. Diyatmika,* National Taiwan University of Science and Technology (NTUST), Taiwan*; G. Greczynski,* Linköping University, Sweden

We report on the difference between Zr Cu Al Ni thin film metallic glasses (TFMGs) prepared by single target DC

and High Power Impulse Magnetron Sputtering (HiPIMS). Three deposition variations are investigated. DC at

1kW, HiPIMS at 1kW and 2.5kW average deposition power. It is found that the microstructure of the thin films

varies between DC and HiPIMS, which influences the films mechanical properties. The films mechanical

properties investigated are hardness, modulus, as well as film ad- and cohesion. Hardness and modulus of the

film increases in respect to DC when HiPIMS is used, with HiPIMS 1kW showing the highest hardness of 9.2 GPa

(a 36% increase over DC). The film's Young's modulus values follow the same trend. Nano scratch results show a

difference in film cohesion with through thickness cracks in the DC samples, whereas none are observed in

HiPIMS samples. TEM and XPS results reveal that a columnar structure exists in the case of DC, which provides

pathways for oxygen. The oxygen content of the DC film is subsequently increased compared to both HiPIMS

films and the oxygen content is relatively high in the gaps between columns. XRD and TEM results show that all

films are fully amorphous, in spite of the presence of a columnar structure in the DC sample

2:20pm **B4-1-WeA2 Effect of Functionally Graded Layers on Tribological Behavior of TiZrN Coatings on AISI D2 Steel***,* ***Jia-Hong Huang (jhhuang@ess.nthu.edu.tw)****, B.-S. Tsai,* National Tsing Hua University, Taiwan

The objectives of this study were to investigate the role of TiN transitional layer and Ti interlayer in the tribological behavior of tri-layer TiZrN/TiN/Ti coatings and to explore the mechanism of stress relief in the tri-layer coatings. TiZrN coatings were deposited on AISI D2 steel by DC unbalanced magnetron sputtering. There were three series of samples, including single layer TiZrN (S), bilayer TiZN/Ti (B), and tri-layer TiZrN/TiN/Ti (Tx) in this study. The TiN thickness of Tx-series specimens ranged from 200 to 400 nm. The N/(Ti+Zr) ratios of TiZrN layer ranged from 0.9 to 1.0 and the Zr/(Zr+Ti) ratio of TiZrN coatings was about 0.5. The hardness of the specimens varied from 28.1 to 31.9 GPa which slightly decreased by introducing TiN transitional layer. The residual stress of TiZrN layer decreased from -8.56 to -3.28 GPa with increasing thickness of interlayer and transitional layer. Scratch test was used to evaluate adhesion strength. The results showed high L_{c2} critical loads for all specimens ranging from 63.2 to 88.6 N. The TiN transitional layer could improve the adhesion strength, and the L_{c2} increased as the thickness of transitional layer increased. The wear rate of the tri-layer coatings was lower than that of TiZrN single layer and bilayer coatings. The results indicated that introducing the interlayer and transitional layer could enhance the wear resistance. The wear rate almost linearly increased with increasing elastic stored energy (G_s) that was related to elastic constants, residual stress and coating thickness [1]. The difference between the fracture toughness (G_c) and G_s can be considered as the capability that the coating can absorb externally input energy. The increase of Gs may decrease the capacity in absorbing energy and thereby decreasing the wear resistance. Therefore, G_s could be taken as an index to evaluate the wear resistance of coatings [2].

Reference

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2:40pm **B4-1-WeA3 Comparative Study of Adhesion Strength of TiC Films Deposited by Sputtering, RF or DC Plasma CVD on Chemically Treated WC-Co Substrate**, ***Kazuki Fuji (kfuji@chemeng.osakafu-u.ac.jp)**, H.M. Matsushima, D.K. Kiyokawa, C.T. Tanaka, N.O. Okamoto, T.S. Saito,* Osaka Prefecture University, Japan; *A.K. Kitajima,* Osaka University, Japan

Cemented carbides (WC-Co) are used for cutting tools, molds, etc. because of high hardness (1200~1500 Hv) and toughness (13~20 MPa・$m^{1/2}$), in which hard film coatings are often employed to improve functionalities. The adhesion strength of the coating film deteriorated due to the large difference in thermal expansion coefficient between the substrate and the coating film, after high temperature deposition. The compressive stress is observed with Physically deposited hard coating films, but is usually not with Chemically deposited the one at high temperature, which dominates adhesion nature of coating layer. The physical properties of the coating layer generally depend on both the film quality and the properties of surface characteristics of the substrate. It is still necessary to clarify the relationship well with the adhesion strength and the well-defined micro-structure of the substrate surface in order to improve the overall hard film coating quality.

In this research, WC-Co substrate is pretreated with an aqua regia or CF_4 plasma to change the composition and microstructure of the surface . TiC is subsequently coated on the substrate and applied to investigate the relationship between film properties and adhesion strength . TiC coatings were carried out by the DC sputtering (at 510°C, target is TiC), RF plasma CVD (at 550°C, from CH_4 and $TiCl_4$) or DC plasma CVD (at 500 ~ 600°C, from CH_4 and $TiCl_4$) method to investigate the influence of various hard films on the substrate . Both the case of pre treated substrate with CF_4 plasma and aqua regia, the longer surface pretreatment time was, the larger Ra resulted in . The maximum Ra by CF_4 plasma treatment was 147 nm, and the maximum Ra by aqua regia treatment was 175 nm . T he maximum critical load of DC sputtered TiC coated on surface treated WC-Co by CF_4 plasma was 12.1N and the arithmetic mean roughness (Ra) was 45 nm, and the critical load of DC sputtered TiC coated on surface treated WC-Co by aqua regia exceeded 60N when the Ra is ca. 100 nm . By using DC plasma CVD, more improvement of adhesion strength is expected because of high power.

3:00pm **B4-1-WeA4 Thin Film Characterization by Picosecond Ultrasonics on High Curvature Surfaces**, ***Frederic Faese (ffaese@neta-tech.com)**, J. Michelon, X. Tridon,* Neta, France

Since the discovery of picosecond ultrasonics by H. J. Maris and his team in 1984, this nondestructive technique continuously expanded and found numerous applications. Where the first application concerned thin film thickness measurement in the semiconductor industries with a complex setup, picosecond ultrasonics technique is now much more efficient, user-friendly and widespread. Indeed, thickness measurement is now easily reachable and this technique also allows the elastic properties measurement of thin films, multilayers and nanostructures, adhesion properties evaluation, etc. Thus, among all the fields that are potentially interested in this new technique are mainly surface engineering, microelectronics and biology.

We will see how the photo-generation and the photo-detection of ultra-high frequency ultrasounds (of the order of THz) can accurately and rapidly measure the thickness of a TiN hard coating on a Ti substrate. This measurement can be performed either locally with a high spatial resolution or by scanning the sample, hence giving a mapping of the thickness measurement on the whole surface. Up to now, the shape of the samples had to be very flat; in this presentation, we will demonstrate that we can also analyze even highly curved samples. Compared to concurrent techniques such as ellipsometry or the Calo tester, picosecond ultrasonics presents the unique advantages to be contactless, nondestructive and able to evaluate the properties of a complex shape sample. To illustrate this last point, results will be presented showing outstanding features such as an advanced 3D mapping of a hard coating thickness on a cylinder or a sphere.

3:20pm **B4-1-WeA5 High Temperature Tribology of Hf Doped c-$Al_{0.67}Ti_{0.33}N$ Cathodic Arc PVD Coatings Deposited on M2 Tool Steel**, *G.C. Mondragón Rodríguez, **Alvaro Enrique Gómez Ovalle (a.gomez@posgrado.cidesi.edu.mx)**, J.M. Alvarado Orozco, J.M. González Carmona, C. Ortega Portilla, J.L. Hernández Mendoza,* CIDESI, Mexico

c-$Al_{(1-x)}Ti_xN$ hard coatings are widely applied due to their thermal stability up to 800 °C, high resistance to wear and oxidation. Due to these characteristics they are frequently deposited on cutting tools used for machining processes. Improvements on the mechanical and oxidation properties are derived from the microstructure characterized by a stable solid solution of Al in TiN. In the present research, undoped a) c-$Al_{0.67}Ti_{0.33}N$ and hafnium doped b) c-$Al_{0.67}Ti_{0.33}Hf_xN$, which were deposited using the cathodic arc technique using 500 sccm of high purity N_2, Temperature = 430 °C, Pressure = 8 x 10-2 mbar, deposition time = 400 Ah, cathode current = 150 A and bias voltage = -80 V. The elemental chemical analysis displays hafnium contents ranging from 1.0 to 2.26 wt. %. The scanning electron microscopy analysis of the surface of both coatings showed similar droplets sizes and defects density produced by the cathodic arc deposition. Through the grazing incidence X-ray diffraction (DRX), the characteristic peaks of a cubic $Al_{1-x}Tix$ N coating were observed for both the reference coating and the doped nitride. Tribology tests of the c-$Al_{0.67}Ti_{0.33}Hf_xN$ coating in an argon jet for 250, 500, 1000, 2500 & 5000 cycles at a temperature of 900 °C showed the evolution and wear behavior under these conditions. The predominant friction mechanisms observed were related to abrasion, showing that hard particle formation and plowing increased wear with increasing distance. Oxidation prevents from further debris formation, while at room temperature debris are oxidized due to friction. The friction coefficients were maintained after the inclusion of hafnium as a doping material, however high temperature wear was reduced. These observations correlated well with the transition and stable oxide phases being formed at 900 °C during the tribology tests.

Keywords: Hf doped, tribology, high temperature tribology, arc PVD.

3:40pm **B4-1-WeA6 Mechanical and Tribological Properties of AlCrN Coating Deposited in a Plasma Nitrided Substrate**, ***Omar Ramírez-Reyna (omar.r.reyna@gmail.com)**,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México; *G.A. Rodríguez-Castro,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, México; *U. Figueroa-López,* Tecnologico de Monterrey, Campus Estado de México, México; *R.C. Vega-Morón, A. Meneses-Amador,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México; *I. Arzate-Vázquez,* Centro de Nanociencias y Micro y Nanotecnologías, Instituto Politécnico Nacional, México

In this study, aluminum chromium nitride (AlCrN) and iron nitrides were formed on AISI 4140 steel by cathodic arc PVD and plasma processes, respectively. Three systems were evaluated by mechanical and tribological tests: AlCrN coating, AlCrN/N duplex coating and only nitrided substrate (N). The structural characterization was performed by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The AlCrN coatings thicknesses were 2.2 and 3 µm for AlCrN and AlCrN/N, respectively; whereas for (N) it was 10 µm. The mechanical properties were obtained by spherical instrumented indentation tests (5 µm radius) applying different load ranges in each sample. An average hardness of 24 GPa was obtained for AlCrN and AlCrN/N whereas 10 GPa for N. Moreover, the adhesion of the coatings was evaluated by progressive load scratch tests (PLST) using a Rockwell C tip. The AlCrN/N coating exhibited superior scratch resistance (L_{C1} = 22.88 N) compared to AlCrN and N coatings. After that, subcritical load (16 N) multipass scratch tests (MPST) were performed on the coatings, applying from 50 to 400 unidirectional cycles for inspection of the damage evolution. In both PLST and MPST, the scratch tracks were analyzed by SEM and optical profilometry. In multipass scratch tests, the AlCrN/N coating exhibited a better behavior, noticeable in less severe failure mechanisms and lower residual depth due to the presence of the iron nitrides interlayer. The applicability of a duplex coating was evaluated.

4:00pm **B4-1-WeA7 Numerical Evaluation of the Contact Fatigue Resistance of AlCrN, N and AlCrN/N Coatings on AISI 4140 Steel**, ***Andre Ballesteros-Arguello (aballesteros_90@hotmail.com)**,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico; *A. Meneses-Amador, G.A. Rodríguez-Castro,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico, México; *D. Fernández-Valdés,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico; *A. López-Liévano,* Grupo SSC Unidad de Simulacion e Ingeniería Mecánica, Mexico; *A. Ocampo-Ramírez,* Grupo SSC Unidad de Simulación e Ingeniería Mecánica, Mexico

An experimental-numerical study of the contact fatigue resistance of coatings over an AISI 4140 steel was developed. Three experimental conditions were carried out: a coating of aluminum chrome nitrides (AlCrN) by physical vapor deposition process (PVD), a coating of iron nitrides (N) by gas nitriding process and finally a multilayer system of AlCrN/N. Contact fatigue tests were performed on a MTS Acumen electrodynamic test system in charge controlled mode, by cyclic loading of a sphere on a flat surface formed by the layer-substrate system. The contact fatigue test methodology consisted of two main stages. First, critical loads were determined under monotonic loads, for each of the systems, where circumferential cracks were considered as the failure criterion. Second, fatigue conditions were performed in a low cycle using subcritical monotonic loads with a frequency of 5 Hz. A numerical model based on the finite element method was developed to evaluate the stress field generated in the systems by cyclic contact loads. The results exhibit a better resistance to contact fatigue in the AlCrN/N multilayer system, due to the presence of the intermediate layer of iron nitrides.

4:20pm **B4-1-WeA8 The Effect of Heat Treatment on Microstructure and Mechanical properties of Sputtering MoSiN Coatings*, Yu-Cheng Liu (com35518617@gmail.com)*,** *F.B. Wu,* National United University, Taiwan

The molybdenum silicon nitride, MoSiN, films were produced by RF magnetron sputtering with structure features varied from columnar crystalline to amorphous as a function of the silicon contents and gas flow ratio during the manufacturing process. During sputtering, the gas flow ratios, Ar/N_2, were controlled at 10/10, 12/8 and 15/5. The input power for Si target was changed from 0 to 150 W with a fixed 135W on Mo target. The structure evolved from crystalline to preferred oriented Mo_2N as input power increased. As the Si contents was around 20-30 at.% the film turned into amorphous. The heat treatment temperatures was controlled at 350, 450, 550 and 650°C for 4 and 9 hours. In addition, the effect of heat treatment environment in vacuum and atmospheres were compared. After heat treatment, the significant enhancement in crystallinity of the MoSiN films was observed. The effect of heat treatment time, temperature, ambient condition, and original microstructure on Hardness, Young's modulus, abrasion characteristics of the MoSiN monolayer films were further investigated and discussed.

4:40pm **B4-1-WeA9 Cross-sectional X-ray Nanodiffraction Characterization of Radiation Damage, Stresses, and Microstructure in Tungsten Coatings*, Kostiantyn Hlushko (kostiantyn.hlushko@unileoben.ac.at)*,** Montanuniversität Leoben, Austria*; A. Mackova,* Nuclear Physics Institute of the Czech Academy of Sciences*; J. Todt,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria*; R. Daniel,* Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; J. Keckes,* Montanuniversität Leoben, Austria

A better understanding of depth-dependent radiation damage in protective coatings which can be used in fusion/fission reactors and in space is essential pending step for further development of novel coating types and microstructures that are capable of withstanding severe environments over long time periods. Tungsten is a perspective material for plasma-facing components of a fusion reactor due to its high radiation resistivity, high thermal conductivity and high melting point. In this contribution, 8µm thick nanocrystalline tungsten coating on WC substrate with columnar microstructure was irradiated using Si^{2+} ions with an energy of 5MeV with a fluence of $2x10^{16}$ ions/cm^2.In order to investigate depth-dependent changes in residual stresses and microstructure induced by the irradiation, cross-sectional X-ray Nanodiffraction (CSnanoXRD) with a beam size of 100 nm was applied at European Synchrotron Radiation Facility in Grenoble, France, to scan 50µm samples at the film cross-section. The experimental results revealed significant changes in the depth-dependent gradients of residual stresses as well as with the changes in unstressed lattice parameters, which will be presented together with the data from transmission electron microscopy.

5:00pm **B4-1-WeA10 Modern Analytical Methods for Characterizing the Tribological Material Properties of Coatings*, Dietmar Schorr (dietmar.schorr@dhbw-karlsruhe.de)*,** Cooperate State University in Karlsruhe, Germany **INVITED**

This paper presents photothermal principle as a new method for determining the tribological properties of hard coatings. The coating properties, which determine the friction and wear behaviour of a tribological system, are the coating thickness, the adhesive strength and the hardness. The known classical analysis methods have disadvantages in determining the respective coating properties and are not applicable for many coatings and surfaces. Furthermore, these methods only provide information on the individual coating properties, but not on the overall tribological behaviour of a coating. With the photothermal method, these limits are exceeded and it also works where classical methods fail. Photothermics works non-destructively and can be used to determine the coating properties over a wide area. The photothermal technology works with thick and thin layers, for cohesive and adhesive adhesion testing and is independent of surface roughness.

In photothermal peripheral zone analysis, an intensity-modulated laser spot hits an object surface. The radiation is absorbed on the surface and generates a heat flux that propagates into the interior of the component in the form of thermal waves. The waves have the same frequency as the irradiated laser light. The further propagation of the thermal waves is influenced by the thermal properties of the coating (thermal diffusivity). These cause the waves to be reflected back and radiated at the surface as heat. The thermal resistance of the material ensures that the thermal waves travel through the material with a time delay and that the phase of the radiated heat is offset from the radiated laser. If the thermal properties of the coating change due to thickness, hardness or adhesion strength, this is measured by the phase shift. This is also almost independent of the surface roughness.

The reflected waves are registered by an infrared detector, which is cooled down to increase sensitivity. The penetration depth of the oscillating thermal waves into the interior of the material is determined by the modulation frequency of the laser and depends on the thermal properties of the material. High frequencies in the kHz range are used for layer analysis and low frequencies in the Hz range for material analysis.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 1-3 - Session C2-1-WeA
Functional Coatings and Thin Films for Electronic Devices I

Moderators: Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, Jörg Patscheider, Evatec AG, Switzerland

2:00pm **C2-1-WeA1 Printed Polymer Heat Sinks for High-Power, Flexible Electronics*, Katherine Burzynski (burzynskik1@udayton.edu)*[1]*,*** University of Dayton and Air Force Research Laboratory, USA*; N.R. Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA*; E.M. Heckman,* Air Force Research Laboratory, Sensors Directorate, USA*; C. Muratore,* University of Dayton, USA

Consumers and military personnel alike are demanding ubiquitous electronic devices which require enhanced flexibility and conformality of electronic materials and packaging, while maintaining device performance. Whether it be high-power devices for faster data speeds, such as fifth generation (5G) wireless communication technology or wearable sensors to facilitate the Internet of Things (IoT), the age of flexible, high performance electronic devices has begun. Managing the heat from flexible electronics is a fundamental challenge. Even on rigid substrates with significantly higher thermal conductivity than polymeric and other flexible substrates, the full potential of semiconducting materials is often thermally limited. The flexible gallium nitride (GaN) high electron mobility transistors (HEMTs) employed in this work are conventionally processed devices that can be released from their growth substrate and transferred to a variety of rigid and flexible substrates. To improve the heat conduction of the flexible substrate material, graphite nanoplatelets were used to improve the thermal conductivity of the polydimethysiloxane (PDMS) by more than 900 percent, from 0.2 to 1.7 W/mK, while maintaining mechanical properties and printability. The GaN HEMTs were directly transferred to this graphite loaded PDMS substrate material and the performance was compared to that of the devices transferred to the unloaded PDMS and the as-grown devices on their sapphire substrates. Using infrared thermography, the GaN HEMTs on graphite-loaded PDMS substrates reach the maximum operating temperature at 60 percent more power than the same device transferred to the PDMS substrate. From the device current-voltage characteristics at 0 gate voltage, the current at saturation is 40 milliamps for devices on the rigid, high thermal conductivity sapphire wafer, compared to 30 and 20 milliamps for devices on flexible, loaded PDMS and unloaded PDMS, respectively. Additionally, the high electrical performance of these devices (i.e., high saturation current) was observed after cyclic bending of these devices on loaded PDMS substrates. These results highlight the fact that high-power device performance is markedly improved when transferred to the higher thermal conductivity flexible substrate. Computational simulations were used to predict flexible substrate architectures to promote point-to-volume heat transfer to further improve device performance. Additive manufacturing for engineered architectures of the flexible, thermally conductive substrate materials was demonstrated to substantially reduce the thermal limitation of high-power flexible electronics.

[1] **Student Award Nominee**

2:20pm **C2-1-WeA2 Ionic Conductivity and Thermal Stability of Nb-Stabilized Fluorite-structure Bi_2O_3 Films**, ***Osmary Depablos-Rivera (osmarydep@yahoo.com)***, Universidad Nacional Autónoma de México, México; *S.E. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, México

The phase of Bi_2O_3 with cubic fluorite-type structure, denoted as delta-Bi_2O_3, is the material with the highest known ionic conductivity. However, this phase is stable above 723 °C up to its melting point (825 °C). It has been reported that the delta-Bi_2O_3 phase can be obtained at room temperature when deposited as a thin film, but its crystalline structure change to tetragonal beta-Bi_2O_3 phase, above 250 °C. Ionic conductors are used as the electrolyte in micro solid oxide fuel cells, whose working temperature range is between 400 - 600 °C. Therefore, the use of the delta-Bi_2O_3 films requires their stabilization at intermediate temperatures, which can be achieved through doping with transition metals or earth rare oxides. We investigated the addition of Nb into the Bi_2O_3 films on the thermal stability and the ionic conductivity. The films were deposited using dual confocal co-sputtering, starting from two independently driven targets, one of Bi_2O_3 and the other one of Nb. The composition of the films was controlled varying the DC power applied to the Nb target at 20, 30 and 40 W, while the radiofrequency power applied to the oxide target was fixed at 30 W. The atomic percentages of Nb in the films were measured by X-ray photoelectron spectroscopy. The amount of Nb increased with the power applied and the values obtained were 5.1, 6.6 and 9.2 at%. The thermal stability of the films was characterized by high-temperature X-ray diffraction (XRD). The XRD patterns showed that the addition of Nb allows keeping the cubic fluorite-like structure up to 400 °C. The surface electrical measurements were carried out by impedance spectroscopy using the method of two probes in contact with concentric platinum electrodes on the surface of the films. The samples were heated in steps of 50 °C from room temperature up to 350 °C. The conductivity increased as the temperature augmented, this is typical in semi and ionic conductors. The highest conductivity was exhibited by the film with 5.1 at.% of Nb, the conductivity was 2.67 $x10^{-3}$ S cm^{-1} at 350 °C. The conductivity was reduced as the Nb content increased. The activation energy determined from the conductivity data was between 1.05 to 1.30 eV, the values of hopping energy were similar that suggest the conduction mechanism was mainly by carriers hopping.

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2:40pm **C2-1-WeA3 Nanostructured CuO/WO_3 Thin Films for Hydrogen Gas Sensing Prepared by Advanced Magnetron Sputtering Techniques**, ***Nirmal Kumar (kumarn@kfy.zcu.cz)***, *S. Haviar, J. Čapek, Š. Batková, P. Zeman, P. Baroch,* University of West Bohemia, Czech Republic

Various architectures of hydrogen sensing multilayers were designed using various combinations of thin films and nanoclusters of both CuO and WO_3. Thin films were prepared using reactive sputter deposition in dc magnetron regime (WO_3) or rf mode (CuO). The nanoclusters were prepared by magnetron-based gas aggregation cluster source which enabled controlling of size and composition of clusters.

There are several architectures described in this work. The combination of two thin films. Decoration of one support film with clusters or thin films overlaying the clusters. By switching the materials in these configurations, various nanostructures were achieved. The sensorial behavior of prepared materials was studied towards hydrogen gas in synthetic air in a form of thin-film conductometric sensor.

The enhancement of the response of WO_3 thin film alone by adding the CuO film on top is described as well as the influence of the amount of nanoclusters deposited on WO_3 thin films. Based on SEM imaging, sensorial behavior analysis, XRD and resistivity measurements, we propose that the sensing mechanism is always based on the formation of heterojunction in between *n*-type WO_3, *p*-type CuO or other phases present in the structures (such as *n*-type $CuWO_4$).

3:00pm **C2-1-WeA4 High-performance Thermochromic VO_2-based Coatings Prepared on Glass by a Low-temperature Scalable Deposition**, ***Tomáš Bárta (bartat@kfy.zcu.cz)***, *J. Vlček, D. Kolenatý, J. Rezek, J. Houška, S. Haviar,* University of West Bohemia, Czech Republic

Three-layer thermochromic VO_2-based coatings were prepared on soda-lime glass by a low-temperature scalable deposition technique. This deposition technique is based on reactive high-power impulse magnetron sputtering with a pulsed O_2 flow control [1] allowing us to prepare crystalline VO_2 layers of the correct stoichiometry under highly industry-friendly deposition conditions: without any substrate bias at a low substrate temperature of 330 °C. Simultaneous doping of VO_2 by W (resulting in a $V_{1-x}W_xO_2$ composition with x = 0.018 in this work) was performed to reduce the semiconductor-to-metal transition temperature to 20 °C. ZrO_2 antireflection layers both below and above the thermochromic $V_{0.982}W_{0.018}O_2$ layers were deposited at a low substrate temperature (< 100 °C). A coating design utilizing a second-order interference in the ZrO_2 layers [2] was applied to increase both the luminous transmittance, T_{lum}, and the modulation of the solar transmittance, ΔT_{sol}. The crystalline structure of the bottom ZrO_2 layer further improved the VO_2 crystallinity and the process reproducibility. The top ZrO_2 layer provided the mechanical protection and environmental stability of the $V_{0.982}W_{0.018}O_2$ layers. The $ZrO_2/V_{0.982}W_{0.018}O_2/ZrO_2$ coatings exhibited T_{lum} up to 60% at ΔT_{sol} close to 6% for a $V_{0.982}W_{0.018}O_2$ thickness of 45 nm, and T_{lum} up to 50% at ΔT_{sol} above 10% for a $V_{0.982}W_{0.018}O_2$ thickness of 69 nm. This study provides a new solution for a low-temperature fabrication of high-performance durable thermochromic VO_2-based coatings for energy-saving smart windows.

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3:20pm **C2-1-WeA5 Thermal and Plasma-Enhanced Atomic Layer Deposition for Nanoscale Coatings**, ***W.M.M. (Erwin) Kessels (w.m.m.kessels@tue.nl)***, Eindhoven University of Technology, The Netherlands **INVITED**

Processing at the nanoscale is becoming increasingly critical for many applications also well beyond electronic devices for computing and data storage. Yet, the semiconductor industry has been the main driving force behind the industrial implementation of the method of atomic layer deposition (ALD) in high-volume manufacturing in the last 2 decades. ALD allows for the preparation of high quality thin films and coatings on challenging surface topologies while precisely controlling nanometer dimensions. It has therefore been key for the materials- and 3D-enabled scaling which has been necessary to continue Moore's law over the last decade.

In this presentation, the developments in the field of ALD will be briefly reviewed including a description of its underlying mechanisms, key features and hallmarks. A particular focus will be given to the technological opportunities provided by the method in terms of materials, processes and applications. An overview will be given of recent and emerging applications of ALD, for example, in energy technologies including solar cells and batteries, in large-area electronics including displays, and in optical and mechanical coating applications. Also the developments in ALD equipment will be presented with respect to ALD configurations (thermal and plasma-enhanced ALD) and with respect to high volume manufacturing including batch and spatial ALD and roll-to-roll ALD for flexible substrates.

4:00pm **C2-1-WeA7 Achieving High Dopant Activation in Doped Semi-conductive Oxide Films by Tuning Compositional and Topological Metastability**, ***Yuyun Chen (chenyuyun@nimte.ac.cn)***, Chinese Academy of Sciences, China

High dopant activation is of great importance to the electrical conductivity in magnetron sputtered doped semi-conductive films. However, the far-from-equilibrium processing conditions, subject to kinetic constraints, would result in compositional and topological metastability to varying degrees, leading to the difficulty in achieving high dopant activation. Here, we attempted to widely vary the compositional and topological metastability in the Ga-doped ZnO (GZO) films by tuning the bias discharge voltages and thuys the Ar^+ bombardment). We further utilized X-ray Diffractometry, X-ray photoelectron spectroscopy, and Raman spectroscopy to examine both metastable evolutions. We found that (i) the difference of the compositional metastability among our GZO films can be negligible; (ii) the Ar^+ bombardment enabled to enhance the dopant activation efficiency, but it also introduced topological disorder into the ZnO lattice; (iii) With increasing Ar^+ bombardment, the carrier concentration increased significantly whereas the Hall mobility decreased, resulting in no evident improvement in the electrical conductivity. Our results can be extended to achieve high dopant activation for the doped magnetron sputtered oxides.

4:20pm **C2-1-WeA8 Structural and Optical Properties of Pulsed-Laser Deposited β-Ga_2O_3 Thin Films**, ***Mallesham Bandi (mbandi@utep.edu)***, Center for Advanced Materials Research (CMR), University of Texas at El Paso, USA, United States of America

In the course of demand for wide band gap semiconductors in modern electronic devices, β-Ga_2O_3 is extensively studied for the last two decades due to its wide range of applications such as field effect devices, switching memories, high temperature gas sensors, photocatalysts, deep-UV photodetector and transparent conducting electrode etc. However, fabricating device quality thin films and understanding the optical properties is an active timely research to exploit β-Ga_2O_3 into wide range of optoelectronic device applications. We report on the effect of deposition parameters on the structure and optical properties of β-Ga_2O_3 fabricated by Pulsed Laser Ablation onto a wide range of substrate materials. Polycrystalline thin films were fabricated on silicon and sapphire substrates with varying substrate temperatures and oxygen partial pressures, which resulted in various morphologies. To study the effect of morphology on optical properties polycrystalline thin films were analyzed using spectroscopic ellipsometry. Moreover, epitaxial thin films of β-Ga_2O_3 were fabricated on C-plane sapphire and MgO (100) oriented substrates. A more detailed account of structure, growth behavior and optical properties of β-Ga_2O_3 will be presented and discussed.

4:40pm **C2-1-WeA9 High k Dielectrics for MIM Architecture: From Capacitors to Non-volatile Memories Applications**, ***Christophe Vallee (christophe.vallee@cea.fr)***, UGA - LTM, France, France; *P. Gonon, M. Bonvalot, A. Bsiesy,* UGA-LTM, France **INVITED**

SC materials were THE materials of SC industry due to their unique properties for switching from conductive to insulator or from transparent to reflective properties thanks to an external stress (most of the time an external voltage applied to the SC device). But nowadays, due to the shrinking of the devices, role of dielectrics materials (such as high k dielectrics) become crucial. First high k dielectrics were developed to improve the SC device performances by increasing the dielectric constant of the capacitor-based device (switching from SiO_2 to HfO_2 in CMOS transistors, from SiO_2 and Si_3N_4 to $ZrO_2/Al_2O_3/ZrO_2$ in DRAM capacitors). The reduction of high k thicknesses below 10 nm also give rises to new potential application of these materials due to unexpected new properties: as for SC materials one can now switch their electrical properties from insulator to conductor. They can be used as memristor (or "memory resistor") which is a Metal-Insulator-Metal (MIM) resistor whose resistance value depends on its past electrical history, i.e. its current-voltage characteristic (I-V) displays a hysteresis loop. In recent years, a large amount of research has been devoted to memristors, focusing on their application to microelectronic non-volatile memories (RRAM - Resistive Random Access Memory). They can also be used as selectors, or MIM diodes, for memories.

With this presentation we will give examples of the use of high k dielectrics and their fabrications for linear MIM capacitors[1], DRAM[2], Resistive Rams[3], MemImpedance[4] and MIM diodes[5]. We will show that whatever the device, due to the very small thickness of the high k dielectrics, the choice of the metal electrodes and the control of the interface is vital.

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5:20pm **C2-1-WeA11 Synthesis and Characterization of Cellulose Acetate Titanium (IV) Tungstomolybdate Nanocomposite Cation Exchanger for the Removal of Selected Heavy Metals from Aqueous Solution**, ***Belay Minase Woldegebriel (belay140@gmail.com)***, National Taiwan University of Science and Technology (NTUST), Taiwan

Cellulose acetate titanium (IV) tungstomolybdate nanocomposite cation exchanger was synthesized by sol-gel method by incorporating cellulose acetate polymer into inorganic exchanger, titanium (IV) tungstomolybdate. Different techniques including FTIR, XRD, TGA SEM and BET were used to characterize the exchanger. The Cellulose acetate titanium (IV) tungstomolybdate (CATTM) behaved as a good cation exchanger with ion exchange capacity of 1.64 meq g^{-1} for Na^+ ions. The sequence of ion exchange capacity for alkali metal ions was found to be K^+> Na^+> Li^+ and that for alkaline earth metal ions was Ba^{2+} > Ca^{2+} > Mg^{2+}. These orders revealed that the ions with smaller hydrated radii acquired larger ion exchange capacity. The pH titration curve indicated that the material obtained as such is a bi functional strong cation exchanger as indicated by a low pH (~2.25) of the solution when no OH ion was added. Thermal analysis of the material showed that the material retained 55% of its ion exchange capacity up to 600°C. Adsorption behavior of metal ions in different solvents with varying concentration has also been explored and the sorption studies revealed that the material was selective for Cr(III) and Pb(II) ions. The analytical utility of the material was investigated by performing binary separations of selected metal ions in a column based on the distribution coefficients of the metals. Cr(III) and Pb(II) were selectively removed from synthetic mixtures of Cr(III)-Co(II), Cr(III)-Cd(II), Pb(II)-Co(II) and Pb(II)-Cd(II). Antimicrobial activity of the synthesized titanium (IV) tungstomolybdate compound was evaluated and showed a considerable antibacterial activity against Staphylococcus aureus, Streptococcus agalactiae, Escherichia coli and Shigella flexneri. The inorganic counterpart has also exhibited a promising antifungal activity against Aspergillus niger and Fusarium oxysporum.

Key Words: Antimicrobial, Cellulose acetate, Cation exchanger, Nanocomposite, Sol-gel method

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E1-4-WeA

Friction, Wear, Lubrication Effects, and Modeling IV

Moderators: Nazlim Bagcivan, Schaeffler AG, Germany, Tomáš Polcar, University of Southampton, UK, Manel Rodriguez Ripoll, AC2T Research GmbH, Austria

2:00pm **E1-4-WeA1 A low-speed Controlled Cycling Impact Test Method for Characterization of Failure Behavior of Films and Coatings**, ***Zhenbing Cai (caizb@swjtu.cn)***, Southwest Jiaotong University, China

A new impact wear test method and tester was developed to investigate the dynamic damage behavior of the impact interface when the coating is damaged. A controlled low kinetic energy impact on the interface continuously,and the parameters such as impact kinetic energy, energy absorption rate and interface failure displacement are obtained. The purpose is to obtain the change of elastic energy and damage energy in the impact process under different parameters as well as the wear and energy absorption of the material changes every cycles. Real-time damage data of impact wear interface of coatings were obtained. In order to accelerate the characterization of thick hard coatings, abrasives were added to the impact interface, which accelerated the failure behavior of materials by more than 100 times. Angle, hardness and impact angle of abrasive obviously affect the impact wear life of coatings.

2:20pm **E1-4-WeA2 Micro-scratch Test of Plasma Nitrided Hadfield Austenitic Manganese Steel**, ***Luis Varela (luisvarelajimenez@usp.br)***, University of São Paulo, Brazil, Brasil; *G. Tressia,* University of São Paulo, Brazil; *E.M. Bortoleto,* Vale Institute of Technology; *C.E. Pinedo,* Heat Tech Technology for Heat Treatment and Surface Engineering Ltd,; *A. Sinatora,* Vale Institute of Technology; *A.P. Tschiptschin,* University of São Paulo, Brazil

Low temperature plasma nitriding (LTPN) of standard and non-standard Hadfield steel was carried out to explore the formation of an expanded austenite phase layer and to assess its effect on the scratch wear resistant and friction behavior of the Hadfield Steels. The Hadfield specimens were plasma nitrided at 420 °C for 20h in 75%N_2 - 25%H_2 gas mixture. The scratch resistance of the nitrided and non-nitrided samples was evaluated by single-pass scratch test simulating the mechanism of material removal under wear-controlled conditions, which corresponds to an abrasive wear event. The scratch tests were performed under various constant normal loads at 50 mN, 125 mN and 200 mN with a 60°diamond cone stylus with a 5 µm tip radius. Structural and mechanical properties of the plasma nitrided specimens were examined using X-ray diffraction, scanning electron microscopy and microha rdness testing. Scanning E lectron Microscopy was used to characterize the microstructure, the wear micromechanisms, and the change of the subsurface structure under the scratches. The results show that the standard nitrided surface specimens consist mainly of γ_N expanded austenite and ε-$Fe_{2\text{-}3}N$ iron nitride. The nitrided surface of the non-standard Hadfield specimen consists of γ_N expanded austenite, ε-$Fe_{2\text{–}3}N$ and CrN. For the non-nitrided specimens, it was observed that at low load (50 mN) the main wear mechanism was microploughing. For greater loads (125 mN and 200 mN) the wear mechanism changed to microcutting. Moreover, for the nitrided specimens, although microcutting was observed for 125 mN and 200 mN loads, the wear severity was lower. The apparent friction coefficient increases with the increase of the normal load from ~0.26 to ~1.1 and ~from ~0.15 to ~0.47, for the non-nitrided and nitrided specimens, respectively.

2:40pm **E1-4-WeA3 Use of Digital Tribology to Design a-C Coated Systems to Achieve Ultra-low Coefficient of Friction under High Contact pressure**, ***Newton Fukumasu (newton.fukumasu@usp.br)**, A.P. Tschiptschin, R.M. Souza, I.F. Machado,* University of São Paulo, Brazil

Carbon-based coatings have attracted significant attention of aerospace, automotive and energy industries, due to low friction and high wear resistance. These tribological characteristics can be tailored based on different levels of sp^2 to sp^3 carbon bond ratios induced by the presence of hydrogen/dopants or deposition process variables, such as power, substrate bias and sample to target distance. Literature reports that ultra-low friction and superlubricity behavior of carbon-based coatings are influenced by the presence of hydrogen and water molecules at the contact during the tribological test. In this work, the digital tribology platform TriboCODE, which is being developed in the Surface Phenomena Laboratory, was applied to understand the stress distribution in coated surfaces in contact, allowing the development of low friction and high efficiency tribological systems under high Hertzian contact pressures (>2 GPa). Ball-on-disk reciprocating tests were used to evaluate friction and wear of designed non-hydrogenated amorphous carbon (a-C) coatings, deposited by a pulsed-DC magnetron sputtering technique. A polycrystalline graphite target was used to deposit the a-C coating over AISI H13 disks and AISI 52100 balls. An interlayer of amorphous silicon, deposited using a single-crystal silicon target, was used to increase the adherence of the coating. Scanning Electron Microscopy (SEM), Raman spectroscopy, optical profilometry and instrumented indentation were applied to characterize the tested surfaces. Tribological tests were carried out under dry contact conditions at room temperature and high relative humidity (>60%). Results indicated a correlation of the G band peak position (GBPP) with the coefficient of friction. When both surfaces were coated, results showed a stable ultra-low coefficient of friction, which decreased with the increase of GBPP (from 0.05 to 0.03). For the cases with one uncoated surface, the increase of GBPP led to the increase of COF, in the range between 0.1 and 0.2, associated with the formation and transference of carbon-based tribo-films at the wear track. The digital tribology platform TriboCODE allowed the evaluation of stress distribution at the contact, indicating lower shear stresses along coating thickness when both surfaces were coated. For one uncoated surface system, the friction induced shear stress at the coating/substrate interface was higher, promoting the failure of the interface and the increase of the COF.

3:00pm **E1-4-WeA4 Evaluation of the Wear Resistance of Borided AISI 1018 Steel Exposed to the Diffusion Annealing Process**, ***Erick Japhet Hernández-Ramírez (ehernandezr1601@alumno.ipn.mx),*** Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; I.E. Campos-Silva,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México, Mexico*; A. Ruiz-Rios, A.M. Delgado-Brito, A.D. Contla-Pacheco,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; J. Oseguera-Peña,* Tecnologico de Monterrey, Campus Estado de México, México

Several studies have recognized that the formation of boride layers (FeB/Fe_2B) increases the mechanical and chemical properties on the surface of steels. Nevertheless, for industrial applications, a Fe_2B layer instead of a $FeB\text{-}Fe_2B$ is more desirable, because the discontinuity of the shear stress on the $FeB\text{-}Fe_2B$ interphase inducing shear failure during specific loading applications. Nowadays, a solution for this problem is the application of post-treatments to dissolve the FeB layer.

In the present study, the wear resistance on the surface of AISI 1018 steels exposed to powder-pack boriding process (PPBP) and to the diffusion annealing process (DAP) were evaluated. Firstly, for the formation of the $FeB\text{-}Fe_2B$ layer, the PPBP was conducted using a powder mixture of 20% B_4C, 10 % KBF_4 and 70% SiC at 1223 K with 6 h of exposure. A total boride layer thickness of 182 µm was obtained at the surface of the borided 1018 steel. The borided specimens were subsequently exposed to the DAP, using a SiC atmosphere at 1223 K with 4 h exposure, obtaining a Fe_2B layer with 250 µm of layer thickness.

Before the wear tests, the boride layers were characterized by the depth-sensing Vickers microindentation technique to determine properties such as hardness, Young's modulus, fracture toughness, residual stresses and *H/E* ratio. The wear tests, for each treatment condition, were carried out in a ball-on-flat configuration, according to the ASTM G133-05 procedure. The tests were done in dry conditions, under a constant load of 20 N, 5 different sliding distances and 10 mm/s of sliding velocity. In addition, the failure mechanisms over the surface of the wear tracks (PPBP and DAP) were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) techniques.

Firstly, the results of indentation test indicated that the borided AISI 1018 steel exposed to DAP revealed a higher fracture resistance (Kc = 2.81 MPa $m^{0.5}$) with the presence of compressive residual stresses along the depth of the borided layer. In contrast, the borided AISI 1018 steel showed a fracture resistance of Kc = 1.28 MPa $m^{0.5}$ with a distribution of tensile-compressive residual stresses along the depth $FeB\text{-}Fe_2B$ layer. The fracture resistance results denoted a correlation with the wear resistance obtained for both treatments; the wear resistance of the boride layer exposed to the DAP showed an increase three-fold compared to the boride layer obtained by the PPBP for the entire set of experimental conditions. Finally, the failure mechanisms developed over the surface of the wear tracks, for both treatment conditions, were plowing, smearing and cracking, principally.

3:20pm **E1-4-WeA5 Numerical-Experimental Analysis of the Tribological Behavior of Borided AISI 316L Steel**, ***Daybelis Fernández-Valdés (ingday1989@hotmail.com),*** Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico*; A. Meneses-Amador,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico, México*; A. Ocampo-Ramírez,* Grupo SSC Unidad de Simulación e Ingeniería Mecánica, Mexico*; A. López-Liévano,* Grupo SSC Unidad de Simulacion e Ingeniería Mecánica, Mexico*; U. Figueroa-López,* Tecnologico de Monterrey, Campus Estado de México, Mexico, México*; I.E. Campos-Silva,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico*; G.A. Rodríguez-Castro,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico, México

Reducing wear on mechanical components that have a metal-metal sliding contact has always been a challenge in the study of tribology. In this context, thermochemical treatments are an effective option to improve surface mechanical properties and prolong the life of mechanisms subjected to wear, corrosion and abrasion. In this study, the resistance to wear of layers of iron boride generated on the surface of AISI 316L steel was evaluated experimentally and numerically. The borurization treatment in AISI 316L steel was carried out by the pack-boriding process at different time and temperature conditions. The tribological behavior of the layer-substrate system was estimated by performing wear tests, with the configuration pin on disk, without lubricant and using an Al_2O_3 ball. Experimental results showed that the borurization treatment significantly improved the wear resistance of AISI 316L steel compared to the untreated material. The wear depth was estimated by Archard's linear wear law. It was found that the results of the numerical model by means of finite element method are consistent with those obtained experimentally.

3:40pm **E1-4-WeA6 Use of Digital Tribology to Design Cu-Ti-Si Interlayers to Increase Adhesion of a:C Coatings on C17200 Copper-Beryllium Alloy**, ***Marcos Santos (mdantas@usp.br)**, N.K. Fukumasu, V. Seriacopi, I.F. Machado,* University of São Paulo, Brazil

Copper-beryllium (CuBe) alloys are widely used in aeronautical and automotive industries due to its good thermal and corrosion properties, however low hardness and wear resistance become critical factors in tribological applications. To overcome those limitations, carbon-based coatings can be applied to increase the wear resistance and reduce the friction coefficient. Nevertheless, the adhesion of carbon coatings on copper substrates are a well-known problem and, in this work, CuTiSi-based interlayers were developed to increase the adhesion of a hydrogen free amorphous carbon coating onto a C17200 Cu-Be alloy. The digital tribology platform TriboCODE, in development by the Surface Phenomena Laboratory, was used to evaluate the stress distribution in a DLC/CuBe system during a reciprocating ball-on-disk test. The C17200 CuBe alloy was used as substrate for the disk, while AISI 52100 steel was used for the ball. Ti-Si interlayers were deposited by a pulsed-DC magnetron sputtering system. A polycrystalline titanium target and a monocrystalline silicon target were used to deposit three interlayer conditions: Ti-Si and Si-Ti independent dual-layers and a stoichiometric TiSi single-layer. After, a polycrystalline graphite target was used to produce a hydrogen free amorphous carbon coating over the engineered interlayers. Dry reciprocating ball-on-disk tests were performed using the Optimol SRV v4 with 10 Hz of frequency, 4 mm stroke and 10N and 20N normal loads. Scanning Electron Microscope (SEM), Raman spectroscopy, coherence correlation interferometry and instrumented indentation were used to characterize the wear track after the test. Scratch tests were performed to evaluate the friction coefficient and critical loads. Using the stress triaxiality parameter, numerical results indicate that more ductile interlayers can improve the adhesion of the coating and, experimental tests corroborate those results, in which a better coating adhesion was obtained for the discrete Ti-Si dual-layer, mainly provided by the high ductility of the discrete titanium layer compared to the other systems.

4:00pm **E1-4-WeA7 Effect of Electrostatic Solid Lubrication on Tribological Behavior of Ti-6Al-4V Alloy***, R.K. Gunda,* BITS Pilani Hyderabad Campus, India*; **Uma Maheshwera Paturi (maheshpaturi@gmail.com)**,* CVR College of Engineering, Hyderabad, India*; S.K.R. Narala,* BITS Pilani Hyderabad Campus, India

The advanced science of tribology offers challenges for the cooling/lubrication of hard-to-cut materials in sliding and machining processes. Modern tribology has facilitated the use of solid lubricants with low cost and eco-friendly, which can sustain and provide lubricity over a wide range of temperature in controlling heat and frictional effect on interface zone. The aim of the paper is to study the effect of innovative ECSL spray technique and the existing results are compare with MQSL and dry sliding conditions under various speed and load conditions. Sliding tests were performed under pin-on-disc tribometer against WC pin and Ti-6Al-4V alloy disc materials. SEM and EDS analysis were used to analyse the morphological and chemical composition of worn surfaces. The present work is expected to form a scientific basis towards developing ECSL spray technique for reducing tribological and environmental perspectives.

4:20pm **E1-4-WeA8 Assessment and Enhancement of Tribocorrosion Behaviour of Aluminum-Titanium Diboride (Al-TiB_2) Metal Matrix Composite***, A. Sheelwant,* BITS-Pilani, Hyderabad Campus, India*; **Suresh Kumar Reddy Narala (nskreddy@hyderabad.bits-pilani.ac.in)**,* BITS-Pilani Hyderabad Campus, India*; P. Shailesh,* Methodist College of Engineering and Technology, India

The unceasing expansion in industrial applicability of innately superior aluminum metal matrix composites (AMMCs) results from their unique structural and functional characteristics. Particulate secondary phase, despite significantly improving thermo-mechanical performance of AMMC, adversely affects its tribocorrsion performance leading to catastrophic events under hostile atmospheres. The current study presents a technique to revamp the tribocorrosion performance of aluminum-titanium diboride (Al-TiB_2) metal matrix composite (MMC) by electrostatic spray coating (ESC) followed by subsequent anodization. A uniform thin film of aluminum was deposited on Al-TiB_2 MMC using the ESC technique for protection against adverse effects of TiB_2 particles present in the aluminum matrix. The tribocorrosion performance was further enhanced by the subsequent anodization, which converts the aluminum coating to aluminum oxide film. The tribocorrosion behavior of Al-TiB_2 MMC was assessed by conducting tribocorrosion tests on a wear and friction test-rig under dry and open-circuit conditions. The effect of ESC and anodization on Al-TiB_2 MMC was examined on the microscopic level using scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Experimental results show significant enhancements in the tribocorrosion behavior of Al-TiB_2 MMC as a result of ESC followed by anodization. The two-step technique explained here may serve to be an effective means for materials scientists and engineers across defense and aeronautical industries to develop highly anticorrosive composites.

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F1-WeA

Nanomaterials and Nanofabrication

Moderator: Vitezslav Stranak, University of South Bohemia, Czech Republic

2:00pm **F1-WeA1 Plasma Based Deposition of Nanostructures and Nanoparticles: From Preparation to Function***, **Oleksandr Polonskyi (polonskyi@ucsb.edu)**,* University of California Santa Barbara, USA **INVITED**

Low-temperature plasma is a versatile tool for a controlled synthesis and deposition of novel nanostructured materials having a broad range of industrial applications. In particular, the unique properties of nanoparticles associated with their dimensions make them very attractive for the growing field of nanotechnology. The methods and approaches of their synthesis allowing a simple and reliable tuning of nanoparticle dimensions, as well as chemical structure, are in high demand. Gas-phase synthesis of metal nanoparticles based on magnetron sputtering became a very attractive tool (known also as a Gas Aggregation Cluster Source) because of its high efficiency, simplicity, high purity of produced nanoparticles and possibility to control their size and deposition rate. However, despite a large number of studies devoted to the deposition of nanoparticles by this method, the knowledge of the mechanisms of nanoparticle nucleation and growth in plasma is limited. To get insight into the nucleation, growth, and transport of nanoparticles in plasma more *in-situ* experimental data is necessary.

In this talk, an overview will be given of the recent progress in the formation and deposition of nanoparticles by the gas aggregation method with emphasis on the mechanism of nanoparticle growth, their properties, and applications [1]. Examples range from noble through reactive to more advanced alloy or core-shell nanostructures including their functional applications (e.g. plasmonics, photocatalysis, gas sensing).

Special focus is set on *in-situ* control and monitoring of nanoparticle formation in plasma volume by utilizing UV-Vis spectroscopy and Small Angle X-ray Scattering techniques [2, 3]. Time- and spatially- resolved measurements reveal that small clusters are formed in close vicinity to magnetron target and part of them are found to be captured in the plasma volume due to electrostatic force acting on the charged nanoparticles.

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2:40pm **F1-WeA3 Deposition of Cu and Pt Metallic Clusters onto Titanium Dioxide Nanoparticles by DC Magnetron Sputtering for Hydrogen Production***, **Glen West (g.west@mmu.ac.uk)**,* Manchester Metropolitan University, UK*; M. Bernareggi, G.L. Chiarello, E. Selli,* University of Milan, Italy*; A.M. Ferretti,* ISTM-CNR Lab Nanotechnology, Italy*; M. Ratova, P.J. Kelly,* Manchester Metropolitan University, UK

A novel technique using pulsed-DC magnetron sputtering has been employed to deposit metal nanoclusters directly onto titanium dioxide nano-particles. Deposition conditions and plasma compositions were varied to produce the desired Cu and/or Pt clusters on the particle surfaces. The nanoparticle powder was placed within an oscillating substrate holder, and a top-down sputter deposition arrangement allowed deposition onto the continuously rotating nanoparticles. HRTEM analyses revealed the presence of well-dispersed, sub-nanometric sized metal clusters, even following extended deposition times, while XRD analysis showed no modification of the TiO_2 crystal structure resulting from the process.

The coated powders were then tested for their ability to produce hydrogen from a methanol photo-steam reforming process via photocatalytic action. The photo-activity of the powders was increased by the presence of Pt clusters with respect to that of bare TiO_2. During Cu sputtering, the plasma composition was found to strongly affect the photoactivity of the materials produced. Copper when deposited as a lone co-catalyst in an Ar-only atmosphere imparted better photo-activity than Cu sputtered in Ar/O_2. When the deposition process coupled both Cu clusters and Pt clusters, an additive effect of the two metals in increasing TiO_2 photoactivity for hydrogen generation was observed under optimised conditions.

3:00pm **F1-WeA4 High Performances Supercapacitor having N, S-doped Soft Carbon Electrodes and Water-in-Salt Electrolyte***, **Yu-Min Fan (awesdr78@yahoo.com.tw)**,* National Cheng Kung University, Taiwan

"Water-in-salt" has known as a novel electrolyte for widening the potential window in energy storage devices. In this work, we present an symmetric supercapacitor based on N, S-doped soft carbon electrode and the use of water-in-salt electrolyte. Soft carbon was first activated by potassium hydroxide to enlarge the surface area and increase active sites. Nitrogen and sulfur were then co-doped to introduce additional functional groups using microwave-assisted hydrothermal treatment. The properties of the treated soft carbon were investigated using scanning electron microscope (SEM), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS). The as-prepared soft carbon was coated onto a carbon cloth substrate and used as electrode in symmetric supercapacitor. Various electrochemical evaluations, such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed. We demonstrate the excellent electrochmeical performce of the symmetric supercapacitor, including a wide potential window of 2.1.

3:20pm **F1-WeA5 Effect of Cu Irradiated Zr/Nb Nanometric Multilayers***, **Nabil Daghbouj (nabildagbouj@gmail.com)**,* Czech Technical University in Prague, Czech Republic

Sputter-deposited Zr/Nb nanometric multilayer films with thin layers (periodicity L=27 nm) and thick layers (periodicity L= 96 nm), were subjected to irradiation using 2.25 Mev Cu^+ ions with low (0.05 at%) and high fluence (0.2 at%) at room temperature. The changes in strain along the c axes (out-of-plane were measured as a function of dose using high-resolution x-ray diffraction. Cu^+ irradiation into thin layers induces a tensile out-of-plane strain in Nb layers and a compressive out-of-plane strain in Zr layers. While the Nb and Zr layers undergo compressive out-of-plane strain (shrink in c-axis)) after Cu+ irradiation when the layers are thick (L= 96 nm). The presented results are well supported by first-principles calculations DFT which shows Cu atoms placed in different interstitials sites as a function of nature of layers (Nb or Zr) and the layer length (thin or thick).

3:40pm **F1-WeA6 Manipulation of Thin Films and Nanostructures on Weakly-interacting Substrates by Selective Surfactant Deployment***, A. Jamnig,* Linköping University, IFM, Nanoscale Engineering Division, Sweden*; N. Pliatsikas, M. Konpan,* Linköping University, IFM, Nanoscale Engineering Division*; J. Lu,* Linköping University, IFM, Thin Film Physics Division, Sweden*; J. Kovac,* Josef Stefan Institute*; G. Abadias,* University of Poitiers, PPRIME Institute, CNRS, France*; I. Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J.E. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan, USA*; **Kostas Sarakinos (kostas.sarakinos@liu.se)**,* Linköping University, Sweden

The ability to control the size and shape of noble-metal nanostructures and the morphology of noble-metal films on weakly-interacting substrates, including 2D materials and oxides, is essential for the fabrication of high-performance enabling devices. The use of less-noble-metal and gaseous surfactants is a known strategy for manipulating growth of noble-metal layers, but the mechanisms by which surfactant atoms affect the complex structure-forming processes are not yet understood. In this work, we study the effect of nitrogen (N_2) gas on the morphological evolution of magnetron-sputter-deposited silver (Ag) thin films on silicon dioxide substrates. We find that presence of N_2 in a mixed argon (Ar)/N_2 gas atmosphere, throughout all film-formation stages, promotes 2D growth and smooth film surface, while the continuous-layer electrical resistivity increases, compared to Ag films grown in pure argon (Ar) ambient. Using a combination of real-time *in situ* film growth monitoring and *ex situ* characterization, we conclude that N_2 is physisorbed on the film growth surface and promotes 2D morphology by suppressing island coalescence rates during initial growth stages. Moreover, our data suggest that physisorbed N_2 causes interruption of local epitaxial growth on Ag crystals, which leads to repeated nucleation and explains the increased electrical resistivity of continuous films. Using these insights, we deposit Ag films by deploying N_2 selectively, either during the early growth stages or after coalescence completion. We show that early N_2 deployment leads to a 2D morphology without affecting the Ag-layer resistivity, while post-coalescence introduction of N_2 in the gas atmosphere further promotes formation of 3D nanostructures and roughness at the film growth front. The knowledge generated in the present study is relevant for the development of single-step growth manipulation strategies in which gaseous and less-noble-metal surfactant species can be deployed with high temporal and spatial precision to selectively target and modify the rates of key structure-forming processes.

4:00pm **F1-WeA7 Novel Type of Bent-Lattice Nanostructure in Crystallizing Amorphous Films Revealed by TEM: From Transrotational Microcrystals to Strain Nanoengineering and Novel Amorphous Models***, **Vladimir Kolosov (kolosov@urfu.ru)**,* Ural Federal University, Russian Federation

Exotic thin crystals with unexpected **transrotational nano**structures [1] have been discovered by transmission electron microscopy (TEM) for crystal growth in thin (10-100 nm) amorphous films of different chemical nature (oxides, chalcogenides, metals) prepared primarily by vacuum evaporation methods. We use TEM bend-contour method [2] combined with selected area electron diffraction. HREM, AFM and optical microinterferometry were used in due cases (preferentially for correlative microscopy).

The unusual phenomenon often can be observed ***in situ*** in TEM column during local e-beam heating or annealing: regular internal bending of crystal lattice planes in a growing crystal, Fig. 1 a-b. It is dislocation independent. Such **transrotation** (**trans**lation of the crystal unit cell is complicated by small **rotation** realized round an axis lying in the film plane) can result in strong regular lattice orientation gradients (up to 300 degrees/μm) of different geometries: cylindrical, ellipsoidal, toroidal, saddle, etc., Fig. 1b

The possible mechanisms of the phenomenon are discussed, Fig. 1d. Initial amorphous state and surface nucleation of the crystal growth are most essential factors. The last fact accompanied by anisotropy of crystal growth rate and obvious tendency for regular change of interatomic distances of the crystal propagating from the surface layers inside the bulk material resembles specific epitaxy, “vacuum epitaxy”. The transrotation phenomenon is the basis for novel lattice- rotation nanoengineering of functional, smart thin-film materials appropriate also for strain nanoengineering. Transrotational micro crystals have been eventually recognized by different authors in some thin film materials vital in applications, e.g. phase change materials (PCM) for memory [3-5].

New nanocrystalline “curved-lattice” concept for amorphous state is proposed: fine-grained structures with lattice curvature, Fig. 1e. Thus the great variety of different possible curved/transrotational lattice geometries inside fine crystal grains in the static model corresponds to different amorphous structures hardly distinguished by known methods. Going to 3D clusters of positive/negative curvature and dynamics we propose the hypothesis of “dilatons”, “contractons” pulsating or/and circulating in amorphous film.

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4:20pm **F1-WeA8 Ultrasensitivity of Self-powered Wireless Triboelectric Vibration Sensor for Operating in Underwater Environment Based on Surface Functionalization of Rice Husks***, **Sz-Nian Lai (snlai712@gapp.nthu.edu.tw)**, C.-K. Chang, C.-S. Yang,* National Tsing Hua University, Taiwan*; C.-W. Su, C.-M. Leu,* Industrial Technology Research Institute, Taiwan*; Y.-H. Chu, P.-W. Sha,* National Chiao Tung University, Taiwan*; J.M. Wu,* National Tsing Hua University, Taiwan

We demonstrate the self-powered wireless triboelectric vibration sensor as made from the naturally nanoporous SiO_2 particles for allowing the detection of the vibrations and movement in the underwater environment. The nanoporous SiO_2 particles are directly converted from rice husks (referred to as RH_{SiO2}), which exhibit strongly interacting surface hydroxyl groups. Through the enzymatic treatments, the surface potential of the RH_{SiO2} can be modulated to obtain either an extremely low or strongly high electronegativity. Specifically, by adding fluorinated groups using fluoroalkylsilane (FOTS) treatment to obtain RH_{SiO2}-F, the charge density of the RH_{SiO2}-F triboelectric nanogenerator (TENG) can be enhanced ~ 56.67-fold as compared to the untreated RH_{SiO2}-TENG. The power density of the RH_{SiO2}-F TENG is increased from 0.077 mWm^{-2} to 261 mWm^{-2}. The RH_{SiO2}-F particles are encapsulated in a quartz cube to fabricate a self-powered wireless sensor that can be stabilized for operating in water at various temperatures. The theoretical calculation further demonstrates that the triboelectric potential is dramatically established between the surface functionalized RH_{SiO2}-F particles and the quartz’s surface. With porous nature of rice husks covered with nano-Si is of a high functionality for designing a new-type TENG which has a great potential to apply in the environmental monitoring.

4:40pm **F1-WeA9 Fabrication and Characterization of Thin-film Metallic Glass/polyacrylonitrile Composite Membrane for Nitrogen Separation***, **Endashaw T. Gizaw (endast09@gmail.com)**,* National Taiwan University of Science and Technology, Taiwan*; H.-H. Yeh,* Chung Yuan Christian University, Taiwan*; J.P Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan*; C.-C. Hu,* Chung Yuan Christian University, National Taiwan University of Science and Technology (NTUST), Taiwan

An amorphous alloy coated membrane composed of primarily a composite polymeric membrane coated with thin-film metallic glass (TFMG) is introduced in this work as an inexpensive alternative for Pd-based metallic membranes in gas separation applications. The $Zr_{60}Cu_{25}Al_{10}Ni_5$ TFMG was successfully coated on Polyacrylonitrile (PAN) membrane using RF sputter deposition without external heating. The membranes surface morphology, crystallography, and thermal stability were characterized using FE-SEM, XRD, and TGA, respectively. From these studies, it was understood that the permeability of the TFMG/PAN composite membrane was controlled by the inherent structure of top ultra-thin selective TFMG coatings layer within several thicknesses ranging from 30 nm to 100 nm. The separation performance of TFMG-coating PAN composite membranes was examined with N_2/O_2 and N_2/CO_2 binary gases using Bubble foam meter. The high permeation and weaker interactions properties of nitrogen through the pore walls of the TFMG/PAN composite membrane potentially make these materials more attractive for N_2 selective. Therefore, a new material, TFMG could be a promising candidate to enhance gas separation performance based on its comprehensive property.

5:00pm **F1-WeA10 Multi-element Hydroxides Grown on Ni-Foam As Binder-Free Electrodes for Supercapacitor***, Yi-Xin Lin (shelly2828666@gmail.com)*, National Cheng Kung University, Taiwan

In this work we have investigated multi-element transition metal hydroxides synthesized using a hydrothermal method. The existence of multiple metals offers unique electrochemical properties due to diversified valence states. Nickel-foam was used as the substrate for the growth of multi-element transition metal hydroxides to obtain binder free-electrode under different hydrothermal temperatures, hydrothermal times, and precursor concentrations. The charge storage mechanism of the resulting samples was investigated. Likewise, the valence state and crystal structure transformation of hydroxides during charge/discharge were thoroughly investigated using ex-situ X-Ray diffractometry and X-Ray photoelectron spectroscopy, respectively. The morphology of the resulting samples was characterized using field emission scanning electron microscopy and transmission electron micrsocopy. The obtained samples were then used as electrodes in supercapacitors. The electrochemical properties of electrodes were investigated using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The long-term stability of the electrode was also investigated up to 5,000 cycles. The results show that the multi-element transition metal hydroxides materials are promising candidate electrode materials for next generation supercapacitors.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific Salon 2 - Session G6-WeA

Application-Driven Cooperations between Industry and Research Institutions

Moderators: Tobias Brögelmann, Surface Engineering Institute - RWTH Aachen University, Germany, Joern Kohlscheen, Kennametal GmbH, Germany, Kumar Yalamanchili, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

2:00pm **G6-WeA1 Success Factors for Collaborative Industrial Coating Development***, Marcus Morstein (marcus.morstein@hightechzentrum.ch)*, Hightech Zentrum Aargau AG, Switzerland **INVITED**

Mastering the development of a truly innovative thin-film coating and combining it with a highly sophisticated pre- and posttreatment process can turn into a task challenging the resources of a single player, such as a coating company. Seen from inside a corporate structure – especially a big one – it may appear convincing to solve such a mission independently. This approach is however often negatively connotated ("silo mentality") and bears the risk of failure when aiming at complex, novel breakthrough coatings or coating technologies. In contrast, the "open innovation" [1] approach offers additional resources through an active strategic use of external collaborations in order to increase the innovation potential by including external ideas, methods and resources.

Knowledge and technology transfer institutions enable this process by supporting companies in getting access to the latest knowledge of research institutions. They also mitigate intellectual property issues and facilitate access to public research funding sources, which helps bearing R & D risks of companies [2,3].

Many research projects have obstacles to overcome before becoming actual success cases. Yet they frequently illustrate the general benefit of open innovation: Sparking good research by including external as well as internal ideas. This presentation will address chances and challenges of the mutual technology transfer in an open innovation approach and outline the most common collaborative constellations. Example success cases from the PVD community will be presented, such as

- Establishing a stable process chain for advanced PVD coating of blanking and forming tools, including substrate surface preparation and coating post-treatment, within different consortia
- Exploring a new coating system using a combinatorial approach in a consortium of two enterprises and one university.

Knowledge-based coating development also benefits from the know-how of innovative end-user project members ("creative consumers") and further actors, such as providers of advanced analytical equipment or services. The role of these for successful coating development will be addressed, too.

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[2] A. Spescha, M. Woerter, *Innovation and firm growth over the business cycle*, Industry and Innovation, **26**, 321-347 (2019).

[3] N. Bloom, C.I. Jones, J. Van Reenen and M. Webb, *Are ideas getting harder to find?*, National Bureau of Economic Research Working Paper No. w23782 (2017).

2:40pm **G6-WeA3 (Cr,Al,Mo)N Coatings for Higher System Stability under Minimum Quantity Lubrication***, K. Bobzin, T. Brögelmann,* ***Christian Kalscheuer (kalscheuer@iot.rwth-aachen.de)***, Surface Engineering Institute - RWTH Aachen University, Germany*; K. Stahl, T. Lohner, M. Yilmaz,* Gear Research Centre – Technical University of Munich, Germany

In todays mobility applications, efficiency is a key requirement. This applies not only to conventional, combustion engine driven mobility, but also to e-mobility. While in conventional mobility, increased efficiency contributes to reduce greenhouse gas emissions, in e-mobility every increase in efficiency translates also directly into increased battery range. To achieve this aim, different approaches are pursued. One approach is the reduction of lubricant viscosities. Another approach is the reduction of lubricant quantities towards minimum quantity lubrication which allows the reduction of no-load losses e.g. in gearboxes. However, both approaches lead to more extreme lubrication conditions, which often exceed the load limits of conventional steels. A promising approach to meet the increasing demands are (Cr,Al)N and triboactive (Cr,Al,Mo)N coatings. In fundamental research the potential of triboactive (Cr,Al,Mo)N coatings was shown, which can interact with sulphur containing lubricants and enable the in situ formation of MoS_2.

Within this work (Cr,Al)N and triboactive (Cr,Al,Mo)N coatings were investigated in a twin-disk test rig in highly loaded rolling-sliding contacts, with regard to gear applications. The coatings were deposited in an industrial scale coating machine by means of cathodic arc evaporation on the case hardened steel 16MnCr5E (1.7131). Tribological tests were conducted under minimum quantity lubrication with an oil volume of V = 0.1 ml of a low viscosity oil at Hertzian contact pressures of p_H = {600; 1,200} MPa. Friction curves were obtained by varying the slip ratio for different sum velocities. The lubricant was doped with sulphur and phosphor. Compared to the uncoated steel, the coatings show a higher system stability and wear reduction. Tribochemical interactions between coatings and lubricant were analyzed by means of Raman spectroscopy. Besides tribochemical interactions, also the thermal insulation effects of the coatings were investigated, since these effects are known to contribute to friction reduction. Therefore, the thermophysical properties were determined by means of differential scanning calorimetry (DSC) and laserflash method. Based on that, simulations of the thermo elasto-hydrodynamic contact were conducted following the operating conditions of the tribological tests. The results show the high potential of (Cr,Al)N and triboactive (Cr,Al,Mo)N coatings for higher system stability and wear reduction under high tribological load.

3:00pm **G6-WeA4 Performance and Characterization of PVD Coatings with Different Al/Ti Ratio During High Speed Turning of Stainless Steel 304***,* ***Qianxi He (heq19@mcmaster.ca)****, J.M. Paiva,* McMaster University, Canada*; J. Kohlscheen,* Kennametal GmbH, Germany*; G. Fox-Rabinovich, S.C. Veldhuis,* McMaster University, Canada

In this study, three AlTiN PVD coatings with different Al/Ti ratio (60/40, 70/30 and 73/27) obtained by arc cathodic system were applied on high speed finishing turning of stainless steel 304 (SS304) under different cutting speeds and lubricious conditions. This material is well known to be hard-to-cut, and therefore applying PVD coatings on cemented carbide is an effective way to improve the cutting tool life. Coatings' characterizations such as phase orientation and residual stresses were evaluated by XRD analyses while coating architecture, coating topography and thickness were performed out by SEM. In order to understand the influence of the mechanical properties of the coatings on the tool wear performance, the adhesion, hardness and elastic modulus of the coatings were evaluated using a scratch and nano-indentation testers. The wear performance study shows that the crater wear leads to the tool failure instead of flank wear. Based on the tool life results, Al60Ti40 coating shows the best tool life, which has 2 times longer than the benchmark, and its tool life increases over 140% under different turning conditions.

Keywords

AlTiN PVD coating, Al/Ti ratio, high speed turning of SS304, wear performance.

3:20pm **G6-WeA5 Mechanical and Tribological Properties of CVD α-Al_2O_3 Coatings at Ambient and Elevated Temperatures**, ***Rachid M'Saoubi (Rachid.Msaoubi@secotools.com),*** Seco Tools AB, Sweden **INVITED**

Recent advances in nucleation and chemical vapour deposition (CVD) technology have led to the development of highly textured -wear and temperature- resistant protective surface coatings for cutting tool applications. In particular, it has been demonstrated that the performance of alumina coatings produced by the CVD technique can be enhanced substantially by controlling crystal orientation and growth texture. Furthermore, the failure of these coatings is often preceded by a degree of plastic deformation that is found to depend on the crystallographic orientation of the film. In the present investigation, the mechanical and tribological properties of texture-controlled CVD α -Al_2O_3 layers with (0001), (01-12), and (10-10) growth textures were investigated using a combination of mechanical and tribological testing methods at ambient and elevated temperatures (up to 600° C). Nanoindentation experiments were carried out using an ex-situ high temperature berkowich type nanonindenter. Micropillar compression of the thin film coatings were performed using a flat punch nanoindenter under Scanning Electron Microscope. The tribological characterisation of the coatings was carried out with the help of conventional single pass scratch testing equipment where friction coefficient and acoustic emission were continuously recorded. The results indicate a strong dependence of the thin films crystallographic orientation on the mechanical and tribological properties of the thin films and seem to correlate reasonably well with their machining performance.

4:00pm **G6-WeA7 Mo-Si–B Based Coatings: Alloying Concepts and Architectural Designs**, ***Elias Aschauer (elias.aschauer@tuwien.ac.at),*** TU Wien, CDL-SEC, Austria*; V. Dalbauer, P. Felfer,* FAU Erlangen, Germany*; V. Moraes,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Primetzhofer,* Uppsala University, Sweden*; C. Fuger,* TU Wien, CDL-SEC, Austria*; H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Environmental sustainability is the driving force for scientific progress. A decisive factor is an economical use of resources as well as a reduction of emissions, often linked to highly–stable materials. Especially, in jet engines and turbines, higher combustions temperatures are a key factor for an efficient operation, simultaneously needed in combination with an excellent lifespan. Next to the well-established protective coatings such as Ti–Al–N and Al-Cr-N, novel thin film material classes arising. Here, especially B containing coatings are getting more and more into the focus.

One of these promising coating materials are boron enhanced Mo–Si based alloys, well investigated as a bulk material, and known for their outstanding creep resistance in combination with a stable oxidation up to 1600 °C. Decisive for their oxidation performance is a well–balanced phase composition, enabling the formation of a boro–silicate based oxide layer. Here, an ideal B/Si ratio is provided by the intermetallic T_2–Mo_5SiB_2 phase. However, contrary to the synthesis of bulk materials at temperatures >1000 °C, where the system reaches the phase equilibrium, PVD processes typically lead to amorphous films. Hence, the addition of T_2 stabilising elements can possibly support a distinct crystallisation.

Therefore, we studied the influence of Ti as well as the bias voltage on sputtered Mo–Si–B based thin films and analysed in detail the effects on the morphology and the crystal structure as well as the phase formation upon annealing in vacuum. The coating performance was tested by analysing the thermomechanical properties as well as the oxidation resistance, showing an extremely stable oxidation resistance up to 1300 °C.

As shown in our previous studies [1], a further improvement can be achieved by implementing this system into a Ti–Al–N based matrix, forming a nano–scaled multilayer. However, within this system, the process management needs particular attention: Different atmospheres for the individual films, varying bias voltages, and differing deposition techniques are influencing the final coating significantly. This complex syntheses process leads to a changing droplet formation, cross–contamination effects of the respective coating systems and a complex phase formation within the Mo–Si-B layers.

Therefore, we also had a look on the synthesis parameters of the multilayer system, in order to learn how to control the performance defining process parameters and the resulting coating performance.

[1] H. Riedl, et al., Ti-Al-N/Mo-Si-B multilayers: An architectural arrangement for high temperature oxidation resistant hard coatings, Surf. Coat. Technol. 328 (2017) 80–88.

4:20pm **G6-WeA8 Hard Protective Coatings Inside Narrow Tubes and Cavities in Aircraft Engine Components**, *A. Kilicaslan, O. Zabeida, E. Bousser,* Polytechnique Montreal, Canada*;* ***Jolanta-Ewa Klemberg-Sapieha (jsapieha@polymtl.ca),*** Polytechnique Montrtreal, Canada*; L. Martinu,* Polytechnique Montreal, Canada

There is an ever-growing interest in the use of functional coatings to protect surfaces of materials and workpieces against harsh environments such as corrosion, abrasion or solid particle erosion (SPE), making surface engineering solutions a very attractive balance between performance and cost. Numerous vapor-based fabrication techniques have been developed, namely PVD, CVD, and PECVD, that can be used to achieve the high hardness and high wear resistance while being compatible with substrate materials such as metals, and different substrate shapes. This is increasingly important in the case of inner surfaces of tubular components, such as parts of aircraft engines, oil pipelines, mining components, and numerous others.

In the present work, we study a novel Non-Line-Of-Sight (NLOS) technique to coat the inner parts of non-linear surfaces and cavities with hard, wear- and erosion-resistant coatings possessing high SPE resistance, a hardness significantly higher than the hardness of the particles impacting the surface, as well as a large thickness (more than 8 µm).

Specifically, we review, study and demonstrate the fabrication process of hard SPE-resistant TiN protective coatings on the inner surfaces of narrow tubes using an NLOS approach yielding a uniform film thickness and properties along the tube axis (better than 20%). The deposition process indicates the importance of applying pulsed-DC PECVD when uniform hard TiN films are prepared at low-frequency in the kHz range. The TiN films (about 12 µm thick), exhibit high hardness and relatively low Young's modulus (25 and 225 GPa, respectively), corresponding to the (111) preferred crystallographic orientation. We show that the SPE resistance on the inner surface decreased by a factor of more than 15 compared to the bare substrate and that the process is well suited for the protection of aerospace, manufacturing, 3D printed and other critical components with a complex shape of inner surfaces.

Topical Symposia
Room Pacific Salon 3 - Session TS3-1-WeA

In-Silicio Design of Novel Materials by Quantum Mechanics and Classical Methods (jointly sponsored by ICMCTF and AQS) I

Moderators: David Holec, Montanuniversität Leoben, Austria, Davide Sangiovanni, Linköping University, Sweden

2:00pm **TS3-1-WeA1 Evolutionary Structure Prediction of Transition Metal Borides**, ***Dmitry Rybkovskiy (D.Rybkovskiy@skoltech.ru),*** *A.G. Kvashnin, Y.A. Kvashnina,* Skolkovo Institute of Science and Technology, Russian Federation*; H.A. Zakaryan,* Yerevan State University, Armenia*; A.R. Oganov,* Skolkovo Institute of Science and Technology, Russian Federation

One of the most important problems in modern materials science is the ability to synthesize materials with desired properties, which are, in turn, defined by their atomic structure. Traditional experimental methods of structure determination are nowadays supported by state-of-the-art computational techniques. Mathematically, the task of theoretical structure determination can be formulated as a global optimization problem - one needs find the lowest energy value of the system as a function of its atomic coordinates. A number of algorithms has been developed for the search of the most stable crystal structures, including minima-hopping, simulated annealing, random structure search, particle-swarm optimization, metadynamics and evolutionary algorithms [1]. Compared to other structure prediction methods, evolutionary global optimization algorithms have the benefit of using both the broad coverage of configurational space and subsequent modification of the best candidate structures. When combined with robust quantum chemical total energy calculation techniques, such an approach allows to perform experiment-independent determination of crystal structure.

In the present work we apply the evolutionary structure prediction algorithm USPEX [2] for the study of the transition metal borides in the whole composition range from pure metal to pure boron. These materials attract considerable attention as potential superhard compounds for use in various technological applications. However, the crystal structure of higher borides is often difficult to assess by experimental methods. By using the evolutionary global optimization algorithm USPEX, density functional theory total energy calculations and approximate total energy models we investigate the structural peculiarities of transition metal borides.

The work was supported by Russian Science Foundation (№ 19-12-00414). This work has been carried out using the Arkuda and Pardus supercomputers of Skolkovo Foundation.

[1] A. R. Oganov, C. J. Pickard, Q. Zhu, and R. J. Needs, Nat. Rev. Mater. **4**, 331 (2019).

[2] A.R. Oganov, A.O. Lyakhov, and M. Valle, *Acc. Chem. Res.* 2011, *44*, 227.

2:20pm **TS3-1-WeA2 Design of Ultrastrong 5d Transition Metal Diborides***,* ***Dominik Legut (dominik.legut@vsb.cz),*** VSB - Technical University of Ostrava, Czech Republic*; N. Wang, Z. Fu, B. Wei,* Beihang University, China*; T. Germann,* Los Alamos National Laboratory, USA*; R. Zhang,* Beihang University, China

Much effort was devoted towards the rational design of ultrastrong transition metal borides (TMBs)with remarkable mechanical properties and excellent stabilities, owing to promising applications inmachining, drilling tools and protective coatings for the aerospace industry. Although an enormousnumber of investigations have been performed on these TMBs under normal conditions, studies on thestability and mechanical strength in harsh high-pressure environments, which are critical for safe servicebehavior and a realistic understanding of stabilities and strengthening mechanisms, are yet nearly absent.In this work, taking 5d TMB2 (TM = Hf, Ta, W, Re, Os, Ir and Pt) as an illustration, we performedcomprehensive high-throughput first-principles screening for thermodynamically stable and metastable

structures under various pressures. Four experimentally observed structures are found to be thermodynamically feasible for most 5d TMB2 (TM = Hf, Ta, W, Re, Os and Ir) at 0 and 100 GPa. By exploiting orbital-decomposed electronic structures, we reveal that the pressure-induced stabilization and phase transitions of 5d TMB2 can be rationalized by the splitting of bonding and antibonding states around the Fermi level. Further investigations on the pressure-induced strengthening indicate that 5d TMB2 in the hP6[194] structure exhibit a profound strengthening effect under high pressure, which can be rationalized by the proposed strengthening factor Z, but Z fails in the oP6[59] structure due to the changed instability modes at different pressures. These findings suggest the necessity to explore the plasticity parameters for a realistic understanding of pressure-induced strengthening in TMBs, providing

a strong argument for rules based on bond parameters at equilibrium in designing strong solids.

2:40pm **TS3-1-WeA3 Bill Sproul Award and Honorary ICMCTF Lecture: Are Protective Coatings Predictable? A Mid-Career Assessment***,* ***Jochen Michael Schneider (schneider@mch.rwth-aachen.de)*** [1] *,* RWTH Aachen University, Germany **INVITED**

Designing the next generation of protective coating materials without utilizing trial and error-based methodologies requires truly predictive computational approaches. Important design criteria for crystalline and amorphous protective coating materials are the mechanical behavior as well as thermal and chemical stability. In this talk an effort is made to describe the good, the bad and the ugly of our predictive capabilities: Which predictions have been validated experimentally, and which experimental data cannot be described theoretically. Implications for future design efforts will be discussed.

3:20pm **TS3-1-WeA5 Influence of Impurities on Mechanical Properties of Nitride Multilayer Coatings***,* ***Lukas Löfler (lukas.loefler@unileoben.ac.at),*** Montanuniversität Leoben, Austria*; J. Buchinger, P.H. Mayrhofer, M. Bartosik,* TU Wien, Austria*; D. Holec,* Montanuniversität Leoben, Austria

Thin films and coatings are used to protect surfaces of tools and components from harsh environmental and/or tough application conditions. To push the mechanical properties of such films to a point where they can fulfil the increasing requirements of modern applications, we need to find new materials or optimize the design and microstructure of the already established material systems. A very effective design is to prepare multilayers of two different thin film materials. If these grow coherent or at least semi-coherent superlattice films with outstanding properties are accessible. For such superlattices, with their typically very thin layers, the interfaces become important elements influencing the overall material behaviour.

Most successful nitride-phases used for protective coatings are either, CrN, TiN or AlN based. Due to their significantly different shear moduli, the superlattice effect (on hardness as well as toughness) is promoted and could be verified experimentally. Ab initio calculations using Density Functional Theory (DFT) of such superlattices were used to investigate their mechanical properties (such as tensile strength for example), based on calculating their stiffness tensor. The tensile strength was obtained by cleaving the cells along various planes, to determine the weakest region. Additionally, the planar strength was also evaluated perpendicular to the superlattice-interfaces, which allows for comparisons with micromechanical experiments (where the crack propagation is typically perpendicular to such interfaces). We furthermore added B and O impurities at and near these interfaces to verify their impact on the mechanical properties.

3:40pm **TS3-1-WeA6 Strength, Transformation Toughening and Fracture Dynamics of Rocksalt-structure $Ti_{1-x}Al_xN$ (0 ≤ x ≤ 0.75) Alloys***,* ***Davide Sangiovanni (davide.sangiovanni@liu.se)****, F. Tasnadi, M. Oden, I.A. Abrikosov,* Linköping University, Sweden

We employ density-functional molecular dynamics simulations to determine the elastic response, ideal strength and toughness, and ability to plastically deform up to fracture of defect-free rocksalt-structure (B1) TiN and B1 $Ti_{1-x}Al_xN$ (x = 0.25, 0.5, 0.75) solid solutions subject to [001], [110], and [111] tensile deformation at room temperature. Overall, TiN exhibits greater ideal moduli of resilience and tensile strengths than TiAlN alloys. Nevertheless, the binary compound systematically fractures by brittle cleavage at its yield point. The simulations also indicate that 25% Al substitutions in $Ti_{1-x}Al_xN$ have negative effects on mechanical performances; the alloy remains brittle, while both strength and resilience slightly decrease. In sharp contrast, $Ti_{0.5}Al_{0.5}N$ and $Ti_{0.25}Al_{0.75}N$ solid solutions exhibit inherently high resistance to fracture and greater toughness than TiN due to the activation of local B1 → wurtzite-like structural transformations beyond the elastic-response regime. The results of this work illustrate the inadequateness of elasticity-based criteria for the prediction of strength, brittleness, ductility, and toughness in materials able to undergo phase transitions at extreme loading. Furthermore, we discuss rationales for design of hard ceramic solid solutions that are thermodynamically inclined to dissipate extreme mechanical stresses via transformation toughening mechanisms.

4:00pm **TS3-1-WeA7 Multiscale Modelling of Thin Metal Film Growth on Weakly-interacting Substrates***,* ***Victor Gervilla (victor.gervilla@liu.se)****, M. Zarshenas, B. Lü, G. Almyras,* Linköping University, Sweden*; J.E. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan, USA*; D.G. Sangiovanni, K. Sarakinos,* Linköping University, Sweden

Controlled growth of thin metal films on weakly-interacting 2D materials and oxide substrates is an essential step in the fabrication of novel devices and requires a fundamental understanding of the atomic-scale processes that govern the dynamics of film morphological evolution. Here, we model key initial stages of group 10 and 11 transition-metal film growth across multiple length and time scales. Using a stochastic kinetic Monte Carlo (kMC) algorithm, supported by deterministic classical molecular dynamics simulations, we study formation and growth of Ag islands on a weakly-interacting substrate. Our simulations reveal the initial formation of 3D nuclei, followed by the development of sidewall facets bounding the islands, which facilitates upward diffusion from the base to the top of the islands. We show that the limiting atomic process which determines the island height is the temperature-dependent rate at which adatoms cross from sidewall facets to the island top. The kMC model is then used to simulate coalescence of 3D faceted island pairs in the presence of a deposition flux. We find that the initial faceted island structure is maintained, which leads to formation of a facet/facet intersection between the two islands. The island pair reshaping then proceeds via repeated facet migration through the intersection leading to a new compact island with a smaller total in-plane size compared to the original islands. Above a critical deposition rate, facet migration and coalescence are inhibited, such that agglomeration results in an in-plane expansion of the new compact island. The results explain

[1] **Bill Sproul Awardee**

multiple experimental observations for film growth as a function of temperature, which are contrary to morphological evolution data available for homoepitaxial film/substrate systems. Finally, the fundamental process that governs island nucleation, i.e., adspecies surface migration, are followed using *ab-initio* molecular dynamics (AIMD) simulations of Ag, Au, Cu, Pt, and Pd monomer and dimer diffusion on graphene. Anomalous transition-metal adspecies diffusion patterns are obtained for flat potential energy landscapes on graphene. This suggests that static diffusion barrier values reported in the literature for multiple metal/graphene systems are not representative quantities of the complex adspecies migration dynamics on weakly-interacting 2D materials.

4:20pm **TS3-1-WeA8 Computational Modeling of 3D Thin Film Growth Morphology: Influence of Angular and Energy Distribution of Particle Flux***,* ***Grégory Abadias (gregory.abadias@univ-poitiers.fr)****, C. Mastail, C. Furgeaud, F. Nita, R. Mareus, A. Michel,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France **INVITED**

Considerable work has been done in recent years, both experimentally and theoretically, to characterize and predict

the properties of thin films from external conditions, including substrate temperature, deposition rate, angular distribution of atoms, and incident kinetic energy. The interplay between some deposition parameters often renders the task to obtain the desired film morphology challenging. On the other hand, the control of the desired morphology is essential for the applications searched for. Predictions from computational approaches are therefore very helpful in this sense.

We have developed a 3D kinetic Monte Carlo (kMC) atomistic code to help understand the role of the elementary atomistic diffusion mechanisms and impact of deposited energy on the resulting thin film growth morphology. The simulation model aims at mimicking the full sputter-deposition process, from ejection of atoms from the target, their transport in the gas phase, and film formation. First-principle calculations are also implemented to determine the potential energy landscape for preferable adsorption sites, or energy barrier for surface diffusion.

In the work presented here, the code has been applied to simulate the growth of TiN and Cu thin films. Examples will be provided for the growth at either normal or oblique angle incidence. The code is capable of reproducing the development of TiN columnar morphology, with column tilt angle in good agreement with experimental findings. For the case of Cu, the growth proceeds in a 3D mode, with nucleation of isolated islands, percolation and formation of continuous layer. The influence of kinetic energy on film morphology and defect incorporation will be also discussed.

5:00pm **TS3-1-WeA10 Benchmarking Simulational Approaches to Predict High-Temperature Elastic Constants of Ti(0.5)Al(0.5)N Alloy***,* ***Johan Tidholm (johan.tidholm@liu.se)****, F. Tasnádi, I.A. Abrikosov,* Linköping Univ., IFM, Theoretical Physics Div., Sweden

The cutting industry is aiming for more efficient cutting, which increases significantly the operating temperature. The applied hard coating should withstand higher heat, stresses, etc. Therefore, the need for knowing the properties of alloys used as coatings at operating temperatures is increasing. Ab-initio molecular dynamics simulations are known as a reliable tool for investigations of thermodynamic and mechanical properties of alloys. Unfortunately, it is a computational demanding approach. Because of this, various approximations have been suggested to predict elastic properties of materials relevant for coating applications at finite temperature. In particular, Elastic constants of Ti(1−x)AlxN have been calculated using static 0 Kelvin density functional theory (DFT) calculations[1] and also in the framework of the temperature-dependent effective potential (TDEP) method[2–4] with an ”effective average force constants” Hamiltonian.[5] However, their accuracy is not analysed considerably. In this study, we carry out direct ab-initio molecular dynamics simulations to predict high-temperature elastic constants of Ti0.5Al0.5N at 300, 600, 900, and 1500 Kelvin. In this way, we obtain the most accurate reference data, which can be used to benchmark other, perhaps more efficient approximations. We compare the obtained elastic constants and analyse the computational demands of the different approaches.

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Awards Convocation and Honorary Lecture
Room Town & Country - Session HL-WeHL

Bunshah Award Honorary Lecture
Moderator: Ivan Petrov, University of Illinois, USA, Linköping University, Sweden, USA

6:05pm **HL-WeHL2 R.F. Bunshah Award and ICMCTF Lecture Invited Talk: A Journey from Trial & Error to the Knowledge-based Design of Coatings and Thin Films***, Christian Mitterer (christian.mitterer@unileoben.ac.at)* [1] *,* Montanuniversität Leoben, Austria **INVITED**

In the 1980-ies, when I have grown my first transition metal boride based hard coatings by sputter deposition, process and materials development were essentially based on trial & error. Nevertheless, that time already led to innovations which established the basis for the present state-of-the-art in hard coating materials, for example TiN, TiC_xN_{1-x}. $Ti_{1-x}Al_xN$, Al_2O_3 and even the first nanocomposite coatings based on the TiB_2-TiN system. Progress in process technology and characterization methods enabled to add more and more functionalities to the films. Prominent examples are age-hardening of metastable $Ti_{1-x}Al_xN$ coatings and self-lubrication by the in-operando formation of lubricious Magnéli phase oxides. Starting in the early 2000s, the utilization of quantum mechanics methods provided a deeper understanding of phase stability and properties. Modern high-resolution characterization methods like X-ray synchrotron nanodiffraction and atom probe tomography came up in the last decade, enabling a previously impossible insight into depth-resolved composition and microstructure on the nanoscale. In parallel, micromechanical test methods have been introduced to assess coating properties like fracture strength and fracture toughness. Nowadays, the available modern process technology coating deposition in combination with quantum mechanical and advanced characterization methods provide the key for the knowledge-based design of coatings and thin films. Within this talk, a personal retrospective on a 35 years long journey will be given, highlighting and exemplifying the change in our approaches for the development of advanced coatings and thin films. Special emphasis will be laid on hard coating materials like transition metal diborides, $Ti_{1-x}Al_xN$ and Al_2O_3 as well flexible Mo-based thin films, where ultimately these combined experimental and theoretical methods led to breakthroughs in our understanding of materials behavior and their application.

[1] **R.F. Bunshah Awardee**

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-1-ThM

PVD Coatings and Technologies I

Moderators: Frank Kaulfuss, Fraunhofer IWS, Germany, Qi Yang, National Research Council of Canada, Canada

8:00am **B1-1-ThM1 Influence of the Period of a Multilayer TiN / TiAlN Coating System on its Microstructure and Electrochemical Behavior for Potential Applications in Hot Work Steel***, **Hernán Darìo Mejía Vásquez (hdario.mejia@udea.edu.co)**, G. Bejarano Gaitan,* University of Antioquia, Medellín, Colombia*; M. Arroyave Franco,* University EAFIT, Colombia

In order to improve the wear resistance of hot-working AISI H13 steel, different surface modifications such as plasma nitriding and hard coatings of TiN, TiCN and TiAlN, among others, have been used. TiAlN is perhaps one of the most commonly used coatings due to its high resistance to wear and oxidation at high temperatures. However, the evaluation of its corrosion resistance has been poorly studied. This research work focused on the design of a TiN / TiAlN multilayer coating system deposited by the DC magnetron sputtering technique deposited on AISI H13 steel to evaluate the influence of the bilayer period on the microstructure and corrosion resistance of the multilayer system. For this purpose, coatings with periods of 20, 30, 40 and 50 nm were deposited for a total thickness of 1500 nm. The coatings presented a columnar growth structure whose density and column width decreases with the bilayer period as determined by SEM. The XRD patterns show a crystalline structure with well-defined peaks of TiN and TiAlN grown in the preferential orientations (111) and (220), whose crystallite size decreases with the number of bilayers, which was confirmed by TEM analysis. The roughness and grain size went from 15 to 5 nm and from 30 to 10 nm for periods of 50 nm to 20 nm, respectively, as evaluated by AFM. Polarization curves and electrochemical impedance spectroscopy exhibited lower corrosion currents and much greater polarization resistance as the bilayer period decreases. The greater resistance to corrosion of the multilayer system, as the number of bilayers increases, is associated with the smaller grain size, greater density of the coatings and greater number of interfaces with the decrease of the period, which progressively hinders the penetration of the electrolyte from the surface of the coating until the interface with the substrate. On the other hand, oxygen diffusion is also inhibited. All deposited coatings exhibited greater corrosion resistance than uncoated H13 steel.

8:20am **B1-1-ThM2 ScAlN-Based Multilayer Structure for High K² SAW Devices***, **Ping-Ho Lee (benli850713@gmail.com)**, Y.H. Huang,* National Cheng Kung University (NCKU), Taiwan*; S. Wu,* Tung-Fang Design University, Taiwan*; J.L. Huang,* National Cheng Kung University (NCKU), Taiwan

ScAlN films are high potential materials for surface acoustic wave (SAW) devices due to its high piezoelectric coefficient (d_{33}) caused by the lattice distortion of the larger Sc^{3+} ions. In this study, ScAlN thin films were deposited on Y-128° $LiNbO_3$ substrate by reactive magnetron co-sputtering using Al and Sc targets. All the films show highly c-axis preferred orientation with columnar structure under SEM and XRD images. Thin metal stacks with different thicknesses were then introduce into the structure to form the ScAlN-based multilayer structure. The quality of ScAlN thin films was improved because of the lower lattice mismatch. A high d_{33} value 37.4 pm/V was measured, which corresponds to the enhanced quality of ScAlN film. The electromechanical coupling coefficient (K^2) also increases with the use of multilayer structure. The highest K^2 (22.55%) value shows four times larger than IDT/ $LiNbO_3$ (4.9%) structure.

8:40am **B1-1-ThM3 Coating Design and Mechanical Properties of Multicomponrnt AlTi(X)N Hard Coatings***, **Yin-Yu Chang (yinyu@nfu.edu.tw)**,* National Formosa University, Taiwan **INVITED**

Due to economical demands to further increase the efficiency of production processes, it is essential to exploit the full potential of wear resistant hard coatings. TiN and AlTiN-based coatings are widely used as protective material for cutting tools, molds, and mechanical components in mechanical industries. Low chemical reactivity of these hard coatings with workpiece materials protects against sticking and thus reduces the adhesive wear. The most widespread wear resistant coatings are those with the following chemical formula Ti-X-(N,C and B) (X = Al, Cr, C, Si, and B etc.) which have proven to have excellent properties for industrial applications in the cutting, forming and stamping fields.

In this study, the coating design, mechanical property, high temperature oxidation behavior and cutting performance of multicomponent and multilayered AlTi(X)N coatings, which X= Cr, Si and B etc., will be discussed. These high performance coatings can be deposited by using cathodic-arc deposition with arc cathodes or unbalanced magnetron sputtering. Various cathode targets, such as Ti, Cr, TiAl, TiAlSi, CrAlSi, and AlSi, are used for the deposition. The microstructure of the as-deposited and high temperature annealed coatings was characterized by field emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD) using Bragg-Brentano and glancing angle parallel beam geometries. The mechanical properties including hardness and elastic modulus of the coatings were analyzed by a nanoindenter with Berkovich indenter tip.

Depending on the coating design, the deposited AlTi(X)N coatings showed B1-NaCl crystal structure and have multiple orientations of (111), (200), and (220). The nanohardness, which measured by nanoindentation, of these coatings possessed hardness higher than 30 GPa, depending on the gradient and multilayered structures. The high temperature oxidation test showed the oxidation rate during annealing depends on film composition and microstructure. The oxide layer formed on the AlTiSiN coatings consists of large TiO_2 and AlTiSiN grains at the oxide-coating interface, followed by a layer of protective Al_2O_3 in the near-surface region. Interestingly, after oxidation, the AlTiBN coating contained an oxide layer composed of nanocrystalline Al_2O_3 and TiO_2. No crystallite growth or phase transformation occurred in the unoxidized AlTiBN coating part after oxidation. The gradient, multilayered, and nanocomposite AlTi(X)N show significantly improvement of the lifespan of cutting tools and mechanical parts.

Keywords: Hard coating; Mechanical property; AlTiN; Multicomponent; Multilayer

9:20am **B1-1-ThM5 Investigation of the Influence of the Thickness of Nanolayers in Wear-resistant Layers of Ti-TiN-(Ti,Cr,Al)N Coating on Destruction in the Cutting and Wear of Carbide Cutting Tools***, **Alexey Vereschaka (dr.a.veres@yandex.ru)**, S. Grigoriev,* MSTU Stankin, Russian Federation*; N. Sitnikov,* National Research Nuclear University MEPhI, Russian Federation*; J.I. Bublikov,* Ikti Ran, Russian Federation

The paper presents the results of the investigation into the formation of the nanolayer structure of the Ti-TiN-(Ti,Cr,Al)N coating and its influence on the thickness of coatings, their resistance to fracture in scratch testing, and the wear resistance of coated tools in turning 1045 steel. The structure of the coatings with the nanolayer thicknesses of 302, 160, 70, 53, 38, 24, 16, and 10 nm was studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution (HR) TEM. It is shown that the grain sizes in the nanolayers decrease to certain values with an increase in the thickness of the nanolayers, and then, with a further decrease in the nanolayer thickness, the grain sizes of the nanolayer grow as the interlayer interfaces cease to produce a restraining effect on the growth of the grains. The study found that the nanolayer thickness influenced the wear of carbide cutting tools and the pattern of fracture for the Ti-TiN-(Ti,Cr,Al)N coatings.

9:40am **B1-1-ThM6 Key Importance of the Controlled Reactive HiPIMS for Low-temperature Preparation of Tunable Oxynitrides and Thermochromic Oxides***, **Jaroslav Vlček (vlcek@kfy.zcu.cz)**, J. Houška,* University of West Bohemia, Czech Republic

Reactive high-power impulse magnetron sputtering (HiPIMS) with a feedback pulsed reactive gas (oxygen and nitrogen) flow control and to-substrate reactive gas injection into a high-density plasma in front of the sputtered metal target was used for a low-temperature deposition of highly optically transparent Al-O-N films (substrate temperature of 120 °C) and thermochromic VO_2-based films (substrate temperature of 330 °C) onto unbiased substrates.

A modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, was used to produce high-quality Al-O-N films with a gradually changed elemental composition (from Al_2O_3 in AlN), structure and properties. We give the basic principles of this controlled deposition, maximizing the degree of dissociation of both O_2 and N_2 molecules in a discharge plasma, which leads to a replacement of very different reactivities of the O_2 and N_2 molecules with metal atoms on the surface of growing films by similar (high) reactivities of atomic O and N.

We developed a low-temperature scalable deposition technique for high-performance durable thermochromic $ZrO_2/V_{0.982}W_{0.018}O_2/ZrO_2$ coatings. The $V_{0.982}W_{0.018}O_2$ layers were deposited by controlled HiPIMS of V target, combined with a simultaneous pulsed DC magnetron sputtering of W target (doping of VO_2 by W to reduce the transition temperature to 20-21 °C), in an argon-oxygen gas mixture. The effective pulsed oxygen flow control of the reactive HiPIMS deposition makes it possible to utilize the enhanced energies of the ions bombarding the growing $V_{0.982}W_{0.018}O_2$ layers for the support of the crystallization of the thermochromic phase in them at the low substrate surface temperature of 330 °C and without any substrate bias voltage. We present the basic principles of this controlled deposition.

10:00am **B1-1-ThM7 Dynamic Feedback Control for *In Situ* Process Monitoring and System Optimization in Complex Thin Coatings Manufacturing***, Christopher Metting (cmetting@accustrata.com),* AccuStrata, Inc., USA

Process stabilization and tuning are critical to the viability of large-scale manufacturing of today's thin film coatings. As coating compositions become increasingly complicated, their manufacturing processes become more difficult to control. Legacy monitoring methods such as quartz crystal or direct optical monitoring are limited quality control solutions as they lack sufficient capability to provide real time information for very thin, very thick, compound, gradient and optically opaque films. AtOMS, or Atomic Optical Monitoring System, is a highly customized, *in-situ* monitoring and control method for in-line quality assurance that represents a significant upgrade for optimization of physical vapor deposition processes.

By monitoring atomic flux through the deposition region, AtOMS provides real-time, dynamic feedback process control with information about film thickness, chemical composition, and deposition rate. AtOMs is able to detect and correct for inherent system and long-term process drifts, allowing for better process tuning and more consistent coating quality. This in turn reduces manufacturing wastes and allows for more rapid and cost-effective scaling.

The AtOMS system consists of a hardware box with a hollow cathode lamp and spectrometer with an optical sensor and collector to be mounted to the chamber and connected by fiber optic cables. The cables allow the flexibility to multiplex the system to monitor several elements and chambers simultaneously without significant additional space requirements. Each system is tailored according the unique chamber geometries for each customer. Installation can often be accomplished with minimal engineering modifications and downtime.

This talk will discuss the system's operation, recent experimental results from monitoring of Yttrium, Zirconium and MolySilicide during sputtering deposition, and use cases including protective thermal barrier coatings for aerospace and corrosion-resistant coatings in the energy industry.

10:20am **B1-1-ThM8 On the Synthesis and Characterization of (Ti,Zr)n+1AlCn MAX Phase Coatings using Elemental and Compound Targets***, Clio Azina (clio.azina@liu.se), A. Petruhins, M. Yildizhan, B. Xin, P.O.Å. Persson, J. Rosen, P. Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

$M_{n+1}AX_n$ phases (where n =1, 2, or 3) form a group of inherently nanolaminated carbides and nitrides where M is an early transition metal, A is an A-group element and X is nitrogen or carbon. MAX phases crystallize in hexagonal structures composed of $M_{(n+1)}X_n$ layers interleaved with atomic layers of A-element. Depending on the value of n, the number of $M_{(n+1)}X_n$ layers is different. MAX phases are considered for a variety of applications because of their unique combination of ceramic and metallic properties, which results from their crystal structure and atomic arrangement. In addition to the pure ternary phases, there are numerous synthesized isostructural solid solutions of MAX phases which, by tuning the composition, can have tunable physical properties.

We have investigated the possibility of depositing $(Ti,Zr)_{n+1}AlC_n$ MAX phase coatings on sapphire substrate, using a $(Ti,Zr)_2AlC$ compound target on one part and elemental Ti:Zr, Al, and C targets on the other, through magnetron sputtering. The compound target has resulted in aluminum-containing (Ti,Zr)C carbides after 30 min of deposition. However, 60 min and 90 min of depositions have resulted in MAX-phase containing films, indicating the need of a buffer layer for the growth of the MAX phase.

On the other hand, depositions carried out from elemental targets have resulted in MAX phase-containing films, although the films were not phase pure. Furthermore, depending on deposition conditions, both the $(Ti,Zr)_2AlC$ and the $(Ti,Zr)_3AlC_2$ MAX phases were identified.

10:40am **B1-1-ThM9 Deposition of Crystalline Alumina Thin Films without Substrate Heating by Reactive Magnetron Sputtering***, Fangyuan Gao (fygao516@uwindsor.ca),* University of Windsor, Canada*; G. Li,* Chinese Academy of Sciences, China*; X.Y. Nie,* University of Windsor, Canada*; Y. Xia,* Chinese Academy of Sciences, China

Compared with amorphous alumina films, crystalline alumina films have better mechanical properties and wide-band optical transmission performance, which could be better used for such as high speed cutting tool coatings and infrared window transparent protective films. In order to obtain crystalline alumina films by magnetron sputtering method, it is generally necessary to operate at temperature over 500℃or heat treatment after deposition. Such high temperature environment in the process limits the choice of substrates, and greatly restricts the application scope of alumina film as a multi-functional material. In this paper, alumina thin films were reactively sputter deposited using an unbalance magnetron and intermediate frequency (40 kHz) power supply equipped with a plasma emission monitoring (PEM) feedback system. The intensity of the Al (396-nm) emission line was maintained at a given value (PEM setpoint) by regulating the introduced oxygen flow rate. The application of PEM method eliminated the hysteresis effect, and transferred the aluminum oxidation reaction originally occurring on the target surface to the substrate. As a result, γ-Al_2O_3 thin films with distinct columnar crystal structure were successfully prepared less than 60℃ The influence of PEM setpoints on the chemical composition, deposition rate, microstructure, and mechanical properties of the crystalline alumina thin films were systematically investigated. The analyses revealed that ideal stoichiometric alumina films were obtained when the PEM setpoints reduced to 40% or less. The deposition rate could be achieved as high as that of pure Al film (at 40% setpoint). The results of nanoindentation test also suggested that the hardness and Young's modulus were comparable to those in other literatures for the mechanical properties of crystalline alumina films deposited at 300-500℃ This study thus demonstrates the potential application of PEM system for tailoring the rapid growth of crystalline alumina films without a need of substrate heating.

11:00am **B1-1-ThM10 Microstructural and Biological Behavior of TiAlVN(Ag) Nanocomposite Coatings***, Francisco Giraldo (francisco.giraldom@udea.edu.co), G. Bejarano,* Universidad de Antioquia, Colombia

In the area of biomaterials, surface treatments such as plasma nitriding or deposition of hard coatings by PVD are commonly used in martensitic stainless steel and titanium alloys, among others, due to the need to increase surface hardness, wear resistance, the chemical stability and enhanced biocompatibility of surgical instruments and bone implants. On the other hand, the reduction of the risks of release of undesirable ions from the surface of the substrate that can generate a cytotoxic response in the patient, and the improvement of biocompatibility are other purposes of current research. The content of Ag in the coatings was modified with the power variation applied to the Ag target of 30 W, 45 W, 60 W and 75 W with a fixed bias of -70 V, working pressure of 0.4 Pa and temperature of 200°C. SEM images of the cross-section of the coated samples showed a columnar growth structure, whose columns initially showed a decrease in width for low silver contents and then increase again with higher silver contents. The superficial images exhibited a cauliflower-type topography whose domes increase with the silver content. Additionally, Ag particles are observed on the surface of the coatings and that are located in the grain boundaries and exhibit larger sizes with increasing power applied to the silver target. The surface roughness, determined by AFM, presented an average value of 10 nm for the sample deposited with 30W applied to the Ag target and is increased up to 50 nm for that manufactured with a power of 75W. The X-ray patterns show the peaks (100) and (101) of the α-Ti phase and (110) of the b-Ti phase, as well as the peaks (111) of the TiN and Ti2N. The independent peaks (111) and (200) of the fcc phase of silver are also observed, which suggests that this metal is insoluble in the TiAlVN matrix, as confirmed in the TEM images of the sample deposited with a 60W power supplied to the silver target. Wettability tests show a change in the surface behavior of the coating from hydrophilic to hydrophobic behavior with increased silver content. In vitro tests of the adhesion and inhibition of P. aeruginosa bacteria were carried out. It was found that the deposited coatings with powers of 45 W, 60 W and 75 W present an important bactericidal and bacteriostatic effect against the selected bacteria. The evaluation of cytotoxicity by means of the MTT cell viability test with the Saos-2 osteoblastic cell line (ATCC HTB-85) showed that the samples deposited with 30W, 45W and 60W applied to the silver blank presented a cell viability greater than 80%.

11:20am **B1-1-ThM11 Injection of Pulse Pressure Dependence on Surface Sintering Process – the Origin of W-B-C Films Synthesis in Magnetron Sputtering from a Single Powder Target***, Bartosz Wicher (Bartosz.Wicher.dokt@pw.edu.pl), R. Chodun,* Warsaw University of Technology, Poland*; M. Trzciński,* UTP University of Science and Technology, Poland*; A. Lachowski,* Polish Academy of Sciences, Poland*; K. Nowakowska-Langier,* National Centre for Nuclear Research, Poland*; K. Zdunek,* Warsaw University of Technology, Poland

A three-dimensional (3D) sintering method of bulk magnetron targets has been developed recently. However, the use of bulk target had the following limitations: limited chemical-phase composition, constrained geometry, small size and cost-effectiveness. Thus an unique approach of surface sintering (2D) is elucidated here by a method of electromagnetic discharge evolution without applying a mechanical press. In this method, dependence of pulse pressure oscillations in a range of 25 - 125 Pa is related to theirs absolute flux energy of 87.8 J - 253.5 J and provides a form of well-sintered body within following powder target stoichiometry compositions; WB-C, WB_2-C and WB_4-C, respectively. Among the densified tungsten-boron-carbon targets, mass transport effect is estimated through a thermal diffusivity measurements, giving up to 3.7 mm^2/s for the most pronounced sinter, obtained for 75 Pa injection setup. Surface-consolidated W-B-C targets, that constitute the origin of unconventional vapor source here, are subsequently used in the films synthesis by Gas Injection Magnetron Sputtering (GIMS). Quantitative analysis examined by X-ray photoelectron spectroscopy (XPS) shows, that the films are more or less equally divided into four of a kind elements (18 - 40 at. %), where the W and B concentrations are changed in line with the previously defined stoichiometry's. Chemical bonding state analysis reveals the C-W, B-W, B-O and W-O bonding, respectively. Structural circumstances provided through transmission electron microscopy (HRTEM) presents, that the thermodynamically-metastable WC_{1-x} and/or W_2BC nanoclusters (1 - 3 nm) are dispersed in amorphous carbon host matrix with regards to the identified Raman spectra results (D_{band} ~ 1358 cm^{-1} and G_{band} ~ 1552 cm^{-1}). These suggest, that surface-sintering approach becomes worth of attention particularly due to its simplicity of any material target fabrication. Accordingly, in this work, an application issue of the unique bonds formation within W-B-C films, is emphasized by means of Vickers result (1780 - 2650 HV) as a sensing microhardness feedback.

11:40am **B1-1-ThM12 Sub-critical Hotspots to Quench Rapid Reactions in Sputter Deposited Nanoscale Ni-Al Multilayer Foils**, *I.E. Gunduz,* Naval Postgraduate School, USA*; **Claus Rebholz (claus@ucy.ac.cy)**,* University of Cyprus, Cyprus

Exothermic reactions in sputter deposited multilayer films/foils or powder mixtures of reactive metallic systems such as Nickel (Ni) and Aluminum (Al) can be utilized for joining temperature-sensitive components or for bulk combustion synthesis of intermetallic parts. The application of such heating sources requires a thorough understanding of the reaction steps to enable performance estimation and design under different boundary conditions.

The identification of intermediate reactions in sputter deposited reactive Ni-Al multilayer foils is challenging due to the rapid thermal front velocities of up to 13 m/s and very thin reaction zones estimated to be on the order of 5-20 µm. Here, we present a novel method to quench reactions at rates beyond 10^8 K/s, which are comparable to the self-heating rates in these foils. A thin aluminum wire is used to produce a microscale spark-affected spot on the surface of the foil with an energy below the self-propagation threshold. Upon the application of the spark that lasts approximately 50 ns, the reactions that are initiated are rapidly quenched due to the conductive heat losses to the rest of the foil and stop the conversion of intermediate species. SEM micrographs and TEM analysis using selected area diffraction show a transition zone of 3 µm, where amorphous Al solid solutions, $NiAl_3$, Ni_2Al_3 and NiAl are sequentially formed at the bilayer interfaces. The reactions appear to propagate faster along smoother bilayers, compared to the kinked sections that develop during the sputtering process, forming a fingered reaction front in the thickness direction starting from the ignited spot.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-2-ThM

Properties and Characterization of Hard Coatings and Surfaces II

Moderators: Naureen Ghafoor, Thin Film Physics Division, IFM, Linköping University, Sweden, Marcus Günther, Robert Bosch GmbH, Germany, Fan-Bean Wu, National United University, Taiwan

8:00am **B4-2-ThM1 Structure and Properties of VSiCN Coatings Deposited by Plasma Enhanced Magnetron Sputtering***,* ***Forest Thompson (forest.thompson@sdsmt.edu)**,* South Dakota School of Mines and Technology, USA*; F.M. Kustas,* NanoCoatings, Inc., USA*; K.E. Coulter,* Southwest Research Institute, USA*; G.A. Crawford,* South Dakota School of Mines and Technology, USA

Hard coatings containing vanadium have been studied extensively for use in high-temperature applications due to the desirable tribological properties of various vanadium oxides. However, vanadium-rich coatings in which vanadium nitride (VN) or vanadium carbide (VC) is the majority phase can exhibit poor wear resistance at elevated temperatures due to excessive oxidation. Thus, the ability to control oxidation behavior in vanadium-rich hard coatings through variation of composition and microstructure is of technological interest. Here, we report on VN-based composite coatings deposited by plasma enhanced magnetron sputtering under different reactive gas flow conditions. Microstructural characterization was conducted using atomic force and electron microscopy. Energy dispersive X-ray spectroscopy and X-ray diffraction were used for composition and phase determination, respectively. Coating hardness and indentation modulus were measured using nanoindentation. Relationships among reactive gas flow rate, microstructure, and mechanical properties are identified and potential influences on coating performance in oxidizing conditions are discussed.

8:20am **B4-2-ThM2 Spinodal Decomposition of Reactively Sputtered VAlN Thin Films**, ***Marcus Hans (hans@mch.rwth-aachen.de)**, H. Rueß,* RWTH Aachen University, Germany*; Z. Czigány,* Centre for Energy Research, Hungary*; J. Krause, P. Ondračka, D. Music, S. Evertz, D.M. Holzapfel,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; J.M. Schneider,* RWTH Aachen University, Germany

We investigate the decomposition mechanisms of metastable cubic (c–)$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ thin films, grown by reactive high power pulsed magnetron sputtering, by combination of structural and compositional characterization at the nanometer scale with density functional theory (DFT) calculations. Based on thermodynamic considerations of $d^2G/dx^2 < 0$, spinodal decomposition is expected for c-$V_{1-x}Al_xN$ with $x \geq 0.35$. While no indications for spinodal decomposition are observable from laboratory and synchroton diffraction data after annealing at 1300°C, the formation of wurtzite (w–)AlN is evident after annealing at 900°C by utilizing high energy synchrotron X-ray diffraction. However, the complementary nature of elemental V and Al maps, obtained by energy dispersive X-ray spectroscopy in scanning transmission electron microscopy mode, imply spinodal decomposition of c–$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ into V- and Al-rich cubic nitride phases after annealing at 900°C. These chemical modulations are quantified by atom probe tomography and maximum variations of x in $V_{1-x}Al_xN$ are in the range of 0.36 to 0.50. The magnitude of the compositional modulations is enhanced after annealing at 1100°C as x varies on average between 0.30 and 0.61, while the modulation wavelength remains unchanged at approximately 8 nm. Based on DFT data, the local x variation from 0.30 to 0.61 would cause lattice parameter variations from 4.111 to 4.099 Å. This difference corresponds to a shift of the (200) peak from 44.0 to 44.1°. As the maximum decomposition-induced peak separation magnitude of 0.1° is significantly smaller than the measured full width at half maximum of 0.4°, spinodal decomposition cannot be unravelled by diffraction data. However, consistent with DFT predictions, spinodal decomposition in c–$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ is revealed by chemical composition characterization at the nanometer scale.

8:40am **B4-2-ThM3 Residual Stress Measurement on Coatings by 2D-XRD with Single Sample Tilt***,* ***Bob He (Bob.he@bruker.com)**,* Bruker AXS, Inc., USA, United States of America

Measurement of residual stresses in coatings and thin films by X-ray diffraction is always a challenging task due to weak diffraction signals from the limited diffraction volume, sharp stress or strain gradients, preferred orientations, anisotropic grain shape and the inhomogeneous phase and microstructure distribution. For a given material, the X-ray penetration depth is dependent on the incident angle. The lower the incident angle, the smaller the penetration depth. When residual stresses are measured on a coating or thin film sample, it is preferable to keep a small incident angle to get the most X-ray scattering from the thin film layer. This is very difficult or impossible with the conventional $\sin^2\psi$ method. This presentation introduces a method to accurately measure residual stress of thin films or coatings by two-dimensional X-ray diffraction with a single sample tilt.

In general, high 2θ peaks are preferred for stress measurement due to the more significant 2θ shift and less sensitive to the sample height error. But for thin films and coatings, high 2θ peaks may not be available or appropriate for stress measurement. With low 2θ peaks, it is difficult or even impossible to measure stress with the conventional $\sin^2\psi$ method. The iso-inclination method allows only a limited angular range for the tilt, while the side-inclination method is extremely sensitive to the sample height error. As a result of large angular coverage with a 2D detector, residual stress may be measured with a single tilt angle. The diffraction vector coverage from low 2θ angle diffraction ring can satisfy the stress or stress tensor measurement with single tilt. The single tilt method can avoid the sample height error associated to multiple sample tilt angles, which is especially critical when measuring stress with a low 2θ peak. Another advantage is the consistent depth of penetration due to a constant incident angle, which is beneficiary for thin films or samples with steep stress gradient. Since no tilt change during the data collection and low spherical error of Φ rotation, the stress or stress tensor can be accurately measured with low 2θ diffraction rings. This presentation introduces the single tilt method for stress evaluation with two-dimensional detectors, including experimental examples on coatings.

Reference:

Bob He, *Two-dimensional X-ray Diffraction*, 2nd Edition, John Wiley & Sons, 2018.

9:00am **B4-2-ThM4 Nanoscale Stress and Microstructure Distributions across Scratch Track Cross-Sections in a Brittle-Ductile CrN-Cr Bilayer Film on Steel Revealed by X-ray Nanodiffraction***,* ***Michael Meindlhumer (michael.meindlhumer@unileoben.ac.at),*** Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; J. Todt, Z. Zalesak,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; M. Rosenthal,* ESRF, Grenoble, France*; H. Hruby,* eifeler-Vacotec GmbH, Düsseldorf, Germany*; C. Mitterer,* Montanuniversität Leoben, Leoben, Austria*; R. Daniel,* Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; J. Keckes,* Montanuniversität Leoben, Austria

Nanocrystalline hard films benefit from a combination of extraordinary multifunctional properties, such as high hardness, elastic modulus, thermal stability and wear resistance. Although scratch tests are routinely used to obtain qualitative data on adhesion and abrasion of thin films, it is not trivial to correlate the scratch-test-response of the films with their composition, microstructure and residual stress state. In order to relate the microstructure and residual stress state to elastic-plastic deformation of a CrN/Cr film induced during a scratch test, cross-sectional X-ray nanodiffraction (CSnanoXRD) in transmission geometry and a beam size of 50 nm was applied. The experiment focused on the characterization of a brittle/ductile CrN/Cr bilayer thin film consisting of 1.2 and 2 µm thick CrN and Cr layers, respectively, deposited on a high-speed-steel substrate and loaded at 200 and 400 mN by a diamond sphero-conical indenter with a radius of 5 µm. In order to assess the microstructure variations and stress distributions in the deformed volume, cross-sections of the scratch traces were extracted and subsequently ex-situ probed by CSnanoXRD at the ID13 beamline of the European Synchrotron Radiation Facility in Grenoble, France. Crack patterns in individual layers were characterized by small-angle X-ray scanning microscopy and revealed crack formation in the CrN layer predominantly at the load of 400 mN, which corresponds to the complementary scanning and transmission electron microscopy data. The results further revealed a gradual increase of the compressive stress from ~-3 to -4 GPa from the interface towards the surface of the CrN toplayer and a rather constant stress state of ~-1 GPa within the Cr sublayer in the as-deposited state. On the contrary, complex variations of in-plane stress in the deformed volume were observed in the CrN toplayer reaching magnitudes up to -6 GPa in the near CrN/Cr interface region. The film volume next to the groove of the residual imprint close to the film surface was almost stress free, indicating full stress relaxation of the deformed zone. Within the Cr sublayer, tensile in-plane stress of ~0.5 GPa near the CrN/Cr interface and compressive stress of ~-1.5 GPa near the film/substrate interface were detected. Further insights into the deformation behaviour of the bilayer system during scratching were gained by correlating the experimental results with a finite-element model. In summary, the experiments revealed that the ductile Cr sublayer served as a stabilizing component for the CrN/Cr bilayer structure upon mechanical loading, effectively suppressing catastrophic failure of the otherwise brittle CrN.

9:20am **B4-2-ThM5 Microstructure and Mechanical Investigation of Textured CVD Alumina Coatings***,* *S. Shoja,* ***Olof Bäcke (obacke@chalmers.se),*** Chalmers University of Technology, Sweden*; O. Alm,* Seco Tools AB, Sweden*; L. von Fieandt, S. Norgren,* Sandvik Coromant R&D, Sweden*; M. Halvarsson,* Chalmers University of Technology, Sweden

Most of the cutting tools used today in industry are coated with materials that have high wear resistance. These coatings improve machining properties and prolong the service life of cutting tools. One of the most widely used materials in wear-resistant coatings is alumina, due to its chemical inertness and high wear resistance. Alumina is often combined with other materials, such as TiCN and TiN, in multilayered coatings that are deposited by CVD (chemical vapour deposition). The most frequently used phases of alumina for protective coatings are κ-Al_2O_3 and α-Al_2O_3 and alumina can nowadays be deposited with different textures using different deposition conditions. It is well known that the texture of α-Al_2O_3 has a large impact on the cutting performance of a wear resistant coating. The right choice of texture for an application can improve tool life several times. Despite the importance of texture, the underlying reason for why texture influences the wear properties of α-Al_2O_3 is today poorly understood. Moreover, there is lack of understanding of the main wear mechanisms for α-Al_2O_3 coatings during metal machining.

To gain a better for understanding for the degradation of α-Al_2O_3 coatings, the microstructure and degradation characteristics of as-deposited and worn CVD TiCN/α-Al_2O_3 coatings, with different textures of α-Al_2O_3, have been in investigated using X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and transmission Kikuchi diffraction (TKD). Using these techniques, the microstructure of the as-deposited and worn coatings with different α-Al_2O_3 textures have been compared and the deformation mechanisms of the latter ones investigated.

9:40am **B4-2-ThM6 Effect of Boriding Medium Composition on Microstructure and Mechanical Properties of Borided AISI 4140 Steel***,* ***Luciana Silveira (luciana.llsilveira@gmail.com),*** Pontifícia Universidade Católica do Paraná, Brazil*; A.G.M. Pukasiewicz,* Universidade Tecnológica Federal do Paraná, Brazil*; P. Brum,* Fiven GmbH, Brazil*; R.D. Torres,* Pontificia Universidade Católica do Paraná, Brazil

In this study, three different powder-pack boriding mixture compositions were used for boriding of AISI 4140 steel. The used boron potentials were: 1% B_4C (low), 5% B_4C (intermediate) and 10% B_4C (high). The boriding treatment was carried out at 900 °C for a treatment time of 2 h. The boride layers were characterized by SEM, XRD analysis and hardness testing. The adhesion to the substrate and the cohesive properties of the borided layers were investigated by scratch testing with a progressive load from 1 to 200 N. The boride layers presented saw-tooth morphology, and a single Fe_2B phase layer resulted from the boriding with the low boron potential. The intermediate and high boron potential created polyphase Fe_2B/FeB layers. The average layer thickness of the boride layers increased with boron potential, reaching 39, 52 and 62 µm for the 1% B_4C, 5% B_4C and 10% B_4C samples, respectively. The hardness of the samples decreased from the surface to the substrate, and higher hardness was obtained by the higher boron potential, 1612 $HV_{0.1}$, compared to the low and intermediate samples, which presented hardness values of 1377 $HV_{0.1}$. This suggests that probably the hardest FeB layer did not form homogeneously in the 5% B_4C sample. Thus, 5% B4C sample has similar surface properties to the 1% B_4C sample. The scratch tests of the borided samples led to different cohesive failure mechanisms. It was observed, in all borided specimens, propagation of arc tensile cracks and forward chevron tensile cracks. Chipping appeared at lower applied loads for the 10% B4C sample, indicating a likely detaching of the outermost and most fragile FeB layer.

10:00am **B4-2-ThM7 The Erosion Resistance of Boride Layers on X12CrNiMoV12-3 Stainless Steel***,* ***Adán Ruíz-Ríos (aruizr1403@alumno.ipn.mx),*** Instituto Politécnico Nacional Grupo Ingeniería de Superficies, México*; I.E. Campos-Silva,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico*; A.M. Delgado-Brito, E.J. Hernández-Ramírez, A.D. Contla-Pacheco,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, México

The stainless steel X12CrNiMoV12-3 is widely used in steam generators, turbines, turbine blades and some engineering parts. These components are exposed to erosive wear by solid particles and is becoming an increasingly severe economic problem. One solution is to protect these components with erosion-resistance layers.

In this study, new results about the erosion wear resistance of borided X12CrNiMoV12-3 stainless steel were estimated. A $FeB-Fe_2B$ layer, with ~60 µm of thickness was formed at the surface of the material using the powder-pack boriding process (PPBP) at 1223 K with 6 h of exposure. Before the erosion tests, the boride layers were characterized by the depth-sensing Vickers microindentation technique to determine properties such as hardness, fracture toughness and residual stresses along the depth of the layer-substrate system.

Otherwise, the erosion tests were carried out according to the standard ASTM G76-13 procedure, in which the tests were performed at room temperature and 673 K. The tests were conducted on the X12CrNiMoV12-3 stainless steel (reference material) and borided X12CrNiMoV12-3 stainless steel. Three impact angles of 30°, 60° and 90° and impact speed of 30 m/s were used over the surface of both materials, considering a quartz particle around 50 µm. In addition, the test time was 10 min; the mass loss of both materials was estimated every 2 min using an analytical balance. Finally, the erosion tracks developed on both materials, were analyzed by scanning electron microscopy technique to determinate the failure mechanisms for the overall set of experimental conditions.

According to the overall set experimental conditions, the influence of the hardness of the $FeB-Fe_2B$ layers (22 GPa) increase drastically the erosion resistance at the surface of the stainless steel in comparison to the reference material. At room temperature, and for an impact angle of 90°, the borided X12CrNiMoV12-3 stainless steel showed the higher material loss (2.2 mg), than that of the other impact angles; for the impact angle of 60° the material loss was of 1.5 mg, and for the impact angle of 30° the material loss was ~1.1 mg. In contrast, the erosive tests performed at 673 K, revealed a minimum erosion damage for the borided stainless steel, in which the maximum value of material loss was ~1.7 mg for the impact angle of 90°.

The main failure mechanism developed at the surface of the borided X12CrNiMoV12-3 stainless steel was cracking, resulting in material loss by flaking. Finally, for the entire set of erosion conditions, the reference material showed predominant failure mechanisms such as plastic deformation combined with cut, plowing and pitting.

10:20am **B4-2-ThM8 Combinatorial Approach for the Synthesis of Thermally Stable High Si-containing Nanocomposite AlCrSiN Coatings***,* ***Michal Zítek (michal.zitek@unileoben.ac.at)****, N. Jäger, M. Meindlhumer,* Montanuniversität Leoben, Austria*; F. Nahif,* voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany*; C. Mitterer, R. Daniel,* Montanuniversität Leoben, Austria

High-performance cutting tools are subjected at high cutting speeds to high loads and temperatures typically exceeding 1000 °C. AlCrN alloyed with Si has been shown to be a perspective coating system for protection of cutting tools operating in such harsh industrial environments as it exhibits promising mechanical properties and thermal stability. Especially low Si-containing AlCrN coatings are known for their enhanced mechanical properties as well as improved thermal stability and oxidation resistance due to their nanocomposite structure.

Unlike Si concentrations far below 10 at.% Si, which are frequently reported in literature, the focus of this work is to systematically study arc-evaporated AlCrSiN coatings with a high Si content of about 15 at.%, varying the Al/Cr ratio from 50/50 to 90/10. Elemental composition was controlled by co-evaporation of $(Al_{50}Cr_{50})_{75}Si_{25}$, $(Al_{70}Cr_{30})_{75}Si_{25}$ and $(Al_{90}Cr_{10})_{75}Si_{25}$ cathodes in an industrial-sized deposition system (alpha400P, voestalpine eifeler Vacotec GmbH). This combinatorial approach allowed for a synthesis of coatings with a wide range of elemental composition from $Al_{19}Cr_{21}Si_{16}N_{44}$ to $Al_{30}Cr_5Si_{16}N_{50}$.

XRD measurements revealed that the AlCrSiN coatings display a nanocomposite structure consisting of a mixture of cub-CrN and hex-AlN phases. The observed gradual increase of the Al/Cr ratio led to an increasing compressive residual stress and fraction of softer hex-AlN phase. These two competing mechanisms resulted in hardness of about 25 GPa irrespective of the coating composition, which was preserved even after annealing at 1000 °C in vacuum. That makes this coating system interesting for various high-temperature applications. The thermal stability and oxidation resistance were furthermore studied in detail by differential scanning calorimetry and thermogravimetric analysis in inert atmosphere and in synthetic air to enlighten the origin of the mechanical and structural stability at elevated temperatures. The results show that especially high Si-containing AlCrSiN coatings with Al/Cr ratios higher than 80/20 exhibit excellent oxidation resistance with negligible mass gain up to 1250 °C.

The combinatorial approaches used within this study are powerful in seeking perspective coatings with specific elemental and phase compositions and can be effectively applied also in industrial-sized deposition systems. Moreover, they enable to understand various mechanisms responsible for high thermal stability and oxidation resistance of coatings while combined with modern characterization methods.

10:40am **B4-2-ThM9 Influence of the Period of the Substrate Oscillation on Thin CrN Films Obtained by RF Physical Vapor Dynamic Glancing Angle Deposition technique***,* *M.J.M. Jimenez,* UNICAMP, Brazil, Brasil*; F. Cemin, A. Riul, L.F. Zagonel,* UNICAMP, Brazil*; C.A. Figueroa,* Universidade de Caxias do Sul, Brazil*; D. Wisnivesky,* UNICAMP, Brazil*; **Fernando Alvarez (alvarez@ifi.unicamp.br)**,* Instituo de Física-UNICAMP, Brazil

The control of physical properties of hard coatings, such as micro- and nanostructure, morphology, residual stress, hardness, texture, and crystallite size is mandatory to obtain good performance in applications such as molds, cutting tools, corrosion, and wear resistance. In this paper, we report the results of CrN thin films deposited by *RF Physical Vapor Dynamic Glancing Angle Deposition* (PVDGLAD). In previous works, it was shown that the above-cited physical properties can be tailored by both appropriated selection of the oscillation frequency and the shape of the temporal function moving the substrate in front of the sputtering target. Indeed, due to the back and forward motion of the substrate, a "multilayered" periodic columnar crystalline structure of the *same material* is obtained. The frequency and angular span oscillation ($-85° < \phi(t) < +85°$), where $\phi = 0°$ corresponds to the substrate parallel to the sputtering target, strongly influence on the material properties such as growth rate, crystallite s size, stress, hardness, and texture. This is due to the angular and time dependence of the momentum of the precursors impinging the substrate during deposition. In this paper, we explore the remarkable effects prompted by the substrate oscillations at relatively low periods ($1<T<10$ minutes) on the nano- and micro-structure of the CrN material, as well as its influence on the physical properties on the columnar multi-structured film coatings. A comprehensive study by Scanning Electronic Microscopy, Atomic Force Microscopy, X-Ray Diffraction, nano-hardness, and Photoelectron Emission Spectroscopy was used to draw conclusions about the elastic and plastic deformation resistance properties, the crystallite size on hardness and morphology of the CrN studied samples. Specific details are reported in the Supplementary Information.

Keywords: Hard Coating, Chromium Nitride, Dynamic Glancing Angle Deposition

11:00am **B4-2-ThM10 Composite Iron Matrix Layers Reinforced with TiC Particles Obtained *In situ*by Reactive Coatings***,* ***Łukasz Szymański (lukaszszymanski14@gmail.com)****,* Innerco sp. z .o.o., Poland*; E. Olejnik,* Innerco sp. z .o.o, Poland*; J.J. Sobczak,* AGH University of Science and Technology Krakow, Poland*; N. Sobczak,* Polish Academy of Sciences, Poland*; G. Bruzda,* Łukasiewicz Research Network, Poland*; A. Wójcik,* Polish Academy of Sciences, Poland*; P. Kurtyka,* Pedagogical University of Krakow, Poland*; H. Krawiec,* AGH University of Science and Technology Krakow, Poland

Composite layers on the surface of fabricated details can improve their complex of properties significantly. In order to manufacturing such layers, the techniques with high energy density such as thermal spraying, laser plating, laser alloying or welding methods (TIG - Tungsten Inert Gas) are used. Perspective seems to be the application of casting methods in the techniques of surface engineering. In this paper, authors present the method of fabrication iron matrix composite layers reinforced by TiC particles.

Composite layers were obtained by reactive coatings based on aqueous solutions of carboxymethyl cellulose with addition of powders substrates of the forming reaction of titanium carbide (TiC). Synthesis of phase reinforcement was introducing by covering mold cavity by reactive casting coatings. The temperature of the iron casting alloy was the factor initiating the synthesis reaction of the TiC. During this research, the fragmentation phenomenon of the composite layer which is revealed by a non-uniform structure in the whole length was identified. Undoubtedly, is related to high exothermic reaction of TiC with heat effect at the level near -187 kJ/mol. In order to restrict the fragmentation of the composite layers resulting from the reactive infiltration phenomenon, the addition of a moderator was introduced into the initial powder mixture. Moderator treated as an "internal chilling" changed significantly the crystallization process within the area of the composite layer and decreased enthalpy reaction of TiC carbides. The produced layers are locally of a maximum thickness up to 2 mm. The performed mechanical measurements indicated more than a two-fold increase in the mechanical properties on example of hardness within the composite layer zone as compared to the base alloy. The wear index of composite zones indicated by both *ball on disc*and erosion methods was several times lower compared to the iron matrix. The surface of composite layers was characterized in the view of roughness. Corrosion resistance of composite layers and base alloy were determined with electrochemical method. Novel techniques of high temperature wettability and reactivity testing between TiC substrates and drop of liquid metal has been adopted. This method allowed to conduct online observation and processes during synthesis reaction of phase ceramic.

The production of composite layers using the presented process is characterized by low cost. The spray mold cavity method is fast and does not require specialized equipment, which can be a big plus during implementation in industrial scale.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 1-3 - Session C1-ThM

Optical Materials: Design, Synthesis, Characterization, and Applications

Moderators: Nikolas Podraza, University of Toledo, USA, Juan Antonio Zapien, City University of Hong Kong, Hong Kong

8:00am **C1-ThM1 Metrology for Emerging Semiconductor Devices and Processes***, **Ndubuisi George Orji (ndubuisi.orji@nist.gov)**,* National Institute of Standards and Technology (NIST), USA **INVITED**

As semiconductor device design undergoes a transformation from laterally-aligned to vertically-aligned gates, and from CMOS-based to beyond CMOS-based architectures, the increased number of materials and device-structure complexity pose new challenges for the metrology needed for characterization and process control. Patterning techniques such as extreme ultraviolet (EUV) lithography, which is expected to be the leading-edge high-volume lithography method for the next decade, also pose a host of measurement problems. In addition, new architectures, such as those based on 2D heterostructures, crossbar memristors, and carbon nanotubes have been proposed. Although the metrology and process control tools needed for some of these new architectures are not yet developed, the challenges are well known. These include smaller sizes, hard-to-obtain optical properties, materials and films with low imaging contrast, and atomic scale defects, among others.

This confluence of small dimensions, new materials and processes, and complex structures requires new approaches. This talk will give an overview of key metrology and characterization requirements for emerging semiconductor devices and processes. The goal is to highlight possible solutions and approaches.

One approach is hybrid metrology, which refers to the use of different techniques to determine the value of a parameter. The large number of process-control parameters for new and proposed device structures means that no single instrument has the required level of resolution, range, and sensitivity needed to adequately characterize the material properties and three-dimensional structure of the devices. I will describe some of the benefits of hybrid metrology and show application examples. I will also describe metrology needed for EUV lithography. Feature sizes and tolerances from EUV lithography are now approaching a level where the molecular size of the resist material affects the printability and size variability of the final features. These variabilities, which are stochastic in nature and show up as surface, linewidth and line edge roughness and defects, are in some cases beyond the detection limits of optical inspection tools.

The importance of metrology in semiconductor manufacturing cannot be overstated. This is underscored by the number of processes where the unavailability of adequate metrology could be a potential showstopper. Although some emerging semiconductor devices fall under this category, there are a variety of new and old techniques and approaches that could be helpful in addressing their metrology needs.

8:40am **C1-ThM3 Enhancing Plasmonic Sensing with Nanostructured Thin Films Containing Au Nanoparticles***, **Marco Rodrigues (marcopsr@gmail.com)**, J. Borges, F. Vaz,* University of Minho, Portugal

Localized Surface Plasmon Resonance (LSPR) phenomenon in materials with noble metal nanoparticles is a hot topic due to the unique optical properties of the nanoparticles. Their optical response can be tailored by changing the size, shape and distribution, as well as the refractive index of the surrounding dielectric matrix. If the nanoparticles are embedded in a porous host matrix produced using a GLancing Angle Deposition (GLAD) system, analyte molecules can easily diffuse to the vicinity of the nanoparticles and induce subtle changes in the refractive index. These interactions can be detected in transmittance spectra by monitoring the shape of the LSPR extinction band (T-LSPR) and, therefore, several transduction mechanisms can be used to build T-LSPR sensors. This work combines (i) the preparation of nanostructured plasmonic thin films using GLAD up to an angle of 85º, (ii) sensitivity studies and (iii) LSPR extinction band processing. Refractive index sensitivity studies were conducted in a controlled atmosphere chamber with real-time T-LSPR monitoring. The obtained signals were then processed using an algorithm that analyses changes in several parameters of the LSPR extinction band. The results showed that the films deposited with a higher angle manifested enhanced sensitivities to gaseous atmospheres, thus confirming the possibility of using these nanostructured plasmonic thin films as T-LSPR sensors.

9:00am **C1-ThM4 Chemical Bath Deposition of ZnO Nanorods on Ion-plated ZnO:Ga Seed Layers and Their Structural, Photoluminescence and UV Light Detecting Properties***, **Tomoaki Terasako (terasako.tomoaki.mz@ehime-u.ac.jp)**, S. Obara, N. Hashikuni, S. Namba,* Ehime University, Japan*; M. Yagi,* National Institute of Technology (KOSEN), Kagawa College, Japan*; Y. Furubayashi, T. Yamamoto,* Research Institute, Kochi University of Technology, Japan

Zinc oxide (ZnO) has many excellent properties, such as a wide band gap (E_g) of ~3.37 eV, a large exciton binding energy of ~60 meV, high transparency, piezoelectricity and thermoelectricity. Among various techniques for preparing the ZnO nanostructures, we have paid our attention to chemical bath deposition (CBD) because this technique is usually performed at low temperatures (<100 °C), which allows us to use polymers as substrate materials. In our previous paper, successful CBD growth of vertically aligned ZnO nanorods (NRs) on ion-plated Ga doped ZnO (IP-GZO) seed layers has been reported. Moreover, we reported that the PEDOT:PSS/CBD-ZnO NRs heterostructures exhibited rectifying characteristics in dark and photocurrent under the light illumination [1]. In this paper, structural and PL properties of the NRs and the device performance of the PEDOT:PSS/ZnO NRs/GZO heterostructures will be discussed in terms of the average width of the NRs (W_{av}).

The ZnO NRs layers were grown on the IP-GZO seed layers by CBD using the aqueous solution of 0.05 M $Zn(NH_3)_2{\cdot}6H_2O$ and 0.05 M $C_6H_{12}N_4$. Bath temperature was kept at ~86 °C. The growth time was varied in the range of 5-360 min. The PEDOT:PSS layers were deposited on the NRs layers by spin-coating (3000 rpm, 30 sec), followed by thermal annealing in the air at 80 °C for 20 min.

It was confirmed that the photocurrent was effectively generated by the illumination of the UV light corresponding to the E_g of ZnO, indicating that both the electrons and holes contributed to the photocurrent generation. It was also found that the increase in W_{av} led to the decrease in the barrier height (Φ_B) and the increase in ideality factor (n). The larger the W_{av}, the lower the density of the surface states capturing electrons by forming adsorbed oxygen molecular ions (O_2^-s). Therefore, the band bending at the surface region becomes smaller with the increase in W_{av} [2]. Time response curves for the PEDOT:PSS/CBD-ZnO NRs heterostructures exhibited very long response and recovery times, which cannot be explained without the help of the surface reaction. These results indicate that the adsorption and desorption of the O_2^-s to the surfaces of the NRs dominate the device performance [3].

This work was supported by JSPS KAKENHI Grant Number JP17K04989.

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9:20am **C1-ThM5 Optical Probing of Vanadium Oxide Thin Film Composition and Phase***, M. M. Junda, **Nikolas Podraza (nikolas.podraza@utoledo.edu)**,* University of Toledo, USA

Vanadium oxides have a range of compositions and phases made possible by multiple valence states of vanadium and the high defect tolerance of some phases. Several types of vanadium oxides have found application or are of interest as imaging layers in infrared sensors (VO_x), phase change materials (VO_2), and electrodes for energy storage (V_2O_5). For each application, different optical and electronic characteristics are required which depends strongly upon the chemical composition, crystal structure (if applicable), and amorphous vs. crystalline ordering of the material. Optical property variations with these characteristics are complicated but enable the use of spectroscopic ellipsometry as a diagnostic of film deposition, post-deposition processing, and operational use. Here, infrared to ultraviolet range spectroscopic ellipsometry is performed on vanadium oxide materials to extract the optical response in the form of the complex dielectric function spectra and relate its characteristics to amorphous film composition, crystal phase after annealing, and changes during temperature driven phase transformations. Amorphous VO_x films are deposited via reactive sputtering of a pure vanadium target in an $Ar+O_2$ ambient onto glass substrates at room temperature. Composition is deduced from variations in the amorphous phase complex dielectric functions. Initially amorphous films are then annealed into polycrystalline materials with the phase dictated by starting composition; in two examples room temperature orthorhombic V_2O_5 and monoclinic VO_2 are produced from initially amorphous x = 2.5 and 2.0 VO_x, respectively. VO_2 exhibits temperature-dependent opto-electronic properties resulting from a metal-insulator transition (MIT) at the easily accessible temperature of ~67ºC from the rutile phase at high temperatures to the monoclinic phase at room temperature. Taking advantage of this switching capability, VO_2 is used for infrared imaging, thermochromic infrared-selective filtering in windows, and has shown potential to be useful in memory and transistor computing electronics. *In situ* SE measurements of VO_2 films are collected as a function of temperature over the infrared to the ultraviolet (0.08 – 5.9 eV) spectral range. In addition to determining the optical response of the metallic and semiconducting VO_2 phases, incremental changes in the complex optical response are tracked as VO_2 is cycled through the MIT.

9:40am **C1-ThM6 ZnO/SnS_2 Composites for Tunable UV and Blue Light Shielding Properties***, **Shih-Ming Tseng (anniezeng1111@gmail.com)**, S.B. Brahma,* National Cheng Kung University (NCKU), Taiwan*; H.H. Lu,* National Chin-Yi University of Technology, Taiwan*; J.L. Huang,* National Cheng Kung University (NCKU), Taiwan

We successifully synthesize ZnO/SnS_2 composites to be used as a filter that shield both UV and blue light. Using hydrothermal method to produce SnS_2, and ZnO has been synthesized by simple precipitation process, ZnO/SnS_2 composites process is adding SnS_2 into ZnO precursor with the precipitation process. These samples are well dispersed in the glass cement and curing agent then curing at 200℃30 minutes to form the transparent flakes. Compare to ZnO, which can only absorb a portion of UV light, these transparent flakes appear the absorb spectrum over the wavelength range of UV and blue light, and the absorption range can be tunable by adjusting Zn/Sn molar ratio. These ZnO/ SnS_2 composites can be used as the UV and blue light shielding materials in the optical applications. Moreover, they are also low toxicity and low cost.

Keywords：ZnO/SnS_2 composites、transparent flakes、tunable UV and blue light shielding

10:00am **C1-ThM7 Upconversion of Core–shell-nanoparticles on Diatom as Micro-Optical Trapping Device***, **Yen-Hsun Su (yhsu@mail.ncku.edu.tw)**, Ting Wei Shen, K.B Lin,* National Cheng Kung University (NCKU), Taiwan

In this research, we fabricate the gold nanoparticles by bottom-up procedure. The gold nanoparticles are fabricated onto the functionalized diatom frustules by self-assemble process. And describing the influence of gold nanoparticle on diatom frustules both experimental and simulating. Ultrathin-thickness single-junction Si-based solar cells can be developed to enhance photoelectric conversion efficiency (PECE) approaching to Shockley–Queisser limit. Loss of short circuit current is a crucial factor that dramatically affects PECE improvement. An upconversion materials is fabricated on the sustainable micro-optical trapping device . Using a systematic procedure, a high upconversion performance core–shell-nanoparticles (CSNPs) structure is synthesized. Accordingly, silica diatom microporous frustule is a good electromagnetic field localization chamber, upon which CSNPs are embedded through a microassemble synthesis. Using a systematic procedure, a high upconversion performance core–shell-nanoparticles (CSNPs) structure is synthesized. Accordingly, silica diatom microporous frustule is a good electromagnetic field localization chamber, upon which CSNPs are embedded through a microassemble synthesis. The upconversion optical field density by surface plasmon resonance of Au nanoparticle's enhancement can be increased five-time greater than that of $NaYF_4$ without SiO_2 coating.

10:20am **C1-ThM8 Measurement of Feature Dimension and Shape for Nanowire Test Structures Using Mueller Matrix Spectroscopic Ellipsometry based Scatterometry and Small Angle X-Ray Scattering***, **Alain C. Diebold (adiebold@sunypoly.edu)**,* SUNY Polytechnic Institute Albany, USA **INVITED**

One of the most difficult measurement challenges is non-destructively determining the feature dimensions and shape for complicated 3D structures. An interesting and challenging example structure is the Nanowire Test Structure which is used to develop etch processes which produce vertically stacked nanowires from a multi-layer film stack of Si/SixGe1-x/Si/SixGe1-x/Si .(1, 2, 3) This presentation will review Mueller Matrix Spectroscopic Ellipsometry based scatterometry which uses the Rigorous Coupled Wave Approximation (RCWA) to solve Maxwell's equations for a model structure and the resulting Mueller Matrix elements are compared to experimental results. We also present the use of critical dimension –small angle X-ray scattering characterization. This method uses high energy synchrotron X-Ray scattering to obtain diffraction results from the same periodic array used for scatterometry.

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Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E2-1-ThM

Mechanical Properties and Adhesion I

Moderators: Megan J. Cordill, Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria, Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, Ming-Tzer Lin, National Chung Hsing University, Taiwan

8:00am **E2-1-ThM1 Effect of Residual Stress on the Mechanical Properties of Nitride-Based Protective Coatings Deposited by Pulsed-Plasma Sputtering Techniques***, **Etienne Bousser (etienne.bousser@polymtl.ca)**, E. Herrera-Jimenez, L. Martinu, J.E. Klemberg-Sapieha,* Polytechnique Montreal, Canada

Materials exposed to harsh environments face ever increasing economic, technological and, environmental challenges. The field of coatings and surface engineering technologies has thus been very active, addressing numerous challenges related to the stringent requirements of high-performance protective coating (PC) systems. Despite the progress in PC fabrication processes and coating architectures, the acceptance and further advances in this area are frequently limited by high residual stress (RS) in the coating systems, primarily related to the lack of fundamental and comprehensive knowledge of the stress generating mechanisms, their complex relation to the microstructure, and the availability of pathways to compensate it, and even to include it in the design.

Solid Particle Erosion (SPE) occurs in situations where hard solid particles present in the environment are entrained in a fluid stream, and impact component surfaces. Since the performance of surfaces against SPE is determined by mechanical properties such as hardness, toughness and coating adhesion, hard nitride-based PC are often used in such harsh environments. In this study, we will present our work on improving the understanding of the effects of RS amplitude and distribution on the mechanical properties of hard nitride-based PC deposited using pulsed-DC and High Power Impulse Magnetron Sputtering onto aerospace alloy substrates (Ti-6Al-4V and SS410).

First, we investigated the effect of three different interface treatments on the microstructure and mechanical properties of TiN coatings. We show that the interface treatments induce RS at depths of several microns within the substrate and microstructural changes to the substrate material significantly affecting the microstructure, mechanical properties and adhesion of the overlying coating. Moreover, we also show the effect of RS on the measurement of coating toughness using conventional indentation methods. The effect of coating composition and deposition process will be discussed with respect to RS and the measured toughness values. The microstructural characterization was done using Transmission Electron

Microscopy, Transmission Kikuchi Diffraction and X-Ray Diffraction (XRD). The RS depth profiles were measured using the multireflection grazing incidence XRD method and Focused Ion Beam (FIB) micro-hole drilling. Finally, the coating mechanical properties were measured by depth-sensing indentation and micro-scratch testing while the toughness was also evaluated using Scanning Electron Microscopy with *in situ* mechanical characterization of micro-machined samples produced by FIB.

8:20am **E2-1-ThM2 Influence of polyamide type film former and alkoxysilane association on the surface and adhesion properties of PA 6-6/Glass***, **Nour Halawani (nourhalawani88@gmail.com)**,* Solvay R&I Lyon, France*; O. Gain, Y. Gabet, S. Al Akhrass,* Université de Lyon, France*; L. Trouillet-Fonti,* Solvay R&I Lyon, France*; E. Espuche,* Université de Lyon, France

Sizing formulations, used to improve interfacial properties in glass fiber-based composites are generally composed of two main components: an alkoxysilane and a film former. In this work the influence of using these components separately and in association was investigated on PA 6-6/glass interfacial properties. For this purpose, two different alkoxysilanes: (3-Aminopropyl)triethoxysilane (A) and (3-Glycidyloxypropyl)trimethoxysilane (G) and a polyamide copolymer type film former (cPA) were used. Moreover, the influence of the final temperature in the coating process was investigated. Increasing the setting temperature from 110°C to 150°C did not provide significant surface properties modifications with the use of alkoxysilanes only, as observed by contact angles and AFM, but had an important effect on alkoxysilane condensation at the glass surface, leading to improve glass/PA 6-6 adhesion. The critical importance of the setting temperature of the coating was also evidenced for cPA: a homogeneous surface was obtained for this coating after heating at 110°C, whereas the formation of finger-like surface morphologies was evidenced after heating at 150°C due to partial dewetting. Using both cPA and alkoxysilane allowed to avoid dewetting process due to the specific location of alkoxysilane species at the glass surface. For these cPA/alkoxysilane sizings used with 150°C as final temperature of the coating process, the formation of a highly condensed alkoxysilane layer at the glass surface, combined with an interpenetrated interphase between the alkoxysilane network, the film former and the matrix, led to particularly interesting adhesion properties.

8:40am **E2-1-ThM3 Molecular Dynamics Investigation of Adhesion Between MoS2 coated AFM tips***, **J. David Schall (jschall@ncat.edu)**, S.R. Toom,* North Carolina Agricultural and Technical State University, USA*; T. Sato, R.W. Carpick,* University of Pennsylvania, USA*; Y.R. Jeng,* Changcung University of Science and Technology, Taiwan*; N.R. Glavin,* Air Force Research Laboratory, USA*; C. Muratore,* University of Dayton and Air Force Research Laboratory, USA

Van der Waals (vdW) materials such as MoS_2 have been proposed as release layers in the crucial transfer process in manufacturing flexible electronics devices as well as candidates for the active materials in the flexible devices themselves. Fundamental studies of the adhesion mechanics of these materials (how they stick together and separate) are needed as the growth, processing, and functioning of such devices at high strains all hinge on their adhesive and mechanical properties. A collaboration with the Air Force Research Laboratory Materials and Manufacturing Directorate and University of Pennsylvania has recently succeeded in producing MoS_2-coated AFM probes; allowing adhesion between MoS_2-MoS_2 interfaces to be probed experimentally in an in situ transmission electron microscope (TEM)-based atomic force microscope (AFM). In this talk we will present results from supporting molecular dynamics (MD) simulations of adhesion between two MoS_2 coated Si AFM tips. The MD simulations were designed to optimally match the in situ TEM-based AFM experiments in terms of tip size, number of layers, layer orientation, and other effects. We observe significant differences in adhesion when making contact at different points on the tip and with different tip orientations, which may have important ramifications in device design when utilizing vdW materials.

9:00am **E2-1-ThM4 Controlled Spalling of Microscale, Single-Crystal Films of High-Quality, High-Value Semiconductors***, **Corinne Packard (cpackard@mines.edu)**,* Colorado School of Mines, USA **INVITED**

Controlled spalling is a method to produce thin, continuous single-crystal films at semiconductor wafer scale. A stressed material with excellent adhesion to the wafer transmits forces sufficient to propagate a near-surface fracture in the crystal, resulting in the removal of a microscale-thickness, single-crystal film and leaving the remainder of the wafer intact. This talk illustrates the impact of nickel stressor film and laminate processing conditions on spall depth and fracture surface morphology, using germanium and gallium arsenide wafers as example high-value semiconductors. Fracture surfaces exhibit various features across nanometer- to centimeter-lengthscales; their morphology is characterized and cross-correlated to local optoelectrical performance in testbed photovoltaic cells.

9:40am **E2-1-ThM6 Thin-film Adhesion: A Comparative Study Between Colored Picosecond Acoustics and the Stressed Overlayer technique***, **Arnaud Devos (arnaud.devos@isen.fr)**,* Iemn, Umr Cnrs, France*; M.J. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Thin-film adhesion is a main issue for a broad range of industrial applications due to the crucial role it plays for final device reliability. Adhesion of thin films can be easily checked with qualitative methods like tape test. In a very efficient manner one can compare the adhesion of different samples. But to identify which interface is the most critical from the adhesion point of view, more sophisticated methods are needed.

One way of measuring quantitatively the adhesion energy is to analyze the geometry of buckles that appear either spontaneously or by adding a stressed overlayer following the pionneer work of Hutchinson and Suo[1].

Alternatively, acoustic waves can be used to probe adhesion at a buried interface through an analysis of their reflection coefficient. To do acoustic measurement at the sub-micronic scale, one needs ultra-high frequency waves typically in the range of a few 10 to a few 100 GHz. Colored Picosecond Acoustics (APiC) is a technique that implements an acoustic pulse-echo technique at the nanoscale using a tunable ultrafast laser. The laser directly excites an acoustic pulse in the sample where it propagates at sound velocity. When such a pulse reaches an interface a part is reflected and a second laser is used to detect optically the returning echo. Such hypersonic waves can be used first to measure the acoustic time-of-flight in each layer of a stack. That gives informations about film thickness or elasticity. They can also be used to detect adhesion defect at an interface [2].

In this paper, the two techniques are compared by applying both of them to the same set of samples. Resolution and their respective capabilities to identify the critical interface and quantify the adhesion energy will be discussed.

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[2] A. Devos, Ultrasonics 56, pp. 90-97 (2015) DOI 10.1016/j.ultras.2014.02.009

10:00am **E2-1-ThM7 Hyperelasticity and Viscoelasticity in Thin Organic Semiconductor Coatings***, **Steve Bull (steve.bull@ncl.ac.uk)**,* Newcastle University, United Kingdom of Great Britain and Northern Ireland*; A. Yadav, H. Gonabadi,* Newcastle University

A wide range of organic semiconductor coatings have been developed for optical and electronic applications and have been extensively characterised for their electronic and optical properties. What mechanical measurements have been made are focused on assessing the average properties of a film (e.g. using buckling to assess elastic moduli) but are not suitable to assess point-to-point variation in mechanical response which may be related to changes in coating microstructure due to crystallisation and/or phase separation or to understand the deformation mechanisms occurring. The assessment of non-linear elasticity and time-dependent mechanical response is also lacking. This presentation will address the strain and time-dependent mechanical properties of 100-300nm thin films of a range of organic semiconductors on a glass substrate using nanoindentation at very low loads (peak loads less than 50µN) with a relatively blunt indenter (500nm tip radius). Although a well-defined indentation is produced in many cases it is not clear that plastic deformation occurs (and by what mechanism) but viscoelastic deformation is significant in making the observed indent. The use of load and displacement control during a hold period to determine the relaxation modulus for very thin films will be discussed. Finite element modelling of the load-displacement curves reveals that including both viscoelasticity and hyperelasticity (rather than simple linear elasticity) is necessary to explain the measured load-displacement curves in for several different organic semiconductor materials.

10:20am **E2-1-ThM8 Effect of Functionally Graded Layers on the Stress Relief of TiZrN Coating on Silicon Substrate**, ***Matthew Wei-Jun Liu (matthew111195@gmail.com)***, *J.-H. Huang (jhhuang@ess.nthu.edu.tw),* National Tsing Hua University, Taiwan

Residual stress is usually generated in hard coatings deposited by physical vapor deposition methods. A common technique to alleviate the residual stress is by introducing a metal interlayer between the coating and the substrate. Owing to its suitable mechanical properties and good adhesion, Ti has become a popular choice for the interlayer material. In a previous study [1], we proposed a physical model to explain the mechanism of stress relief from the perspective of plastic deformation of Ti interlayer. To further improve the tribological properties of hard coatings, functionally graded materials (FGMs) was introduced in the hard coating as a transition layer. FGMs are known for enhancing the overall mechanical properties of two joining materials, because the continuous change in FGMs can compensate for the abrupt structural and compositional mismatch between the two different materials. However, the underlying stress-relief mechanism of the functionally graded layers has not been fully explored. This study aimed to further understand the stress relief mechanism in the Ti/TiZr/TiN/TiZrN coatings where a TiN transitional layer along with a Ti/TiZr bi-metal interlayer were introduced, and to investigate the effect of the Ti/TiZr/TiN functionally graded layer on the mechanical properties of the TiZrN coatings. Ti/TiZr/TiN/TiZrN coatings with various TiN layer thickness were deposited on Si (100) substrate by unbalanced magnetron sputtering. The residual stress of each layer was measured and evaluated by the average X-ray strain combined with nanoindentation methods [2,3]. $Ti_{0.15}Zr_{0.85}N$ was chosen for the composition of the top coating, in order to better differentiate the X-ray diffraction peaks of TiN and TiZrN, and thus obtain more reliable residual stress values. A physical model based on the previous coating/interlayer bilayer model was developed for understanding the stress-relief mechanism.

REFERENCES

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[3] A.-N. Wang, C.-P. Chuang, G.-P. Yu, J.-H. Huang, Surf. Coat. Technol., 262 (2015) 40.

10:40am **E2-1-ThM9 Comparing the Residual Stress Gradient Measurement of ZrN using FIB-DIC and Xray Diffraction**, *W-Y. Lin, Y.-C. Chou,* National Chung Hsing University, Taiwan*; J.-H. Huang,* National Tsing Hua University, Taiwan*;* ***Ming-Tzer Lin (mingtlin@nchu.edu.tw),*** National Chung Hsing University, Taiwan

Reliable measurement and modeling of residual stresses at the micrometer scale is a great challenging task for small scale structures and nanostructured thin films. Moreover, the specific location on micro scale evaluation of residual stress gradients is a very critical issue in the hard coating of thin films. The analysis of the residual strain depth profiles requires detailed knowledge of the in-depth lattice strain function, so the residual stress profile calculation can be carried out in a manner that takes into account the mechanical anisotropy and texture of the materials. The development of a microstructure independent procedure for depth resolved measurement of residual stress is an issue of strategic interest. Here, we perform a digital correlation (DIC) of the specimen images acquired by incremental focused ion beam (FIB) ring-core drilling with various depth steps. 2 um thick sputtered ZrN thin films deposited on the silicon substrate were used for this measurement. To observe the depth resolved residual stress profiles of each step on thin film samples, two FIB images of the specimen, one before and one after being drilled, were processed to extract the surface deformation from tiny changes in the FIB images using DIC. This combined with high-resolution in situ SEM imaging of the relaxing surface and a full field strain analysis by digital image correlation (DIC). A parallel residual stress measurement was also performed using both wafer curvature and a four-circle diffractometer with grazing incidence X-ray diffraction (XRD) cos^2asin^2j method at several azimuthal angles to obtain the average X-ray strain (AXS). The stress gradient of ZrN films along the X and Y-axis of the wafer were revealed and compared to evaluate the stress gradient of ZrN deposition.

11:00am **E2-1-ThM10 Effect of Si Addition to DLC on the Sliding Interface Structure between the DLC-Coated Disk and Bearing Steel Ball Slid under Dry Condition in Ambient Air**, *T. Ikeda,* ***Hiroyuki Kousaka (kousaka@gifu-u.ac.jp),*** *T. Nakano,* Gifu University, Japan*; I. Tanaka,* University of Hyogo, Japan

We investigated the effect of Si addition to DLC (Diamond-Like Carbon) on the sliding interface structure between the DLC-coated disk and bearing steel (SUJ2, JIS) ball slid under dry condition in ambient air. Hydrogenated DLCs with a-C:H and a-c:H:Si structure were deposited on mirror-polished steel disks (SUJ2, JIS) by using plasma CVD, where about 5 at% silicon is included into a-c:H: si structure. Sliding tests were conducted by using pin-on-disk type friction tester at relative humidity from 10 to 50 %. For a-C:H:Si films, all the friction test showed stable friction coefficients around μ=0.05-0.1 after running-in, where the contact point of mating ball was covered by a lot of Si and O atoms. On the other hand, for a-C:H films, all the friction test showed stable friction coefficients around 0.2-0.5 after running-in, where the contact point of mating ball was covered by a lot of O atoms. 2D image of the O-covered surface obtained by SEM-EDS observation suggested that the O atoms therein is bonded to Fe atoms to form ion-oxide layer on the contact point of mating ball. These results suggested that the Si addition to DLC prevents the formation of ion-oxide layer on the contact point of mating steel ball to achieve the resultant low-friction around μ=0.05-0.1. For confirming the hypothesis, we conducted further friction test between a-C:H film and a mating steel ball made with stainless-steel (SUS440, JIS) which is expected to suppress the formation of ion-oxide layer on the contact point of the ball. Sliding test was conducted by using pin-on-disk type friction tester at relative humidity of 10 %., showing that the stable friction coefficients around 0.08 is achieved by changing steel ball from bearing steel to stainless-steel. 2D image of the contact-point of the mating ball obtained by SEM-EDS observation clearly indicated that the existence of O atoms therein can not be confirmed.

11:20am **E2-1-ThM11 Structural, Nanomechanical and Tribological Properties of Manganese Phosphate Coatings**, ***Esteban Broitman (esteban.daniel.broitman@skf.com)***, *I. Nedelcu,* SKF Research & Technology Development Center, Netherlands*; T. von Schleinitz,* SKF Research & Technology Development Center, Germany

Manganese Phosphate (MnPh) coatings are nowadays being used in rolling bearings applications due to their advantages such as wear resistance, corrosion resistance, improved fatigue life, and anti-fretting performance. There has been extensive research on their preparation methods, however, there is only one publication describing their nanoindentation hardness, and nothing is known about their elastic modulus.

In this work, MnPh coatings with a thickness of about 5 µm were deposited by a chemical conversion process. AISI 52100 steel substrates were placed in a phosphoric acid bath, where an acid-metal reaction took place locally depleting the hydronium (H_3O^+) ions, raising the pH, and causing a manganese phosphate dissolved salt to fall out of the solution and be precipitated onto the steel surface. Among the many possible grain size settings, a variant with 5-10 µm was chosen to do the measurements as the small grain sizes deliver more repeatable measurement results. Analysis of the surface microstructure and composition of the coatings by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Electron Dispersion Spectroscopy has revealed a polycrystalline coating with prismatic-shaped crystals, and about 20% content of Mn. The nanomechanical properties, studied by nanoindentation, exhibit a surface with hardness H_{IT} ~ 1 GPa and Young's modulus E_{IT} ~ 50 GPa. A method was develop to draw H_{IT} and E_{IT} maps correlated to their SEM morphology. A Mini-Traction Machine (MTM) was used in a ball-on-disc configuration to assess wear performance under severe boundary lubrication conditions. After tribological testing, XRD and SEM analysis has shown that the crystallinity of the original structure in the contact area strongly deteriorated due to the severe deformation of the original grains, while the hardness and elastic modulus inside the wear track increased to H_{IT} ~ 7.5 GPa and E_{IT} ~ 225 GPa, respectively.

11:40am **E2-1-ThM12 Effect of Substrate on the Evolving Mechanical and Tribological Behavior of a Superhydrophobic Silane Thin Film**, ***Akinsanya Baruwa (darebaruwa@gmail.com)***, *E.T. Akinlabi,* University of Johannesburg, South Africa*; P. Oladijo,* Botswana International University of Science and Technology, Botswana*; J. Dutta-Majumdar,* Indian Institute of Technology Kharagpur, India

A superhydrophobic silane compound was deposited on mild steel, stainless steel, and titanium substrates via atomic layer deposition (ALD) method for evolving properties comparison and determination of the influence of substrates' chemical compositions on films properties. The substrates were pretreated by oxidizing the surface using an organic precursor before silanization. The chemical characterizations were conducted using low-angle X-ray diffraction and Atomic total reflection Fourier transformed infrared. The evolving mechanical property was investigated through nanoindentation, nanoscratch, and water contact angle while the morphologies were examined through A field emission scanning electron microscope. The morphological data revealed that silane film on stainless steel is denser and discreetly clustered when compared to other substrates while the coating on the mild steel substrate looks smoother. Young's modulus and the hardness of the silane coating on the stainless-steel values were better than the mild steel and titanium respectively. The scratch test showed better adherence of the silane film to the stainless steel when compared to the mild steel and titanium. The mechanical and chemical investigations indicated that the responses from the silane-pretreatment-substrate composites pose the film to be very effective on the stainless steel. Therefore, a superhydrophobic coating that can align good mechanical response with stable chemical properties at the nanoscale could be possible.

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F2-1-ThM

High Entropy and Other Multi-principal-element Materials I

Moderators: Diederik Depla, Ghent University, Belgium, Ulf Jansson, Uppsala University, Sweden, Erik Lewin, Uppsala University, Sweden

8:00am **F2-1-ThM1 High-Entropy Ceramic Thin Films; A Case Study of Nitrides, Oxides and Diborides**, ***Paul Heinz Mayrhofer (paul.mayrhofer@tuwien.ac.at)***, *A. Kirnbauer, R. Hahn,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany **INVITED**

High-entropy materials often outperform their lower-entropy relatives in various aspects, such as thermal stability and fracture toughness. While there are extensive research activities in the field of high-entropy alloys, comparably little is performed for high-entropy ceramics. Here we show, that especially with physical vapor deposition the development of single-phased high-entropy ceramics is straight-forward. Or, are we just lucky? On the definition-basis for high entropy alloys, we use the term "high-entropy" for our nitrides, oxides and borides if at least five corresponding binaries constitute them, and the configurational entropy (per formula unit) amounts to at least 1.5R.

All high-entropy ceramic thin films investigated, outperform their commonly-used binary or ternary constituents in thermal stability and thermomechanical properties.

High-entropy nitrides, sputtered from equimolar powder-metallurgically-prepared targets, are single-phase fcc-structured with a hardness H comparable to those of the constituting binaries and ternaries, but considerably lower indentation moduli E. For example, H = 33 and 31 GPa with E = 450 and 433 GPa for (Hf,Ta,Ti,V,Zr)N and (Al,Ta,Ti,V,Zr)N; while H = 36 GPa with E = 520 GPa for (Ti,Zr)N. But even after vacuum-annealing at 1300 °C, the (Hf,Ta,Ti,V,Zr)N still showed 28 GPa of hardness and no clustering of atoms or indications for decomposition processes (based on atom probe tomography APT and XRD studies). Alloying with ~5 at% Si substantially increased their oxidation and failure resistance.

High-entropy (Al,Cr,Nb,Ta,Ti)-oxides always crystallized in single-phase rutile structure independent on the O_2-to-Ar flow-rate-ratio used (0.4–4; p = 0.4 Pa) during sputtering a metallic equimolar target. Thereby, simply R decreased from 33 to 20 nm/min, H increased from 22 to 24 GPa and E increased from 380 to 410 GPa. Vacuum annealing at 1200 °C solely led to a change of their nearly random crystal orientation towards a highly 101-texture.

The hardness of our as-deposited high-entropy $(Hf,Ti,Ta,V,Zr)B_2$ and $(Hf,Ta,V,W,Zr)B_2$ diborides (non-reactively sputtered from corresponding targets) is very high with 47 and 46 GPa, combined with E of 550 and 610 GPa. Even after vacuum-annealing at 1300 °C, the still single-phased $(Hf,Ta,V,W,Zr)B_2$ exhibits 45 GPa hardness and no indications for recovery and decomposition. Contrary, the ternary $(Ti,Zr)B_2$ already "softened" to 40 GPa upon annealing at 1100 °C.

These results confirm the beneficial effects of high-entropy also for ceramics, especially with respect to the three core-effects, severe lattice distortion, sluggish diffusion, and formation of single-phased crystalline solids.

8:40am **F2-1-ThM3 High Entropy alloy TiZrHfMoW Coatings: Effect of Ti Content on its Microstructure and Mechanical and Tribological Behaviour**, ***Rumana Akhter (r.akhter@student.unsw.edu.au)***, University of New South Wales, Australia*; Z.F. Zhou,* City University of Hong Kong, Hong Kong*; Z.H. Xie,* University of Adelaide, Australia*; P. Munroe,* University of New South Wales, Australia

High entropy alloys (HEAs) have recently attracted considerable attention in the pursuit of high-performance structural materials. In bulk form, these alloys exhibit many attractive physical and mechanical properties. More recently, these alloys have begun to be investigated in the form of thin film coatings. In this study, the relationships between composition, microstructure and mechanical properties were interrogated for TiZrHfMoW coatings. A series of TiZrHfMoW coatings, with variations in coating composition, were deposited onto Ti-6Al-4V substrates using the double cathode glow discharge plasma technique. The phase compositions, microstructure, mechanical, and tribological properties of the as-prepared coatings were characterised by XRD, AFM, TEM/EDS, FIB, SEM, as well as indentation, scratch and wear tests. The coatings were found to be a mixture of bcc and hcp phases. TEM analysis demonstrated that the coatings consisted of fine grains (~ 5 nm in diameter) containing a high density of nanoscale pores. Very high hardness values ranging from ~21 GPa to ~28 GPa was determined in these coatings. The wear tests against a ruby counterface revealed that coating with lower Ti content possessed better wear resistance than with a higher Ti content despite the fact that the coating with higher Ti content had higher H/E^* and H^3/E^{*2} values. It is believed that the evolution of the mechanical and tribological properties is governed by both the composition and microstructure of the coatings.

9:00am **F2-1-ThM4 Surface Characteristics of $Ni_2FeCoCrAl_x$ High Entropy Alloys under Atmospheric Pressure Plasma Treatment**, ***Chi-Ruei Huang (zx8110256zx@gmail.com)***, *F.B. Wu,* National United University, Taiwan

High entropy alloys, HEAs, has been developed with outstanding performance in mechanical properties, thermal stability, sluggishness in diffusion, anti-sticking, corrosion resistance. Atmospheric pressure plasma, APP, is a surface treatment technology that can be used for surface modification, surface cleaning, adhesion enhancement, etc. APP exhibits merits of less treatment time, variety in material and lower production costs, so it is widely used in various fields. However, the knowledge of the evolution of microstructure and surface characteristics of HEAs under treatments through APP was limited. In this work, $Ni_2FeCoCrAl_x$ HEAs is treated with APP under treatment parameter for input power ranged from 700 to 1100 W with a plasma jet gas (N_2 + O_2) of 35 to 50 slm at a working distance of 21 to 25 mm. Stainless steel, copper, and carbon steel are also treated for reference. Properties and diffusion characteristics on these alloys surface were investigated. The surface properties, oxide film thickness, Rockwell hardness, and tribological behavior of HEAs and various other materials are studied. The variation in properties is explained in terms of crystal structure, composition distribution, and surface characteristics.

9:20am **F2-1-ThM5 Structural Properties of AlSiTaTiZr Multicomponent Metallic and Nitride Thin Film Alloys**, ***Felipe Cemin (lipecemin@gmail.com)***, UNICAMP, Brazil*; M.J.M. Jimenez,* UNICAMP, Brazil, Brasil*; L.M. Leidens,* Universidade de Caxias do Sul, Brazil*; R.B. Merlo,* UNICAMP, Brazil*; C.A. Figueroa,* Universidade de Caxias do Sul, Brazil*; F. Alvarez,* UNICAMP, Brazil

The increasing demand for advanced materials combining unique and unusual properties has encouraged the study of new multicomponent alloys. High entropy alloys (HEA) were originally designed as simple solid-solution structures composed of at least five principal elements (3d transition metals) in near-equiatomic composition, yielding exceptional mechanical properties. In recent years, the field has grown to include refractory and noble metals as well as low-density elements. Moreover, these alloys now include intermetallic phases, ceramic compounds, thin films, architected microlattices, *etc*. When considering HEA thin layers composed by functional elements such as Ti, W, and Zr, the as-deposited product is often amorphous (or nanocrystalline), due to the relatively large atomic size difference (resulting in sluggish diffusion) and 'rapid quenching' effect in sputtering deposition, prompting glassy metal formation. With the addition of nitrogen, a solid-solution could be formed based on the involved binary nitride compounds.

In the pursuit of understanding these new materials, we have investigated key parameters leading to film crystallization and phase formation in an AlSiTaTiZr multicomponent system. Therefore, metallic and nitride films were grown by radio-frequency magnetron sputtering with different deposition conditions, *e.g.*, substrate temperature, bias voltage, angle of deposition, and nitrogen concentration, with the goal to tune adatom diffusivity, grain nucleation, and ultimately the microstructure and properties of the films. Although the deposition method is essentially controlled by kinetic factors, thermodynamic calculations can help to predict possible phase formation. Therefore, thermodynamic simulations using the Calphad method were employed in post-annealed samples. The chemical composition of the films was controlled by proper designing of a sectioned, circular target containing slices ("pizza shaped target") of different elements. This approach differs from most of strategies using powder targets or co-deposition methods (multiple metal targets). It was observed that the chemical concentration of the elements in the film is not only determined by the target composition but also by the sticking factor of the different adatoms on the substrate surface. The chemical bonds were analyzed by XPS reveling the presence of silicides and aluminades of the transition metals in both amorphous and crystalline metallic samples. Moreover, a microstructural characterization was performed using XRD and AFM. Mechanical and tribological properties were studied by nanoindentation and FFM. Transport properties are also considered.

9:40am **F2-1-ThM6 Carbon Supersaturated Refractory Multicomponent Nanostructured Coatings***,* ***Stefan Fritze (stefan.fritze@kemi.uu.se)****, P. Malinovskis, L. Riekehr, L. von Fieandt, E. Lewin, U. Jansson,* Uppsala University, Sweden

The combination of ceramic hardness with high ductility is a major challenge in the design of protective thin films and high entropy alloys (HEAs) are a promising pathway to achieve new high-performance materials. While HEA thin films have been studied to some extent by experimental and computational materials science, there is only limited information available about the influence of carbon on HEA thin films, especially when prepared with physical vapor deposition techniques. In this study, we report on the influence of carbon on the structure and properties of two different HEA alloys in the CrNbTaTiW system. The metal composition of these alloys includes a near-equimolar alloy and a Ta/W-rich composition.

We have deposited Cr-Nb-Ta-Ti-W-C thin films by non-reactive magnetron sputtering. The material properties were strongly depending on the composition and the best results were observed for TaW-rich films which crystallise in a bcc structure with a strong (110) texture. TEM analysis revealed that the films exhibit coherent grain boundaries with specific crystallographic directions. The addition of 8 at.% led to the formation of a meta-stable bcc supersaturated solid-solution without the formation of carbide precipitates. The main effect of the carbon addition was a significant grain refinement reducing the column width from 35 to 10 nm, which resulted in an increase in hardness from 14 to 19 GPa while the reduced E-modulus was unaffected. The enhanced hardness will be discussed in terms of solid solution hardening and grain refinement strengthening. Nanoindentation deformation studies revealed that the addition of carbon significantly reduces the plastic deformation around the indents without showing any signs of crack formation which is explained by the special arrangement of the grain boundaries.

Finally, the effect of carbon addition on the corrosion properties was likewise investigated in 1 M NaCl environment. High pitting corrosion resistance was found for the $Cr_3Nb_{10}Ta_{38}Ti_3W_{38}C_8$ composition, with a corrosion potential of 0.23 V (vs. Ag/AgCl) and a transpassive region equal to hyper-duplex stainless steel (i.e. SAF3207HD).

10:00am **F2-1-ThM7 Single-phased High Entropy Oxides for Energy Applications***,* ***Jyh-Ming Ting (jting@mail.ncku.edu.tw)****,* National Cheng Kung University, Taiwan **INVITED**

Since the report of high entropy alloy (HEA), other high entropy materials such as high entropy oxide (HEO), carbide, nitride, fluoride , etc. are being intensively investigated. These new materials were synthesized to have different forms, e.g., film, bulk, or powders. Although limited, these studies have shown interesting results that demonstrate the use of these new materials in different applications including energy storage and catalysis. Here, we report HEO nanopowders produced using a facile synthesis method. HEOs having various groups of 5 elements with different elemental concentrations are reported. The resulting materials were subjected to various microstructural analysis. Depending on the composition, different single crystal structures were obtained. Homogeneous elemental distributions were also obtained. Selected HOE nanopowders were evaluated for use as anode in lithium ion battery and electrode in water splitting cell. Exceptional properties are reported and discussed.

10:40am **F2-1-ThM9 Improving Phase Stability, Hardness and Oxidation Resistance of Reactive Magnetron Sputtered ($Al_vCr_wNb_xTa_yTi_z$)N Thin Films by Si-alloying***,* ***Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at)****,* Institute of Materials Science and Technology, TU Wien, Austria*; K. Yalamanchili,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Rudigier,* OC Oerlikon Management AG, Switzerland, Liechtenstein*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloyed nitrides are promising materials for hard coatings. One major drawback is a lack of oxidation resistance in most coatings, which limits high-temperature applications in ambient conditions. In this work we report a method to increase the oxidation resistance while also improving thermal stability of the alloy, and higher resistance to the hardness drop induced by elevated temperature annealing.

($Al_vCr_wNb_xTa_yTi_z$)N coatings were formed in a cubic (c) solid solution in thin film form by reactive magnetron sputtering in N_2-atmosphere using a powder metallurgically prepared metal target (Plansee) with nominal composition of 20 at% of each element. Si was alloyed by placing different numbers of pieces (about 2x2x0.4 mm^3 each) of Si on the cathode racetrack during deposition. The hardness and indentation modulus of the as-deposited samples were 32.6 ± 2.0 GPa and 462 ± 23 GPa without Si, and 35.4 ± 1.1 GPa and 328 ± 14 GPa with Si, respectively. X-Ray Diffraction (XRD) measurements of the samples after vacuum annealing to temperatures up to 1200 °C revealed that Si delays the decomposition from 1000 °C to 1200 °C. After vacuum annealing to 1100 °C we measured a hardness of 30.3 ± 2.5 GPa and 38.1 ± 1.3 GPa as well as an indentation modulus of 445 ± 25 GPa and 430 ± 11 GPa for the samples without and with Si, respectively.

We gauged the oxidation resistance of the coatings by placing the samples in a furnace in ambient air at 850 °C for 0.5, 1, 5, 10, 30 and 100 h. After these durations we extracted the samples from the hot zone and analysed them with XRD and Energy-Dispersive-X-Ray-Analysis. With increasing Si-content the oxidation resistance improved significantly.

Based on our results we can conclude that this type of high entropy nitride coatings, especially when alloyed with Si, provides excellent thermomechanical properties as well as oxidation resistance.

11:00am **F2-1-ThM10 Electrochemical and Mechanical Properties of Multi-Component Al-Cr-Nb-Y-Zr Nitride Thin Films***,* ***Kristina von Fieandt (kristina.von.fieandt@kemi.uu.se)****,* Uppsala University, Angstrom Laboratory, Sweden, Sverige*; A. Srinath, R. Lindblad, B. Osinger, S. Fritze, L. Riekehr, L. Nyholm, E. Lewin,* Uppsala University, Angstrom Laboratory, Sweden

Multi-component nitrides that are based on the high-entropy concept, with five or more principal elements, have attracted a lot of attention due to their promising material properties regarding e.g. hardness and corrosion resistance. The mixing of the many elements causes a high configurational entropy, which will favor the formation of a solid solution. To gain a fundamental understanding of the high-entropy concept, a large focus has been on exploring single-phase high entropy materials in equiatomic compositions. Recently the research field has also expanded to non-equiatomic high-entropy materials that may consist of several phases, which have demonstrated excellent material properties [1].

In this study, thin films of the Al-Cr-Nb-Y-Zr-N system in non-equimolar concentrations were deposited in order to study their mechanical and electrochemical properties. Films within this material system have previously shown to be both hard and corrosion resistant [2], which makes them suitable for use as protective coatings. The atomic radius difference of the constituent elements is relatively large and thus the solubility to form a single solid solution is limited. Elemental segregation is therefore expected, which may act as an additional design parameter of the mechanical properties.

The films were synthesized by dc magnetron reactive sputtering using elemental and segmented targets of the respective elements and a gas flow of Ar and reactive N_2. The nitrogen gas flow ratio was varied to achieve films with nitrogen contents between 0 and ~50 at.%. For the films without nitrogen the structure was mainly amorphous with a minor crystalline intermetallic phase. For intermediate nitrogen contents, between 15 and 41 at.%, a cubic crystalline phase in an amorphous matrix was found and at higher N contents, i.e. between 46 and 51 at.%, the structure evolved to a highly crystalline nitride solid solution with the NaCl-type structure. Partial elemental segregation was found in all samples by EDX-STEM mapping. Both hardness and corrosion resistance were increased with increasing nitrogen content, as measured by nanoindentation and potentiodynamic polarization respectively. Furthermore, the deformation behaviour was studied by indentations measurements, which showed that the fully nitrided films, with nitrogen contents of ~50 at.%, were highly ductile and no sign of cracks was observed. Thus Al-Cr-Nb-Y-Zr-N based thin films are not only hard and corrosion resistant but also crack resistant, making them very promising for use as protective coatings in harsh environment.

References:

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[2] von Fieandt *et al.,To be published* (2019)

11:20am **F2-1-ThM11 Structural and Mechanical Properties of AlTiTaZr-N Medium Entropy Alloy Films Obtained by DC Magnetron Sputtering via a Combinatorial Approach*, Mohamed EL GARAH (mohamed.el_garah@utt.fr)*,** *S. Achache,* LASMIS, CNRS- Université Technologique de Troyes, France*; A. Michau, F. Schuster,* CEA, Université Paris-Saclay, France*; F. Sanchette,* LASMIS, CNRS- Université Technologique de Troyes, France

Since their introduction by Yeh and Cantor[1, 2], High Entropy Alloys (HEAs) reveal attractive physical and chemical properties. Similar to that, High Entropy Films (HEFs) have been also reported to possess excellent mechanical and physical properties such as good wear[3] and corrosion resistance[4] as well as an excellent thermal stability.[5] They open up new promising possibilities to various functional material applications; especially they can be used as protective coatings to deal with extreme environments.

AlTiTaZr-N medium entropy alloys are deposited by DC magnetron sputtering of pure metallic targets in Ar-N_2 gas mixtures, with a combinatory configuration. The effects of nitrogen flow rate as well as the substrates position on the films properties are investigated and discussed. The substrates are placed in two different positions on the substrates holder. Without nitrogen, AlTiTaZr are amorphous single phased and, when the nitrogen flow rate increases, a face-centered cubic (FCC) solid solution is formed. Preferential orientation depends on both substrates position and nitrogen partial pressure. By increasing the amount of nitrogen in the gaseous mixture, the as-deposited films in the zone near the axes of the targets have a preferential orientation with the (200) planes parallel to the surface. Hardness and Young's modulus of AlTiTaZr-N films reach 21 GPa and 148 GPa, respectively.

(1) Cantor, B.; Chang, I.; Knight, P.; Vincent, A. , , 213.

(2) Yeh, J.-W.; Chen, S.-K.; Lin, S.-J.; Gan, J.-Y.; Chin, T.-S.; Shun, T.-T.; Tsau, C.-H.; Chang, S.-Y. , , 299.

(3) Cheng, J. B.; Liang, X. B.; Xu, B. S.*Coat. Tech.***2014**, *240*, 184.

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(5) Sheng, W.; Yang, X.; Wang, C.; Zhang, Y. , , 226.

11:40am **F2-1-ThM12 Sputter Deposition of High Entropy Alloy Oxynitrides*, Robin Dedoncker (robin.dedoncker@ugent.be)*,** Ghent University, Belgium*; G. Radnóczi,* Hungarian Academy of Sciences, Hungary*; D. Depla,* Ghent University, Belgium

High Entropy Alloys (HEAs) have now been studied for over a decade, both as a bulk material and as thin films. These multi elemental alloys show a great potential for a wide range of applications. Despite the complex chemical composition, they form simple solid solutions. Magnetron sputtering is a convenient way to deposit such alloys as the high quenching rate aids in the formation of a solid solution. This versatile technique also permits to form compounds based on HEAs. The addition of nitrogen [1] or oxygen [2] during the reactive sputtering of CoCrCuFeNi results again in a simple NaCl (B1) structure with all elements homogeneously distributed according to a STEM analysis. This remarkable resemblance between oxides and nitrides of HEAs is intriguing, and is further examined in this study. For this purpose the sputter deposition of CoCrCuFeNi, CoCrFeMnTi and CoCrFeMnNi thin films in argon/dry air was investigated. Each alloy shows a distinct different structural evolution upon introducing dry air. The obtained films of CoCrFeMnNi was intensively studied with HR-TEM, which could unveil the microstructure and the growth of a single phase oxynitride.

[1] Reactive sputter deposition of CoCrCuFeNi in nitrogen/argon mixtures, R. Dedoncker, Ph. Djemia, G. Radnóczi, F. Tétard, L. Belliard, G. Abadias, N. Martin, D. Depla, Journal of Alloys and Compounds, doi: 10.1016/j.jallcom.2018.08.044

[2] Reactive sputter deposition of CoCrCuFeNi in oxygen/argon mixtures, R. Dedoncker, G. Radnóczi, G. Abadias, D. Depla, Surface and Coatings Techology, doi: 10.1016/j.surfcoat.2019.02.045

Topical Symposia
Room Pacific Salon 3 - Session TS3-2-ThM

In-Silico Design of Novel Materials by Quantum Mechanics and Classical Methods jointly sponsored by ICMCTF and AQS II

Moderators: David Holec, Montanuniversität Leoben, Austria, Ivan Petrov, University of Illinois, USA, Linköping University, Sweden, USA, Davide Sangiovanni, Linköping University, Sweden

8:00am **TS3-2-ThM1 From Dry Sliding to Full Coverage: The Role of Water in Molybdenum Disulfide Lubrication Studied in Silico*, Victor Claerbout (claervic@fel.cvut.cz)*,** Czech Technical University in Prague, Czech Republic*; T. Polcar,* University of Southampton, UK*; P. Nicolini,* Czech Technical University in Prague, Czech Republic

The study of the tribological characteristics of molybdenum disulfide (MoS_2) as solid lubricants has been boosted after the discovery of the super-low friction behavior of MoS_2 by Martin et al. in 1993[1]. However, despite numerous experimental and theoretical efforts, the exact mechanisms determining the lubrication characteristics at the nanoscale are still under debate. The picture becomes even less clear in trying to understand the effects of water on the frictional properties of MoS_2. Recently, it has been shown experimentally that such an effect is more pronounced in amorphous structures than on crystalline samples at nanoscale[2]. In this contribution, we aim to elucidate the phenomena taking place at the nanoscale when one layer of MoS_2 slides atop another in the presence of water. In particular, by means of molecular dynamics simulations, we studied the effect of increasing amounts of water molecules, at different loads and for varying sliding velocities, providing an estimation of the dissipated energy due to friction. The wide range of speeds (from 0.2 to 20 m/s), normal loads (from -1 to 4 GPa) and amounts of water molecules (from dry sliding to full coverage) studied will permit a comparison with parts of the Stribeck curve[3], also allowing to identify the different friction regimes simulated (e.g., dry/boundary lubrication) and relating them to the sliding mechanism in presence of discrete water molecules.

References:

[1] J.M. Martin *et al.*, *Phys. Rev. B*, **48**, 10583(R) (1993).

[2] E. Serpini *et al.*, *Trib. Int.*, **136**, 67-74 (2019).

[3] B. Jacobson, Trib. Int., **36**, 781-789 (2003).

8:20am **TS3-2-ThM2 Structural Ordering of Molybdenum Disulfide studied via Reactive Molecular Dynamics Simulations*, Paolo Nicolini (nicolpao@fel.cvut.cz)*,** Czech Technical University in Prague, Czech Republic*; R. Capozza,* Italian Institute of Technology, UK*; T. Polcar,* Czech Technical University in Prague, Czech Republic

Molybdenum disulfide, the most studied member of the transition metal dichalcogenides family, has been used as solid lubricant for several decades, showing extremely low friction coefficients[1] and stability to high temperature. Its lubricating properties are ascribed to the weak van der Waals interactions between sulfur atoms in the crystalline layered structure. Moreover MoS_2, even when prepared in the amorphous state or made of randomly oriented domains, can undergo shear induced structural transitions to the more ordered layered state affecting its tribological properties[2].

Exploiting a reactive classical force field[3] able to treat explicitly formation and breaking of bonds, we investigated by means of molecular dynamics simulations, the shear-induced structural changes and the possible layer formation in amorphous molybdenum disulfide. The ordering process is studied in details, with particular regard to the estimation of the thermodynamic properties that govern the process itself. A connection with crystallization theories is finally found, conferring a predictive power to the achieved results.

Overall, this study aims at gaining an atomic level understanding of the dynamics of layer formation process in MoS_2, thus controlling and possibly improving its tribological properties.

References:

[1] J.M. Martin *et al.*, *Phys. Rev. B*, **48**, 10583(R) (1993).

[2] J. Moser, F. Lévy, *Thin Solid Films*, **228**, 257 (1993).

[3] T. Liang *et al.*, *Phys. Rev. B*, **79**, 245110 (2009).

8:40am **TS3-2-ThM3 Method Development to Enable In-Silico Design of Materials**, ***Susan Sinnott (sinnott@matse.psu.edu)***, The Pennsylvania State University, USA **INVITED**

This presentation describes recent developments of third-generation charge optimized many-body (COMB3) potentials to enable the design and investigation of metal-carbon interactions in classical molecular dynamics simulations. Particular examples are given where the potentials are applied to investigate the interaction of carbon materials, including graphene and metal-carbide-derived-carbons (CDCs) with titanium and aluminum. The results provide new insights into the bonding character at these interfaces and the role of defects, bond-angle, and temperature on interatomic interactions.

9:20am **TS3-2-ThM5 Plasticity and Fracture in Transition Metal Carbides**, ***Giacomo Po (gpo@miami.edu)***, University of Miami, USA; *M. Chen, J. Wheeler,* ETH Zürich, Switzerland; *D. Sangiovanni,* Linköping University, Sweden; *S. Kodambaka,* University of California Los Angeles, USA **INVITED**

Current and future applications in hypersonic flight, re-entry vehicles, propulsion, and power production create an insatiable demand for materials capable to perform in severe environments.Materials for these applications must possess a rare combination of properties, which include high specific strength, elevated melting temperature, high thermal conductivity, and low thermal expansion coefficient . Ultra-High Temperature Ceramics are being considered for applications in extreme environments, especially when oxidation is a major concern. Currently, the factor limiting the use of UHTCs as structural materials is their low-temperature brittleness. This talk focuses on the plasticity and fracture mechanisms of the transition metal carbide TaC, one of the highest melting temperature materials known to mankind. *In-situ* micro-pillar compression experiments carried out at different temperatures reveal unexpected intrinsic ductility of TaC, which contrasts its well-known bulk brittleness. These findings unveil new properties of the material, such as a pronounced non-Schmid behavior and a remarkable temperature/orientation dependence of the yield strength. A variety of multiscale modeling techniques ranging from *ab-initio* to discrete dislocation dynamics simulations are employed to understand the small-scale behavior of TaC. Computer simulations shed light on the room-temperature brittleness of TaC by explaining the link between plastic deformation and fracture.

10:00am **TS3-2-ThM7 Quantitative Description and Electronic Structure Tuning of the Anomalous Thermoelastic Behavior of Elemental V, Nb, Ta, Pd, and Pt as well as Nb-X (X=Zr, V, Mo) Solid Solutions**, ***Philipp Keuter (keuter@mch.rwth-aachen.de)***, *D. Music, V. Schnabel,* RWTH Aachen University, Germany; *M. Stuer,* Manufactures Cartier Horlogerie, Switzerland; *J.M. Schneider,* RWTH Aachen University, Germany

For numerous applications constant physical properties with respect to temperature are required to guarantee consistent performance despite changing environmental conditions. An anomalous thermoelastic behavior was measured for the elastic constant c_{44} of the cubic transition metals V, Nb, Ta, Pd, and Pt, with Nb possessing the most pronounced anomaly in c_{44},which increases from around 500 to 2500 K. To study the anomalous thermoelastic behavior of bcc V, Nb, Ta as well as fcc Pd and Pt a density functional theory based model is used, which allows for the calculation of the elastic constants *c'* and c_{44} as a function of temperature.

Correlative investigation between V, Nb, Ta, Pd, and Pt with anomalous thermoelastic properties and Mo and Cu with ordinary behavior reveals a high density of states at the Fermi level to be a necessary but not sufficient condition for an anomalous thermoelastic behavior. In addition, anomalous metals in contrast to ordinary metals reallocate electronic states in the vicinity of the Fermi level upon lattice distortion, causing an increase in bond strength as identified by crystal orbital Hamilton population analysis. Hence, we have identified the combination of high density of states and electronic reallocation upon lattice distortion to be the physical origin for anomalous thermoelastic behavior in metals. The absence of an anomaly for *c'*-type distortion in V, Nb, Ta, Pd and Pt is suggested to be due to the less pronounced reallocation of states compared to c_{44}-type distortion.

To study the effect of the chemical composition on the thermoelastic behavior in Nb-based solid solutions, the shear thermoelastic constants $c_{44}(T)$ and $c'(T)$ are investigated by systematically varying the valence electron concentration (VEC) and lattice constant through alloying Nb with Zr, V and Mo, respectively. An anomalous thermoelastic behavior is predicted for all binary solid solutions. The onset of the increase in c_{44} remains unchanged for isoelectronic Nb–V indicating the absence of a size effect in the anomalous thermoelastic behavior. On the other hand, the anomalous thermoelastic behavior can be tuned by alloying with Zr or Mo, due to the VEC induced change in the density of states in the vicinity of the Fermi level, leading to a shift in the anomalous trend of c_{44} to lower temperatures. An anomalous temperature behavior is also predicted for the shear elastic constant *c'* for Nb–Mo solid solutions with Mo concentrations between 24 and 33 at%. With increasing Mo concentrations, the anomaly in both elastic constants is suppressed due to the continuous reduction in electronic states at the Fermi level.

10:20am **TS3-2-ThM8 Identifying Fingerprints of Point Defects in X-ray Photoelectron Spectroscopy Measurements of TiN and TiON with *ab initio* Calculations**, ***Pavel Ondračka (ondracka@mch.rwth-aachen.de)***, RWTH Aachen University, Germany; *D. Holec,* Montanuniversität Leoben, Austria; *M. Hans, J.M. Schneider,* RWTH Aachen University, Germany

Point defects have great influence on mechanical, electrical, optical and other properties of (not only) nitrides and oxynitrides. Significant point defect concentrations are produced by highly energetic deposition processes such as high power pulsed magnetron sputtering (HPPMS), or, in the case of oxynitrides, are a direct consequence of the O incorporation. As the direct observation of point defects is complicated, the characterization of point defects is usually based on indirect information, such as the lattice parameter and composition measurements. In this work we explore a new combined theoretical and experimental approach for obtaining information about point defects from the X-ray photoelectron spectroscopy (XPS) measurements and *ab initi*o calculations of cubic TiN and TiON.

Density functional theory calculations using the all electron Wien2k code with the core-hole approach were used to calculate the N 1s and Ti 2p core electron binding energy shifts in TiN_x and TiO_xN_y. Considered point defects include N and Ti vacancies, different N and Ti interstitials and Frenkel pairs. It was shown that the majority of point defects have a significant influence on the binding energy of its first neighbours. For example, a single Ti vacancy decreases the binding energy of its nearest nitrogen neighbours by 0.6 eV. The aim of the *ab initio* calculations was to create a fingerprint database which could be used when analyzing experimental data.

The *ab initio* calculations were later utilized when analyzing XPS data from TiN and TiON thin films deposited by reactive DC and HPPMS magnetron sputtering. Thereby we were able to identify point defect-introduced features in the XPS spectra and, combined with lattice parameter and composition data, propose a quantification method. This work represents an important step on the road towards a more precise point defect identification and quantification in these materials.

10:40am **TS3-2-ThM9 Theoretical Insights into Transition Metal Nitrides for Thermoelectric and Piezoelectric Applications**, ***Björn Alling (bjorn.alling@liu.se)***, Linköping Univ., IFM, Theoretical Physics Div., Sweden **INVITED**

Multicomponent thin films based on transition metal nitrides is a candidate class of materials for thermoelectric applications. In particular, ScN and CrN, being rock-salt structured semiconductors with small bandgaps, have been studied and found to have high power factors and Seebeck coeficients. [1]

In this work I precent our recent theoretical results based on first-principles calculations that are able to explains the anomalous and low thermal conductivity of CrN, which is another crucial parameter for a thermoelectric materials. We have found that there is a non-adiabatic dynamical coupling of disordered magnetic Cr moments in the paramagnetic state with the lattice vibrations that reduces the life time of heat carrying phonons. [2] For ScN, that has a high thermal conductivity, we have studied theoretically which alloying strategies that could reduce it while still keeping suitable electrical properties. Finally, I present the result of our investigations of novel ternary nitrides based on $TM_{0.5}AE_{0.5}N$ (TM=Ti, Zr,Hf; AE=Mg,Ca,Zn) that can combine suitable electrical properties with alloy-scattering of phonons that reduces thermal conductivity.[3] The analogy to our investigations into chemically similar, but structurally different wurtzite nitrides for piezoelectric applications is discussed. [4]

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[2] I. Stockem et al. Phys. Rev. Lett. **121**, 125902 (2018)

[3] M. A. Gharavi, et al. J Mater Sci **53**, 4294 (2018)

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Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-2-ThA

PVD Coatings and Technologies II

Moderators: Frank Kaulfuss, Fraunhofer IWS, Germany, Yen-Hsun Su, National Cheng Kung University (NCKU), Taiwan, Qi Yang, National Research Council of Canada, Canada

1:20pm **B1-2-ThA1 Biased Target Sputter Deposition System using Novel Ion Source and Motion Control***, Jack VanGemert (jvang@rams.colostate.edu), R. Ham, S. Thompson, J. Williams,* Colorado State University, USA, United States of America

Colorado State University is developing a motion controlled, novel biased target sputter deposition system. The system consists of a deposition source and a two-axis motion system that enable uniform coating over large areas. It is designed to grow thin films of controlled thicknesses that exhibit specific optical properties with minimal stress and high adhesion. The deposition system is comprised of a thermionic hollow cathode which supplies electrons that drive a plasma discharge, a novel hidden anode ion source (HAIS), and a tubular metallic target. The HAIS is a comparatively compact and low-cost device that is capable of producing ions with energies up to 200 eV at a significant rate (> 1 Ampere). To the authors' knowledge, an ion source of this design has not been used in any previously developed thin film deposition system. A detailed description of the HAIS, along with the rest of the system, will be provided in the conference paper.

Metallic and dielectric thin films have been grown on glass substrates using the HAIS deposition system. The system has been shown to produce thin films with thickness control and desired thin film properties at high deposition rates. For typical operating conditions, deposition rates have been measured using a crystal deposition monitor. Deposition rates of 2750 nm/min for Cu, 168 nm/min for Ti, 87 nm/min for TiN, and 60 nm/min for TiO2 are routinely achieved at throw distances of 10 cm. The novelty of this ion source is due to its multi-functionality, all while being a low cost and compact device. The HAIS functions as a substrate cleaner by bombarding the substrate surface with ions prior to coating. During deposition the HAIS is used as the ion source for sputtering target material, as well as an ion assist source. The complexity and cost of the deposition system are decreased by using this novel ion source because the use of features inherent to most commercially accepted deposition systems are not required. For example, the use of magnets and water cooling found in magnetron systems, or the costly grids associated with ion beam sputter deposition systems, are not necessary for this system. The features of this deposition system offer the capability of growing comparatively affordable thin films in a timely manner for a broad range of applications.

Analysis of the thin films will be presented to assess the effectiveness of this system. Specifically, analyses of the thickness, roughness, composition, stress, and transmissivity will be presented for several Ti, TiO2, and TiN thin films. These data will be used to evaluate whether this sputter deposition system can compete with the state-of-the-art.

1:40pm **B1-2-ThA2 Monitoring Tantalum Nitride Thin Films Structure by Reactive HiPIMS Magnetron Sputtering: From Microstructure to Properties***, Angeline Poulon-Quintin (angeline.poulon@icmcb.cnrs.fr), B. Giroire, L. Teule-Gay,* ICMCB-CNRS, France*; M. Cavarroc,* Safran Tech, France*; A. Achille,* ICMCB-CNRS, France

Tantalum nitride thin films were deposited onto steel substrates using Reactive High-Power Impulse Magnetron Sputtering (HiPIMS) allowing reaching a high ionization degree of the sputtered metallic material thanks to high power density applied to the target during few tens of microseconds pulse. The influence of target power density, N_2 partial pressure, total gas (Ar + N_2) pressure and target-to-substrate distance on film crystalline structure is reported. The structures obtained were investigated by X-ray diffraction and transmission electron microscopy. Cubic metastable phase or hexagonal stable phase can be successfully isolated in single phase continuous layer. The TaN crystalline phase obtained depends strongly on processing parameters especially pulse parameters. It is well known that TaN hexagonal single-phase continuous layer is difficult to isolate using conventional reactive magnetron sputtering. Our previous study, based on RF magnetron sputtering, has shown TaN hexagonal structure formation to be enhanced in growth conditions promoting adatoms mobility on the substrate surface. With HiPIMS, TaN hexagonal phase layer is much more difficult to obtain due to the increase number of process parameters to select, the specific composition and the energy of the plasma created. Comparison of mechanisms involved during the stabilization of each TaN structure depending on the process is presented as well as characterization of microstructure, and properties (mechanical, electrical and optical).

2:00pm **B1-2-ThA3 On Electron Heating and Ion Recycling in the High Power Impulse Magnetron Sputtering Discharge***, Jon Tomas Gudmundsson (tumi@hi.is),* University of Iceland, Iceland*; D. Lundin,* LPGP, Universite Paris-Sud, France*; M.A. Raadu,* KTH Royal Institute of Technology, Sweden*; T.J. Petty, T.M. Minea,* LPGP, Universite Paris-Sud, France*; N. Brenning,* KTH Royal Institute of Technology, Sweden

In the past it has been assumed that the magnetron sputtering discharge is maintained by the sheath acceleration of secondary electrons emitted from the target, upon ion impact. This is described by the well-known Thornton equation, which in its original form [1] is formulated to give the minimum required voltage to sustain the discharge. However it has been demonstrated recently that Ohmic heating of electrons outside the cathode sheath is roughly of the same order as heating due to acceleration across the sheath in dc magnetron sputtering (dcMS) discharges [2]. Furthermore, for the high power impulse magnetron sputtering (HiPIMS) discharge we find that direct Ohmic heating of the plasma electrons is found to dominate over sheath acceleration by typically an order of magnitude [3]. In HiPIMS discharge a high density plasma is created by applying high power pulses at low frequency and low duty cycle to a magnetron sputtering device. Here we discuss the large discharge currents and the discharge current composition at the target surface in HiPIMS discharges. We discuss the role of self-sputter(SS-) recycling and working gas recycling within the discharge. We find that above a critical current density $J_{crit} \approx 0.2$ A/cm^2, a combination of self-sputter recycling and working gas-recycling is the general case [4]. For high self-sputtering yields, the discharges become dominated by SS-recycling, contain only a few energetic secondary electrons. For low self-sputtering yields, the discharges operated above J_{crit} are dominated by working gas recycling, and secondary electrons play a more important role. We explore a discharge with Al target which develops almost pure self-sputter recycling, a discharge with Ti target that exhibits a mix of self-sputter recycling and working gas-recycling [5] and a reactive Ar/O_2 gas mixture where working gas-recycling is dominating [6].

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2:20pm **B1-2-ThA4 How to Deposit a Porous Thin Film by Magnetron Sputtering ?***, Diederik Depla (Diederik.Depla@ugent.be), R. De Doncker,* Ghent University, Belgium

Without additional efforts, thin films deposited by magnetron sputtering are dense due to the bombardment by sputtered atoms and reflected neutrals. To overcome this intrinsic feature of magnetron sputtering, several routes have been explored to deposit a porous thin film, and still to benefit from the advantages of magnetron sputtering.

Increasing the deposition pressure and/or tilting the substrate belongs to the most common approaches, but these strategies are plagued by technical issues such as enhanced arcing, a low deposition rate, and limited scalability.

Another strategy is based on the deposition of a mixture of materials, or an alloy which is chemically and/or physically treated to remove one of the constituents. Dealloying by applying a heat treatment and subsequently electrochemical etching is one example that belongs to this group of methods. High temperature and/or (electro)chemical treatments limit the substrate choice, and are often environmentally harmful.

This paper suggests an alternative approach based on the sputter deposition of a powder mixture of a metal with NaCl [1]. The deposited layer is simply treated with water to dissolve the deposited salt, leaving a porous metal layer on the substrate. The thin films are deposited from a powder target composed of NaCl and metal powder. Due to the low thermal conductivity of the target, the target gets hot. As a result, the salt is sublimed while the metal is sputtered from the target. The film composition, and therefore the porosity, is controlled by the applied target power.

This one-source approach without the use of film annealing or aggressive chemicals overcomes the major obstacles of other synthesis routes without compromising the benefits of magnetron sputtering.

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2:40pm **B1-2-ThA5 Effects of Nitrogen Concentration on the Microstructure and Mechanical Properties of VNbMoTaWNx High-Entropy Alloy Coatings**, ***Wen-Hau Wang (williampig111@gmail.com)***, National Taiwan University of Science and Technology (NTUST), Taiwan, 台灣; *C.-J. Wang,* National Taiwan University of Science and Technology (NTUST), Taiwan; *B.-S. Lou,* Chang Gung University, Taiwan; *J.-W. Lee,* Ming Chi University of Technology, Taiwan

High-entropy alloy (HEA) is a relatively new material system, which was first reported in 2004. Among the HEA materials, the refractory HEAs have drawn lots of attentions from researchers and industries due to their high hardness, good wear resistance, good corrosion resistance and stable thermal properties.

In this study, the N contained VNbMoTaW refractory HEA coatings were grown using a pulsed direct current magnetron sputtering system. Four $VNbMoTaWN_x$ thin films containing different nitrogen contents were grown using different nitrogen flow rates. The chemical compositions of thin films were analyzed by a field emission electron probe microanalyzer (FE-EPMA). The adhesion of each thin film was measured by a scratch test. The hardness values of thin films were measured by a nanoindenter. The crystalline phases of thin films were analyzed by an X-ray diffractometry. The cross-sectional morphologies of thin films were observed by a field emission scanning electron microscope. The results showed that the nitrogen free VNbMoTaW thin films had a BCC structure, whereas the phase structure of nitrogen contained HEA coating changed to FCC structure with increasing nitrogen concentrations. The highest hardness of 23.7GPa and an adhesion of 34.2N were obtained for the $VNbMoTaWN_x$ thin film when the film was grown at a Ar/N_2 gas flow ratio of 2:30.

3:00pm **B1-2-ThA6 Tribocorrosion Behaviours of VNbMoTaWCr High Entropy Alloy Coatings**, ***Ismail Rahmadtulloh,*** Ming Chi University of Technology, Taiwan; *W.-H. Wang,* National Taiwan University of Science and Technology (NTUST), Taiwan, 台灣; *C.-J. Wang,* National Taiwan University of Science and Technology (NTUST), Taiwan; *B.-S. Lou,* Chang Gung University, Taiwan; *J.-W. Lee (jefflee@mail.mcut.edu.tw),* Ming Chi University of Technology, Taiwan

Recently, tribocorrosion has become an interesting research area for academic researchers and industries. The deep understanding of tribocorrosion behaviour has become important in development of alloys having good wear resistance and corrosion protection. In this work, the VNbMoTaWCr high-entropy alloy (HEA) coatings with different Cr contents were fabricated by a pulsed DC magnetron sputtering system. For tribocorrosion tests, the coatings were immersed in a 3.5% NaCl solution at room temperature under 2 N load using a pin-on-disk tribometer. The potentiodynamic polarization tests were performed to investigate the corrosion potential, corrosion current, and polarization resistance for each coating before and during the tribocorrosion test. The coefficient of frictions of coatings during tribocorrosion were also obtained. The effect of Cr concentrations on the tribocorrosion behaviours of VNbMoTaWCr HEA coatings was explored. The tribocorrosion behaviours such as plastic deformation, wear performance, corrosion attack and failure mode of VNbMoTaWCr HEA coatings are discussed in this work.

3:20pm **B1-2-ThA7 Surface Morphologies and Mechanical Properties of Multicomponent TiNbCrMoZr Thin Films after Laser Texture Oxidation Treatment**, *Y.Y. Chang,* ***Chi-Sheng Chen (40471136@gm.nfu.edu.tw),*** National Formosa University, Taiwan

Recently, the development of novel multicomponent alloy materials, so-called High Entropy Alloy (HEA) has led to a large number of new alloy systems with unique property combinations. Physical vapor deposition (PVD) technologies could be applied for HEA coatings and have been found to be successful in producing quality coatings. Promising properties better than those of conventional alloy coatings could be obtained when proper HEA compositions and deposition processes are designed. In this study, TiNbCrMoZr coatings were synthesized by cathodic-arc deposition (CAD) using Zr, Ti-Nb and Cr-Mo alloy targets. During the coating process of TiNbCrMoZr, Cr-Mo alloy was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. The thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. After deposition, the TiNbCrMoZr coating was annealed to form surface oxides by laser texturing oxidation at different frequency pulses. Laser surface texturing with using short and ultra-short pulses allows for modifications of surface's topography for a wide range of various materials, including surface microstructure as well as a surface's chemistry. X-ray diffraction (XRD) was used to characterize the microstructure and phase identification of the deposited coatings. The surface morphologies, microstructures and bonding states of the prepared coatings was investigated by field emission scanning electron microscope (FESEM), equipped with an energy-dispersive x-ray analysis spectrometer (EDS), and X-ray photoelectron spectroscopy (XPS). The hardness and elastic modulus of coatings was evaluated using nanoindention and Vickers hardness measurement. Ball-on-disc wear tests were conducted to evaluate the correlation between tribological properties and coating structures of the deposited coatings. The adhesion strength of the coatings was evaluated by a standard Rockwell indentation test. Wettability of the surfaces was investigated by water contact angle (WCA), and furthermore it could recognize the hydrophilic and hydrophobic features. The design of TiNbCrMoZr coatings was anticipated for improvement in surface hardness, tribology, and biomedical performance of metal substrates, which may have potential for use in biomedical devices and tools.

3:40pm **B1-2-ThA8 Multifunctional Coatings with Antifouling Properties**, ***Jose Castro (jodcastroca@unal.edu.co)***, *I. Carvalho, M. Henriques, S. Carvalho,* University of Minho, Portugal

Additive manufacturing (AM) is a hot topic nowadays, having a first order in importance in research trends, improving existent technologies and carrying them further. AM can be applied to all family types materials: metals, polymers, ceramics and compounds. Among abovementioned, ceramics have a huge importance and application in our current technologies. Their capability to maintain functional properties for long time periods combined with the easiness to process and abundance of raw materials make them a fundamental part of mankind development. Within this type of materials, one of the most commonly used nowadays is stoneware. This material has a wide range of uses, from everyday usage such as kitchenware and pottery to high tech applications such as pipelines, which in some cases are affected by biofouling. Some ceramics are not able to prevent the formation of biofouling formation which can affect their finish and appearance. Trying to solve this issue, TiN and Ag:TiN with oxygen addition coatings in 3D printed stoneware, were presented as multifunctional solution, in order to extend the performance of base material, offering a variety in an aesthetical point of view and adding antibacterial properties. This study performed the aforementioned films by reactive direct current (DC) magnetron sputtering. Films obtained were characterized physical, chemical and morphologically, as well as their color variation, roughness, wettability, antibacterial and antibiofouling resistance. The results revealed that the Ag doped coatings (with or without oxygen addition) had an enhanced multifunctionality compared with control samples (without Ag). The Ag nanoparticles addition created a surface with antibacterial and antibiofouling, in order to resist outdoors and aqueous environments, making these films able to be applied in architectural pieces as sculptures or other decorative parts, maintaining their properties with good aesthetical properties.

4:00pm **B1-2-ThA9 Multilayer nano-composite Oxidation-resistant Coatings for Accident-tolerant Nuclear Fuel Cladding using Reactive HiPIMS with Positive Kick and Precision Ion Energy Control**, ***Brian Jurczyk (bjurczyk@starfireindustries.com)***, *R. Stubbers, I. Shchelkanov, T. Houlahan,* Starfire Industries LLC, USA **INVITED**

In the wake of the Fukushima nuclear accident in Japan there is worldwide pressure to improve the accident tolerance of fuels used in light water reactors. A near-term pathway is to deposit a thin protective coating directly on existing Zr-alloy fuel cladding trading coating properties (i.e. chemical resistance, wear resistance, fracture toughness, radiation damage), impact on neutron economy and thermal hydraulics, manufacturing feasibility and implementation readiness, per cladding unit, CapEx and operations costs, regulatory acceptance and quality assurance protocols, and applicability for both pressurized-water and boiling-water conditions. In this study we evaluate a high-throughput fabrication method for nanolayered Cr-based corrosion-resistant and fracture-resistant coatings using a high-power impulse magnetron sputtering innovation—namely the IMPULSE® + Positive Kick™. Ultra-fast IMPULSE® switching achieves high instantaneous plasma densities during HIPIMS discharge pulse for easy control over self-sputtering, ionization fraction and reactive gas management. The adjustable Positive Kick™ quickly reverses the polarity on the sputter target to accelerate metal ions to the substrate—increasing delivered ion fraction and rate for higher efficiency. Precision ion energy control results in fully dense films across a wider range of the Thornton diagram controlling film stress and morphology. Metals and ceramics are precision deposited with excellent adhesion, graded composite nanostructure and conformal layering for radiation hardness, thermal shock- and oxidation-resistance. ~10µm Cr-based coatings were deposited via IMPULSE® + Positive Kick™ on 9.5-mm diameter Zr-alloy cladding with Ar and N_2 gas pressure (0.5-5Pa), cathode power density (0.1-2kW/cm^2), main pulse width (5-100µs), Positive Kick™ voltage (+0-600V), kick delay & width (0-100µs), and repetition rates up to 10kHz. Utility of in-situ surface cleaning via the Positive Kick™ is also demonstrated for adhesion. Samples were characterized pre- and post-testing using mechanical testing, optical and scanning electron microscopy (EDS, EBSD) and x-ray diffraction. Thin-film microstructure was evaluated using SEM, EDS, EBSD and FIB. Corrosion tests were performed in an autoclave using boronated and lithiated water at 360°C at 18.7MPa over sequential time periods for weight gain and spallation/delamination inspection. Manufacturability estimates for volume Zr-alloy coating using a patent-pending inverted cylindrical magnetron configuration optimized for conformal HiPIMS deposition is presented.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-3-ThA

Properties and Characterization of Hard Coatings and Surfaces III

Moderators: Naureen Ghafoor, Thin Film Physics Division, IFM, Linköping University, Sweden, Marcus Günther, Robert Bosch GmbH, Germany, Fan-Bean Wu, National United University, Taiwan

1:20pm **B4-3-ThA1 Low Temperature Deposition of TiB-based Hard Coating Films by Pulsed DC Plasma CVD**, ***Takeyasu Saito (tsaito@chemeng.osakafu-u.ac.jp)***, *H.M. Matsushima, K.F. Fuji, D.K. Kiyokawa, N.O. Okamoto,* Osaka Prefecture University, Japan

Cemented carbide is often used for molds and cutting tools based on high hardness (1800 Hv for WC, 1200-1500 Hv for WC-Co) and toughness (4-6 Mpa・m$^{1/2}$ for WC, 13-20 Mpa・m$^{1/2}$ for WC-Co), in which Ti-based hard coating films are generally used to improve functions such as hardness, heat resistance, durability, releasability and lubricity. Typical Ti-based hard films are TiC, TiN and TiCN, in which TiCN has advantages of TiC with high hardness (3000-3800 Hv) and low friction coefficient (0.1) and TiN with excellent oxidation resistance (ca. 600ºC). In addition, TiB_2 has excellent heat resistance, oxidation resistance (over 400ºC), and high hardness (20-70 GPa). However, it is difficult to form TiB_2 thin film with high growth rate and good crystallinity at low temperatures. It is important to deposit TiB_2 coating films with good crystallinity to get enough hardness, by controlling the ratio of Boron, Carbon and Nitrogen, to balance the superior characteristics of TiB_2 and TiCN.

Physical Vapor Deposition (PVD) or Chemical Vapor Deposition (CVD) are mainly used for Ti-based hard coating films. PVD has the advantage of simple and low-temperature growth (up to 550ºC), on the other hand, thermal CVD (ca. 1000ºC) has a limitation of the base material because of high temperature treatment, whereas adhesion strength and uniformity are superior . Therefore, a film deposition method having good adhesion strength and uniformity at low temperatures is required.

In this study, we focused on lowering the film deposition temperature to increase applicable base material. Growth rate, crystallographic structure, film composition and hardness were measured by a surface profiler, X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and a micro-hardness tester, respectively. We carried out Ti-based or TiB-based hard films synthesis from $TiCl_4$, BBr_3, CH_4, and N_2 using RF plasma CVD, DC plasma CVD, and the pulsed DC plasma CVD. For the case of TiB-based hard coating films by RF plasma CVD, growth rate as 350-800 nm/h was obtained, however, XRD exhibited amorphous or microcrystalline. The hardness was lower than the reported value, possibly due to the amorphous phase and existence of oxygen. For the case of TiC hard coating films by DC plasma CVD, growth rate was up to 800 nm/h, also exhibited amorphous or microcrystalline. Pulsed DC plasma CVD can be expected to crystallize the TiB-based hard film, because by introducing pulse, it is possible to control the electron temperature in the plasma, and to control the dissociation reaction in the plasma and the accumulation of charges on the substrate surface.

1:40pm **B4-3-ThA2 TiAlN/TiMoN Multi-Layered-Coatings as Hydrogen Barriers**, ***Motonori Tamura (tamura@uec.ac.jp)***, University of Electro-Communications, Japan

The hydrogen barrier properties of multi-layered coatings of TiAlN/TiMoN and single layer coatings of TiN and TiAlN were evaluated.

Coatings were deposited using the arc ion plating method with multiple evaporation sources. AISI 316L austenitic stainless steel was used as the substrate. The total thicknesses of the coatings ranged between 2.0 and 2.6 µm.

Hydrogen-permeation tests were performed on the coated stainless steel samples. These tests were based on the differential-pressure methods.

The coatings facilitated reductions of the hydrogen permeabilities to 1/100 of that of the uncoated substrate. The experiment confirmed that the coatings composed of fine crystal grains were highly effective as hydrogen barriers, and that this barrier property became even more efficient if multiple layers of the coatings were applied. The crystal grain boundaries of the coating and interfaces of each film in a multi-layered coating can serve as hydrogen trapping sites. It is speculated that fine crystal structures with multiple crystal grain boundaries and multi-layered coating interfaces will contribute to the development of hydrogen barriers.

2:00pm **B4-3-ThA3 Air-based Sputtering Deposition of Gradient Oxynitride Coatings**, ***Fu-Hsing Lu (fhlu@nchu.edu.tw)***, National Chung Hsing University, Taiwan*; Y.-C. Liou, Y.-L. Lee, M.-H. Chan,* National Chung-Hsing University, Taiwan **INVITED**

Oxynitride coatings exhibiting characteristics mainly between nitride and oxide coatings have many technological applications. In the literature, oxynitride coatings have often been prepared by using N_2 and O_2 as reactive gases in sputtering. We previously reported that air could be employed to replace conventionally used N_2/O_2 in producing oxynitride coatings with various O/N compositions. Hence, high vacuum is not required, which can reduce substantially the processing time and cost. Gradient coatings with different O/N compositions were further made by sequentially changing the air/Ar ratio during sputtering in this research. Gradient TiN_xO_y and TaN_xO_y thin films have been selected as model systems. The gradient coatings were designed with the structures varying from crystalline to amorphous, corresponding to the coatings with conductive, semiconductive, to insulating and opaque, translucent, to transparent behaviors. High efficient selective solar absorbers and electrochemical photocurrents were achieved by employing the gradient oxynitride coatings. The facilely air-based sputtering deposition of gradient oxynitride coatings may bring in more technological applications.

2:40pm **B4-3-ThA5 Fabrication and Microstructure Evolution of Sputtering Single Element Transition Metal Nitride Multilayers**, *K.Y. Liu, Y.H. Yang, J.Y. Xiang, Z.X. Lin,* ***Fan-Bean Wu (fbwu@nuu.edu.tw)***, National United University, Taiwan

Transition metal nitride, TMN, layers nowadays is frequently applied for the enhancement in surface protection applications. Amongst versatile TMN films, multilayer systems attracted intense attentions due to its structure feature and specific strengthening mechanisms. In this work, TaN and MoN single transition metal nitride multilayer coatings were deposited through vacuum sputtering process. Layered configuration was identified since distinct crystal structures, like columnar crystalline, nanocrystalline, and even amorphous features, were manipulated for building layers. The film growth mechanism was discussed in terms of deposition parameters, including gas mixture and sputtering power density. The distinguishable interfaces in the multilayers could be established by different microstructure of adjacent layers. The higher power and larger N_2 gas inlet during deposition generated amorphous layers and suppressed the continuous growth of columnar crystals in crystalline layers. In addition, the high power impulse method was also employed to modify the interfaces between building layers. The intact and flattened interfaces were beneficial to the discontinuity of the microstructure of the building layers for the single transition metal nitride multilayer coatings.

3:00pm **B4-3-ThA6 Iron Aluminides Layers Prepared by Ionized Jet Deposition**, ***Jaroslav Čech (jaroslav.cech@fjfi.cvut.cz)***, *P. Haušild, J. Skočdopole, J. Čapek,* Czech Technical University in Prague, Czech Republic*; K. Nová, P. Novák,* University of Chemistry and Technology, Czech Republic

Intermetallic materials are used in wide range of applications for some of their irreplaceable chemical, physical and mechanical properties. One of the most studied materials are the iron aluminides especially due to their low weight and good oxidation resistance comparing to stainless steels or nickel-based superalloys. Less attention was focused on the ternary Fe-Al-Si system because of the brittle behavior of these alloys. In the previous studies, it was found that the system FeAl20Si20 (wt.%) has excellent high temperature oxidation and sulphidation resistance that can outperform the austenitic stainless steels and nickel-based superalloys [1]. Therefore, the Fe-Al-Si alloys can be the potential candidates for their replacement.

As these alloys are very brittle [2], their preparation by standard metallurgical methods and practical application of bulk materials is not very convenient. For this reason, the layers deposited on the substrates with higher toughness can potentially be interesting. One of the promising ways of the layer's deposition is the ionized jet deposition technique (IJD) [3]. This contribution focuses on the characterization of FeAl and FeAlSi layers prepared by this progressive IJD method under different conditions (substrate roughness, substrate temperature, deposition distance etc.). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed to characterize the microstructure and phase composition of the layers. Nanoindentation and the scratch tests were performed to determine mechanical properties (hardness, Young´s modulus) and adhesion of the deposited layers with the aim to identify the optimum deposition conditions.

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3:20pm **B4-3-ThA7 Effect of the Projection Parameters on the Morphology and the Abrasive Wear Resistance to the Nickel-Based Coatings Produced with Thermal Spraying Flame Technique***, **Hector Rojas (hectorf.rojasm@unilibrebog.edu.co)**, F. Orjuela B, E. Gómez,* Universidad Libre, Colombia*; A. Cueca,* Sena - Cme, Colombia

In this work, coatings were produced based on nickel with the flame thermal spraying technique on a brass, using the experimental fractional factorial orthogonal arrangements of the Taguchi methodology $L_9(3^{4-2})$, to evaluate the effect of projection parameters in the morphological changes and abrasive wear resistance of deposits.

For experimental design, were defined as factors flow gases projection (C_2H_2 and O_2), air pressure projection and projection distance; all three evaluation levels as follows: gas flow (3, 4 and 5 slpm), air pressure (50, 60 and 70 psi) and projection distance (120, 185 and 250 mm).

Noise factors considered were the relative humidity of the site of application of the coatings (60 to 80%) and the preheating temperature of the substrate (200 to 250 ° C). Characterization of the coatings made with conventional optical microscopy techniques (COM) and scanning electron microscopy (SEM).

The results showed that, at higher gas flows, average values of air pressure and lower projection distances, the best conditions projection parameters and reduced wear rate of the coatings are obtained.

3:40pm **B4-3-ThA8 Evaluation of the Mechanical Properties of Single Fe2B Phase Formed on 316L Steel by Interrupted Boriding***, G. A. Rodríguez-Castro,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, México*; O. Vázquez-de la Rosa, A. Meneses-Amador,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; **José Arciniega-Martínez (jarciniega@ipn.mx)**,* Instituto Politecnico Nacional ESIME, México*; I. E. Campos-Silva,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; O. A. Morales-Contreras,* Universidad Autónoma de Baja California, México, Mexico

In this work mechanical and contact fatigue behavior of iron borides formed on AISI 316L steel by interrupted boriding were evaluated. The boriding was carried out at 900 °C during 1 h of exposure time resulting in a FeB/Fe2B bi-phase layer. In order to evaluate only the Fe2B phase, the AISI 316L steel was submitted to interrupted boriding process at 900 °C - 4 h of exposure time. Mechanical properties through the coatings were estimated by Berkovich depth-sensing indentation test. The quality adhesion was determined by VDI tests. Static indentations with spherical indenter were developed to determine a critical load generating radial cracks. After, fatigue tests were carried out using 4 different subcritical loads from 10 to 100,000 cycles at 6 Hz. The fatigue marks were analyzed by optical and confocal microscopy and optic perfilometry. The interrupted treatment decreased the layer thickness (5.49 ± 0.33 µm) compared to the conventional boriding (12.18 ± 0.47 µm) and modifies the distribution of the alloying elements in the layer/substrate system but still maintains its flat morphology. In addition, the former reduced the hardness and Young´s modulus from 26 to 22 GPa and 380 to 338 GPa, respectively compared to the conventional boriding. For interrupted treatment, the level of damage decreases since there are no spallings during the VDI test. Load- number of cycles graphs (P-N) was built for both superficial treatment conditions. The boride layer formed by interrupted boriding presented the best fatigue performance, mainly attributed to the mere presence of the Fe2B phase and the residual stress state present in the coating.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 1-3 - Session C2-2-ThA

Functional Coatings and Thin Films for Electronic Devices II

Moderators: Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, Jörg Patscheider, Evatec AG, Switzerland

1:20pm **C2-2-ThA1 Effect of Substrate Bias on the Properties and Microstructure of Nanotwinned Cu Thin Films***, **Sun-Yi Chang (seanny841123@gmail.com)**, F.-Y. Ouyang,* Tsinghua University, Taiwan

With the development of advanced nano-electronic devices, the interconnects are necessary to exhibit excellent mechanical properties and electrical properties in the integrated circuit technology. Recently, nanotwinned Cu has drawn much attention in various research due to its high mechanical strength, good conductivity and thermal stability. In this study, the effect of substrate bias on the properties and microstructure of nanotwinned Cu thin films was investigated. The Cu thin films were deposited on the Si (100) with an adhesion layer of Ti by unbalanced magnetron sputtering(UBMS) system at different substrate bias voltages, ranging from 0 V to -160 V. The samples were analyzed by Focused Ion Beam (FIB), X-ray diffraction (XRD), Atomic Force Microscope (AFM) and four-point probe. The results of Focused Ion Beam (FIB) images show that the columnar nanotwin structure grow straighter as bias increases. For the samples fabricated at non-biased and lower biased conditions, the twin structure was formed randomly, and no clear column structure was observed in the films. Further increase of bias would facilitate the formation of twin structure. The columnar nanotwinned structure can only be observed distinctly under the substrate bias of -100 V and -120 V. Moreover, in the case of -120 V, most twin boundaries were found to be parallel to the substrate. When the bias exceeded -120 V, it shows that the effect of bias would suppress the growth of straight columnar structure. XRD results indicate that all the deposited Cu films exhibit structure with (111) preferred orientation growth. The percentage of (111) orientation increases as the bias increases. In addition, the increase of bias could lower the electrical resistivity of the films and finally reached a minimum value at optimized condition. The mechanism of the effect of the bias on properties and microstructure will be discussed in details in this study.

1:40pm **C2-2-ThA2 Study of Thermal Stability of Highly (111)-oriented Nanotwinned Ag Films by using Unbalanced Magnetron Sputtering***, **Yu-Chuan Hao (max850502@gapp.nthu.edu.tw)**,* National Tsing Hua University, Taiwan, Republic of China, Taiwan*; L.-P. Chang, F.-Y. Ouyang,* National Tsing Hua University, Taiwan, Republic of China

Nanotwinned (NT) metals have recently received a lot of attentions due to their novel properties of excellent thermal stability and enhanced mechanical strength with the nano-scaled twin boundaries. It can be used in nuclear reactors to alleviate radiation damage as well as the next generation of advanced packaging process. In this study, the thermal stability of nt-Ag films on (100) Si substrate with Ti interlayer was investigated by annealing at 150˚C、300˚C、400˚C and 600˚C under the vacuum for an hour, respectively. Firstly, the cross-sectional FIB images showed that the as-deposited nt-Ag films were mainly columnar structures with high density nanotwins. Furthermore, the random-oriented grains were formed near the Ti interface. The HR-XRD analysis results showed that Ag(111) was the main diffraction peak and the ratio of integrated intensities was up to 98.7%. Secondly, nanotwins showed stable columnar structures after annealing at 150˚C for 1h. In addition, it was found that the grain growth occurred in random-oriented grains to reduce the total grain boundary energy. When the annealing temperature increased to the 400˚C, the results showed that columnar structures still remain high thermal stability and some of the (111)-orientated nt-Ag grains grew apparently downward to consume the random-oriented grains. Lastly, abnormal grain growth occurred in almost all grains after annealing at 600˚C for 1h. The microstructure evolution and mechanism of the highly (111)-oriented nt-Ag films at various annealing temperature will be discussed in details.

2:00pm **C2-2-ThA3 Fabrication and Surface/Interface Characterization of Mo-Ga Thin Films***, NLR Lalitha Raveendran,* University of Texas at El Paso, USA, United States of America*; LP M. Porter,* Carnegie Mellon University, USA, United States of America*; **Ramana Chintalapalle (rvchintalapalle@utep.edu)**,* University of Texas at El Paso, USA

High temperature alloy films are desired in a wide range of technological applications in electronics and photonics. The present study explores the surface/interface Mo-Ga thin films fabricated by sputter-deposition under variable deposition temperature (25-700 ^{o}C). Structural analyses made using X-ray diffraction indicate the formation of nanocrystalline Ga-Mo alloy films at 500 ^{o}C; however, crystal quality deteriorates at >500 ^{o}C. The surface characterization using X-ray photoelectron spectroscopic studies combined with energy dispersive X-ray spectrometry indicate the formation of stoichiometric films up to 500 ^{o}C while Ga loss occurs in samples deposited at higher temperature. Depth profiling analysis reveal the surface oxidation is due to sample handling while the films are Ga-Mo alloy. The effect of deposition temperature on the electrical properties of Ga-Mo films will also be discussed.

2:20pm **C2-2-ThA4 Stress Relaxation in the Si-SiO2 System and its Influence on the Interface Properties***, **Daniel Kropman (daniel.kropman@mail.ee)**,* University of Tartu*; V. Seeman,* University of Tartu, Estonia*; A. Medvids,* Riga Technical University, Latvia

The fact that a positive charge formation occurs in SiO_2 film during the process of Si thermal oxidation is already known, with the formation being dependent upon the oxidation conditions which involve temperature, time and ambient conditions. This is connected by oxygen vacancies in the SiO_2 film and unsaturated $Si^{3\bullet}$ bonds at the interface. Until now this process has not been studied in depth at an atomic level. The purpose of the present work is to investigate the charge formation in the Si-SiO_2 system and its diminishing by means of the appropriate choice of oxidation conditions via EPR spectroscopy, IR spectroscopy, CV curves, TEM, and deflection measurements. Laser irradiation and ultrasonic treatment were used for the modification of interface properties. It has been established that, at an oxidation temperature that is within the range of 1125^{0}C-1130^{0}C in SiO2 film with a thickness of 0.2-0.3µ at the interface, there appears a low positive or negative charge which is connected with negatively charged acceptors that are formed by Si vacancies, and the positive charge in the SiO_2 is compensated. The results that were obtained coincide with the point defects generation kinetic model in the Si-SiO_2 system which was proposed in [1] and confirmed experimentally [2]. Integral circuit technology conditions that allow the interface charge to diminish were introduced by the semiconductor plant ALFA (Riga, Latvia) [3]. We supposed that these results, which were obtained during long term collaboration between Estonia and Latvia, constituted a discovery that had been achieved by Si-SiO_2 system investigation no less than thirty years ago: the discovery of the quantum Hall effect on the Si-SiO *2 structure [4].*

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2:40pm **C2-2-ThA5 Materials and Processes for Integration of IC Chips through Advanced Packaging***, **Marcel Wall (marcel.a.wall@intel.com)**,* Intel, USA **INVITED**

Heterogeneous integration of multiple types of Integrated circuit chips on a single package is an emerging area in advanced packaging that has made significant to impact to High Performance Computing (HPC) devices. In this presentation, we will discuss the evolution of heterogeneous System in Package (SIP) packaging technologies. We will provide an overview of key drivers and metrics for enabling advanced die to die and on package interconnect technologies . We will explore the existing heterogeneous SIP packaging technologies and challenges associated with meeting the needs of next generation HPC devices. Finally, we will cover the areas of innovation needed in materials, equipment, process and design in advancing the next generation of heterogeneous SIP packaging technologies.

3:20pm **C2-2-ThA7 P-type Nitrogen Substituted Zinc Oxide Transparent Semiconductor Thin Films Grown on Glass Substrates by Sol-gel Method***, **Chien-Yie Tsay (cytsay@mail.fcu.edu.tw)**, W.Y. Chiu,* Feng Chia University, Taiwan

Transparent oxide semiconductor (TOS) thin films have been widely used in optoelectronic devices and photovoltaic cells. Most of oxide semiconductors are n-type conductivity. Therefore, the development of p-type oxide semiconductors is desired for new transparent active devices and invisible circuitry applications. The substitution of nitrogen ions for oxygen ions in ZnO (ZnO:N) thin films could make the nature of conductivity of the films changed from n-type to p-type. In this study, we investigated the influence of nitrogen substituting concentration ([N]/[Zn] = 0, 0.1, 0.2, 0.3, and 0.4) on the structural, optical, and electrical properties of sol-gel derived ZnO thin films and realized the preparation of p-type ZnO-based semiconductor thin films on glass substrates. Each as-coated sol-gel film was preheated at 300 ^{o}C for 10 min and then annealed at 500 ^{o}C for 1 h in oxygen ambient. XRD examination showed that these as-prepared ZnO-based thin films had only the wurtzite phase. The substitution of N for O sites in ZnO thin films obviously refined the grain size, reduced surface roughness, decreased *electrical* resistivity*, and enhanced transparency in the visible range.* Hall effect measurement showed that the ZnO:N thin films exhibited p-type conductivity when the N substituting level achieved 3 0 % and had mean hole concentration of 1.80 $\times 10^{15}$ cm^{-3}.

3:40pm **C2-2-ThA8 Atmospheric-Pressure Synthesis of Atomically Smooth, Conformal, and Ultrathin Low-k Polymer Insulating Layers by Plasma-Initiated CVD***, **Dominique Abessolo Ondo (dominique.abessolo@list.lu)**, F. Loyer, R. Leturcq, N.D. Boscher,* Luxembourg Institute of Science and Technology, Luxembourg

Owing to their mechanical flexibility, ultrathin low dielectric constant polymer insulating layers have been intensively investigated to reduce the power operation of the electronic devices. However, the down-scalability of polymeric films thickness to few tens of nanometre over large areas suffer from reproducibility and pinhole formation. Yet, the chemical vapour deposition (CVD) processes which meet a wide range of requirements for flexible electronic devices, can produce ultrathin pinhole free films with good uniformity.

We recently developed an atmospheric-pressure plasma CVD approach based on ultrashort plasma pulses for the simultaneous synthesis and deposition of polymer layers. The process, called atmospheric-pressure plasma-initiated chemical vapor deposition (AP-PiCVD) efficiently combines ultrashort plasma on-time (*ca.* 100 ns) and long off-time (*ca.* 10 ms) for the initiation and propagation of the free-radical polymerization reaction, respectively. AP-PiCVD has notably allowed the atmospheric and dry synthesis of conventional polymers layers with molecular weights up to 94,000 g.mol^{-1}. The process, inherently scalable on any substrate, has already ensured the growth of various functional polymer layers, including flame retardant layers and thermoresponsive coatings.

The present work demonstrates the ability to adjust the dielectric constant of the polymer layers from the careful selection of the monomer. AFM and SEM investigations highlight the atomically smooth, defect-free and conformal nature of the as-deposited polymer layers. Among the various thin film synthesized, the polymer layers prepared from 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotrisiloxane display an ultralow dielectric constant (k = 2.8). Low leakage current densities, in the range of 10^{-9} A/cm² at 20 V for thicknesses as low as 12 nm, are measured, confirming the excellent down scalability of the insulating properties of our polymer layers. In addition to the choice of the monomer, the saturation ratio, which is the monomer partial pressure over its saturated vapour pressure, is demonstrated to be a key parameter controlling the polymer growth. Supported by the physico-chemical characterization (FTIR, SEM, growth rate, dielectric constant), and the relationship established between the saturation ratio and the the resulting films properties, a structure-property-processing relationship is shown.

4:00pm **C2-2-ThA9 Sputtered Gold-tantalum Oxide Films with High Electrical Resistivity***, **Alison Engwall (engwall1@llnl.gov)**, L. Bayu Aji,* Lawrence Livermore National Laboratory, USA, United States of America*; J. Bae,* General Atomics, USA, United States of America*; A. Baker, X. Lepró,* Lawrence Livermore National Laboratory, USA*; S. Shin,* Lawrence Livermore National Laboratory, USA, United States of America*; S. McCall,* Lawrence Livermore National Laboratory, USA*; S. Kucheyev,* Lawrence Livermore National Laboratory, USA, United States of America

An attractive inertial confinement fusion (ICF) design based on a target subjected to high magnetic flux works by embedding a seed magnetic field into an implosion. During the ICF implosion, the magnetic flux density is greatly amplified and can reach astonishingly large values >10 kiloTesla. Such high magnetic fields are expected to positively influence hot-spot heating, alpha particle energy deposition, and the growth of hydrodynamic instabilities during the ICF implosion. The realization of this design, however, requires the development of a new generation of non-conductive thin-wall metallic cans, referred to as hohlraums, which are typically made of pure Au. High electrical resistivity in the entire temperature range from cryogenic temperatures (~20 K) to the melting point is an essential requirement for magnetized hohlraums. The current Au hohlraums have low electrical resistivity and, hence, are not suitable. To address this challenge, we demonstrate the deposition of >30-micron-thick coatings of Au-Ta-O alloys by reactive magnetron sputtering on both stationary planar and rotating sphero-cylindrical substrates. We study how film nucleation and growth depend on the deposition conditions. Emphasis is given to the microstructure, stress, and electrical transport properties of the films.

This work was performed under the auspices of the US DOE by LLNL under contract DE-AC52-07NA27344.

4:20pm **C2-2-ThA10 Synthesis and Characterization of Bi4Ti3O12 Films using Hydrothermal Method: A Study on the Piezo-Related and Photoelectrochemical Properties***, **Jeanne Ranny de Guzman (jrannydeguzman@gmail.com)**, K.-S. Chang,* National Cheng Kung University (NCKU), Taiwan

$Bi_4Ti_3O_{12}$ (BiT) films were successfully synthesized on fluorine-doped tin oxide (FTO) substrate by a two-step process, i.e. BiT seed layer was fabricated first on FTO substrate using sol-gel method and then BiT film was grown by a subsequent hydrothermal treatment. The influence hydrothermal conditions and the addition of surfactant on the crystal structure and morphology of BiT films were investigated. X-ray diffraction results confirmed the presence of typical perovskite layered structure of BiT with an orthorhombic phase. Scanning electron microscopy showed a nanoparticle-like morphology for BiT films without any surfactant while a nanosheet morphology with an average side length of 1 um and a thickness of about 100 nm was obtained upon the addition of polyvinylpyrrolidone (PVP). The photocatalytic, optical, electrical, and piezoelectric properties of the as-fabricated BiT films were also explored in this study.

4:40pm **C2-2-ThA11 Nanostructured Multifunctional Architectural Glass Glazing for Future Green Cities***, S. Woodward-Gagne, R. Beaini, B. Baloukas, O. Zabeida,* ***Ludvik Martinu (ludvik.martinu@polymtl.ca)****,* Polytechnique Montreal, Canada

In North America, buildings represent the largest single sector of energy consumption at 39%. This situation can be substantially improved by applying energy-efficient glass and windows provided with smart and multifunctional glazing. In this work, we focus on two types of design-driven nanostructured optical coating systems, namely a) thin films with tailored angular-selectivity (AS) that can be used to tune solar transmission as a function of the sun's position in the sky, or to attenuate parasitic light sources, and b) high performance thermochromic smart radiators (SR).

In the first part, we describe fabrication of slanted columnar thin films (SCTFs) using glancing angle deposition (GLAD) of optically transparent SiO_2 SCTFs overcoated with conformal atomic layer deposited (ALD) TiN films forming a columnar core shell structure. We show that the combination of GLAD and ALD provides an additional degree of freedom to independently adjust the microstructural and optical characteristics, leading to adjustable AS. ALD functionalization of SCTFs can thus be applied for passivation of functional columns, and hence decoupling of device microstructure and surface chemistry, while tailoring the AS independently from the SCTF thickness and density.

In the second part, we use the inherent metal to insulator transition (MIT) of thermochromic VO_2 that allows a coating to act as a lightweight thermal regulator. Using a modeling approach to optimize the optical properties of the individual constituent films, we design an SR with the following architecture: mirror | dielectric resonant cavity | VO_2 | top protective and antireflective film. Using an infrared transparent ultra-low refractive index dielectric materials for the resonant cavity, e.g.: CaF_2 (n @ 10 micron = 1.17), we experimentally demonstrate the largest-reported dynamic variation of the emissivity between the hot and the cold states of 66% in the 3 to 25 wavelength range. We discuss the advantages of the described approaches for architectural glass glazing considered for energy solutions in future green cities.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E2-2-ThA

Mechanical Properties and Adhesion II

Moderators: Megan J. Cordill, Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria, Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, Ming-Tzer Lin, National Chung Hsing University, Taiwan

1:20pm **E2-2-ThA1 Toughening Magnetron Sputtered S-phase Stainless Steel Coatings by Cycling the N_2 Gas Flow Rate***, **Carlos Mario Garzon (cmgarzono@unal.edu.co)**,* Universidad Nacional de Colombia - Bogotá, Colombia*; A.A. Recco,* Universidade do Estado de Santa Catarina, Brazil

Both superficial protective coatings and functional interlayers of stainless steel (SS) are being developed by diverse research groups in pursuit of superior electrochemical corrosion resistance, oxidation resistance, tribological performance, mechanical strength, and tailored optoelectronic properties. In particular, nitrogen-alloyed austenite phase in SS (so-called S-phase) displays superior corrosion resistance associated to anti-scratch capacity. However, S-phase coatings exhibit hampered ductility in comparison with its nitrogen-lean counterparts due to nitrogen-induced ductility dip. Thus, wear resistance of S-phase coatings could be impaired when tested under conditions of high contact loads, it due to early film cracking. In this contribution, we report on magnetron sputtered S-phase stainless steel coatings obtained from an 316L SS target by cycling the N_2 gas flow rate between 2.2 and 0.0 N_2 sccm. Direct-current magnetron sputtering experiments were carried out with a substrate temperature of 573 K, fixed Ar flow rate of 1.2 sccm and power density of 7.0 Wcm^{-2}, obtaining 1.7 µm thick coatings. SS coatings onto either SS or glass substrates were studied. Coatings with N-lean interlayers sandwiched between S-phase regions were thus obtained. Coatings with either one or three N-lean interlayers were studied. Two coating configurations were studied, varying the stacking ordering of N-lean and S-phase interlayers. Coating's cracking resistance was appraised by carrying out Vickers indentations on top of covered samples at increasing test loads, with maximum test load of either 30 kgf (SS substrates) or 15 kgf (glass substrates). On one hand, coatings onto SS substrates showed no crack formation. On the other hand, coatings onto glass substrates showed diverse patterns of crack formation. Radial crack length was recorded for those coatings onto glass, and it was observed an outstanding increase of resistance to indentation-induced cracking in the coatings obtained cycling the N_2 gas flow rate, regarding to the traditional homogeneous S-phase coatings. The observed coating toughening was attributed to a ductile barrier effect exerted onto propagating cracks by the N-lean interlayers and to an adequate distribution of coating residual stress. This contribution shows how the stacking configuration of N-lean and S-phase interlayers and the interlayer thickness affect the overall coating's toughness.

1:40pm **E2-2-ThA2 Nb-containing Diamond-like Carbon Films Fabricated by Radio Frequency (rf) Magnetron Sputtering Technique***, **Adedayo Adeniyi (sherifadeniyi@gmail.com)**, J. Corona, J. Patel, Q. Yang,* University of Saskatchewan, Canada

To enhance the performance of diamond-like carbon (DLC) films, Nb-doped amorphous non-hydrogenated carbon films were deposited on CoCrMo alloys by radio frequency (rf) magnetron sputtering. The films were fabricated to obtain a multilayered structure of Nb/NbC/DLC gradient for improved mechanical and chemical properties. The effect of Nb content (in the NbC gradient layer) on the properties of the films were studied using x-ray photoelectron spectroscopy, x-ray diffraction, Raman and scanning electron microscope to analyze the composition and microstructure of the films. The internal stress was evaluated using the Stoney's equation after obtaining the curvature before and after film deposition (using the profilometer). Mechanical and tribological properties of the films were investigated by, nanoindentation and reciprocating ball-on-disk tribo-tester, respectively. The results indicated enhanced film properties.

2:00pm **E2-2-ThA3 Insights into Indentation-Induced Cracking via 3D-FIB Tomography and HR-EBSD***, **Bo-Shiuan Li (bo-shiuan.li@materials.ox.ac.uk)**,* University of Oxford, UK **INVITED**

Indentation-induced cracking has been a topic of interest to the coating community since the late 70s, as it provides a convenient measure for evaluating fracture properties of the coated layer. The fracture toughness (K_c) calculation based on indentation-induced cracking simply relies on three parameters: fracture load, crack length, and an empirical coefficient which depends on the indenter geometry. Due to the complicated stress state around the indent and subsurface crack geometry, it is difficult to perform conventional stress analysis for obtaining the stress-intensity factor (SIF) used in fracture mechanical analysis. Alternatively, a pre-defined crack geometry (often half-penny or Palmqvist shape) is assumed to simplify the stress analysis. For ideally brittle material, the method generally shows good agreement with macroscopic values, but will starts to deviate when plasticity is significant.

In this work, nanoindentation up to 700 °C was performed on the monolithic 6H-SiC, a promising ceramic for high-temperature structural applications. High-resolution electron backscatter diffraction (HR-EBSD) and 3D-FIB tomography were used to examine the stress state and crack geometry around the nanoindent. Results from both analysis will provide physical validation of the indentation-based fracture toughness model, and gain insights into the brittle-to-ductile (BDT) transition at elevated temperatures.

2:40pm **E2-2-ThA5 Influence of Twin Wire Arc Spraying Process Parameters on Microstructure and Hardness of Steel Coatings***, **Nicole Wagner (njwagner@cpp.edu)**,* Cal Poly Pomona, USA

Twin wire arc spraying offers high deposition and growth rate capabilities, coupled with process robustness and versatility. This technique is therefore desirable in real-life applications of component protection and repair. An Oerlikon Metco FlexiArc 300 twin wire arc spraying system was used to fabricate an array of dense steel coatings. Dual 1.6mm diameter steel wires were used with compressed air as the carrier gas. Coatings with thickness of 100 micrometers were deposited within a few seconds of spraying. Coating structure and morphology were evaluated with scanning electron microscopy (SEM), while energy dispersive x-ray spectroscopy (EDS) was used to assess elemental composition. Vickers hardness was measured on coating cross-sections. The operating conditions were altered to include variations in torch power, standoff distance, carrier gas pressure, and coating thickness. Correlations were made between process conditions and coating morphology, microstructure, element content, and Vickers hardness. Results showed relationships between spray conditions, oxide content, and Vickers hardness. Two distinct lamella regions of varying elemental composition were observed throughout the coatings. These regions displayed a significant difference in Vickers hardness.

3:00pm **E2-2-ThA6 Effect of Transitional Layers on Wear Behavior of $Ti_{0.15}Zr_{0.85}N$ Coatings on AISI D2 Steel***, **Hung-Hsiang Liu (zxc010189@gmail.com)**,* Hsing Hua University, Taiwan*; J.-H. Huang,* National Tsing Hua University, Taiwan

The objective of this study was to investigate the effects of TiN and TiZr transitional layers on wear resistance of TiZrN coatings on AISI D2 steel. TiZrN coatings with Ti interlayer and TiN/TiZr transitional layers were deposited on AISI D2 steel by DC unbalanced magnetron sputtering. The N/(Ti+Zr) ratio of TiZrN layer was about 1.0 and the Zr/(Zr+Ti) ratio of TiZrN coatings was about 0.85 for easily distinguishing the TiN and TiZrN X-ray diffraction peaks. The thickness of TiZrN for all specimens was fixed at 1800 nm such that the effect of coating thickness on the residual stress and wear behavior could be ignored. Moreover, there was sufficient thickness of the TiZrN coatings to obtain accurate results of wear tests. The residual stress of each layer was measured by average X-ray strain combined with nanoindentation methods [1,2]. The adhesion strength was measured by scratch tests, and the wear rate was evaluated by pin-on-disc tests. From our previous study [3], elastic stored energy (Gs) could be taken as an index to assess the wear resistance of coatings because wear rate increased with Gs. The measured residual stress of TiZrN coatings was used to calculate Gs and further verifying the validity of Gs to be a suitable index for wear resistance. From the results of wear test, the effects of TiN, TiZr transition layer and Ti interlayer on tribological behavior of the TiZrN coatings on AISI D2 steel could be understood, and the layer dominated the change of wear rate and adhesive strength was discussed.

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3:20pm **E2-2-ThA7 Effect of the Incorporation of Ag Layers in the Structure of an Hydroxyapatite Coating Deposited by Magnetron Sputtering***, **Julian Lenis (julian.lenis@udea.edu.co)**, F.J. Bolívar,* University of Antioquia, Medellín, Colombia

The use of osteoconductive and antibacterial coatings of materials commonly used in the manufacture of implants has emerged as a way to avoid rejection of these devices in the human body and to prevent bacterial infections. For this reason, surface modification of stainless steel and titanium alloys is currently widely studied. For several years, biological evaluations shown good adhesion, proliferation and cellular differentiation in calcium phosphates, particularly in hydroxyapatite (HA), which is mainly due to its high chemical similarity to bone mineral. Meanwhile, there is a need for elements that act locally to inhibit bacterial adhesion and the formation of biofilm, thereby protecting the implant during surgery and in the post-operative stages. Silver (Ag) appears to be a promising option in this respect, given its wide antibacterial spectrum and bactericidal properties against both gram-negative and gram-positive strains that have been demonstrated for many years. The current work presents the effect of the incorporation of Ag layers in the structure of an HA coating on the mechanical properties and the biological response.

Keywords: Magnetron sputtering**,** Hydroxyapatite, Multi-layer coating, Hardness, Cell viability, Cell adhesion.

3:40pm **E2-2-ThA8 Abrasion Wear Resistance of Low Temperature Plasma Nitrided Inconel 625 Superalloy***, L.B. Varela, M.F.C. Ordoñez,* University of São Paulo, Brazil*; C.E. Pinedo,* Heat Tech & University of Mogi das Cruzes, Brazil*; **André Tschiptschin (antschip@usp.br)**,* University of São Paulo, Brazil

In this work, Low Temperature Plasma Nitriding (LTPN) was carried out in an Inconel 625 superalloy at 420 °C for 20 h, in a 75% N_2 + 25% H_2 atmosphere. After plasma nitriding, the specimens were analyzed by various characterization techniques: X-ray diffraction, scanning electron microscopy, micro-hardness measurement, scratch and micro-abrasion wear tests. Microstructure, hardness and abrasion wear resistance of the untreated Inconel 625 is compared with the properties obtained after the LTPN treatment. Friction coefficient, mechanical failure mode and critical loads for damaging the nitrided case were determined using the linear scratch test, carried out at a linearly increased normal force. Microabrasion tests were conducted to evaluate the abrasion wear resistance. The microstructure of the as received material was composed entirely by polygonal (γ) FCC grains. The results showed that LTPN promotes the formation of a nitrided layer around 8.4 µm thick, 930 ± 20 HV hard, consisting of a nitrogen expanded FCC phase (γ_N), also known as S phase, ε-$Fe_{2-3}N$ and CrN nitrides. Colossal N supersaturation was detected in the expanded FCC layer, which promoted strong hardening and a state of compressive residual stresses. The scratch tests results showed that the nitrided layer strongly decreased the apparent friction coefficient, in comparison with the non-nitrided alloy. Tensile cracking was the prevalent mechanical failure mode of the nitrided layer. Microabrasion results showed that the LTPN treatment decreased the wear volume losses. For the nitrided samples wear coefficients were determined for the nitrided layer and for the substrate, indicating a change in the wear volume loss rate with the sliding distance.

4:00pm **E2-2-ThA9 Effects of Processing Parameters of Plasma Electrolytic Oxidation on the Microstructure, Adhesion Strength and Corrosion Resistance of Oxide Layers on ZK60 Magnesium Alloys***, **Mengesha Getinet Asrat (getgetuw@gmail.com)**,* National Taiwan University of Science and Technology, Taiwan, Ming Chi University of Technology, Taiwan*; J.P. Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan*; J.W. Lee,* Ming Chi University of Technology, Taiwan*; B.-S. Lou,* Chang Gung University, Taiwan

Magnesium alloy has been widely used in industry and daily life. Despite Mg is commonly used in aerospace, automotive, communication devices and biodegradable implants, the poor corrosion resistance and low surface hardness limit its further application. In this study, plasma electrolytic oxidation (PEO) process was used to improve the drawback of ZK60 magnesium alloy. PEO coatings were grown on ZK60 magnesium alloy using a Na_2SiO_3. $5H_2O$, KOH, K_3PO_4 and KF based electrolyte under different duty cycles, different anodic and cathodic currents of a bipolar pulsed direct current power supply at a fixed frequency and working voltage. The corrosion resistance of PEO coatings were studied by a potentiodynamic polarization test in 3.5 wt.% NaCl solutions. The adhesion strength of PEO coatings were measured by a scratch test. The weight gains, the oxide layer thickness and the surface roughness of the PEO grown oxide increased at higher anodic and cathodic on-time, higher cathodic current and higher duty cycle. The corrosion resistance and the adhesion strength of the PEO coatings improved meaningfully with decreasing duty cycle, lower cathodic current and lower anode and cathode on-time. A PEO coating with a compact, less crack and pores surface morphology was obtained at lower duty cycle.

Key words: Plasma electrolytic oxidation, ZK60 Mg alloy, corrosion resistance, adhesion strength.

4:20pm **E2-2-ThA10 Progressive Metallic Coatings for Enhancing Corrosive Properties of Magnesium Alloys***, **Sunil Dutta**, S.K.R. Narala (nskreddy@hyderabad.bits-pilani.ac.in),* BITS Pilani Hyderabad Campus, India

Over the past couple of decades, the state-of-the-art developments in the alloying arena have entirely revolutionized the products of Engineering, Aero, IT, and Defence sectors. Magnesium and its alloys have been evolved as the strongest candidates for various applications/ products which demands weight reduction, high strength, and ductility. However, magnesium alloys have poor corrosive properties, which can lead to structural or mechanical failure. Like most metals, magnesium is also susceptible to corrosion when exposed to air, water, and humidity. Different approaches to combat corrosive property of magnesium involves, the introduction of the alloying element during development, organized deposition of thin-film coatings using an anodic chemical process, mechanical surfacing, deep rolling, low plasticity burnishing, etc. The simplest and sought-after way to evade corrosion on the surface of magnesium-based alloys is to coat the substrate to avert interaction with the environment. However, conventional coatings are susceptible to porosity, permeability, poor hydrolytic stability, etc. This enhances the material's vulnerability to environmental degradation and eventually leads to its chemical decay. Progressive metallic coatings enhance the wear resistance properties manifold thereby making parts robust enough to withstand extreme environmental conditions. The paper deliberates progressive metallic coatings with pros and cons and also presents a decision support module for selection of best metallic coating for a particular Mg alloy. The module has been developed using Mamdani implication in MATLAB with two input variables, and one output variable.

4:40pm **E2-2-ThA11 Nanostructured CVD W/WC Coating with Enhanced Resistance to Water Droplet Erosion and Cavitation***, **Yury Zhuk (yzhuk@hardide.com)**,* Hardide Plc, UK

Water Droplet Erosion (WDE) damages the leading edges of steam and gas turbine blades, increasing turbine rotation drag and leading to costly maintenance. Cavitation Erosion (CE) damages pump and valve components, flow control and marine equipment. Both WDE and CE are complex phenomena which have significant similarity, so materials resistant to CE often show enhanced resistance to WDE. Protection of industrial equipment against WDE and CE is a pressing industry demand and advanced coatings are considered a promising approach to address it. This paper reports the testing of nano-structured CVD WC/W metal matrix composite coating resistance to WDE and CE and discusses the key factors affecting this advanced coating performance.

Two types of WC/W coatings were tested: "A" type is 100 microns thick and has a hardness range of 800-1200 Hv and "T" type is 50 microns thick with a higher hardness of 1100-1600 Hv. Both coating types are made of Tungsten Carbide nanoparticles dispersed in metal Tungsten matrix. This composition and structure enable a combination of enhanced fracture toughness with high hardness and the production of exceptionally thick hard CVD coatings to provide durable protection.

The coatings were tested for WDE resistance using 350 µm water droplets at 300 m/sec velocity. Uncoated 410 SS control samples suffered from major loss of material after just 7-hours of exposure to WDE, forming a 200 µm deep scar across whole tested area. After a much longer exposure of 90 hours, the coating samples showed negligible WDE damage, only measurable on the sample's edges. Thicker and less hard type A coating showed better performance when compared to thinner, harder type T.

The coating CE resistance was tested in accordance to ASTM G32-92 using ultrasonic induced cavitation in distilled water. The sample's weight was measured at regular intervals during the total 330 minutes exposure. All coating types showed a very low maximum CE erosion rate of 0.004….0.010 mg/min as compared to 15.6 mg/min for uncoated Ti6Al4V substrate. Less hard A type coating also shown better performance in this test.

Effects of the coatings' thickness, hardness, microstructure, and residual stresses on the WDE and CE resistance were evaluated.

The testing showed that the CVD WC/W coating can protect steam and gas turbine blades against WDE, and pump and valve parts against CE thus increasing equipment service life and maintaining its optimal performance for longer. The CVD technology produces a uniform coating on complex shaped parts like turbine blades, vanes, pump impellers, including non-line-of-sight areas.

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F2-2-ThA

High Entropy and Other Multi-principal-element Materials II

Moderators: Diederik DeplaUlf Jansson, Uppsala University, Sweden, Erik Lewin, Uppsala University, Sweden,

1:20pm **F2-2-ThA1 Unveiling Microplasticity Mechanisms in Metallic Glasses with the Help of Polymer-supported Thin Films***, **Oleksandr Glushko (oleksandr.glushko@unileoben.ac.at)**,* Montanuniversität Leoben, Leoben, Austria*; C. Mitterer, J. Eckert,* Montanuniversität Leoben, Austria

The main, if not only, mechanism of plastic deformation in metallic glasses is *shear banding* – formation of strongly localized bands with high shear displacement within them. Despite at least a decade of intense research, shear bands are still not fully understood. This unfortunate situation can be explained by the fact that shear banding is a very fast kinetic process which can hardly be temporally resolved in an in-situ experiment. Additionally, the high amount of elastic energy which is released upon shear band propagation leads to catastrophic fracture of free-standing tensile samples through propagation of a single shear band across the whole specimen. Here, we use polymer-supported thin film metallic glasses (TFMGs) to capture the dynamics of shear bands under tensile loading.

By means of in-situ resistance measurements, in-situ optical microscopy as well as quasi-in-situ SEM and FIB characterization, different stages of evolution of shear bands and cracks with increasing strain are detected and described. Two distinct types of shear bands appear in polymer-supported $Pd_{80}Si_{20}$ and $Au_{60}Ag_{20}Si_{20}$ (deposited by co-sputtering) TFMGs with increasing strain: (i) the "out-of-plane" shear bands (the direction of shear is not in the film plane) which are formed at about 2% strain and develop quickly into through-thickness cracks and (ii) in-plane shear bands (the direction of shear is within the film plane) which appear after crack density saturation (at about 10% strain) and do not lead to crack formation. If the film thickness is reduced below 15 nm, the formation of shear bands is suppressed and the film can deform up to strains of about 6% elasto-plastically (i.e. without cracking) showing formation of homogeneously distributed short nanocracks at higher strains [1]. It is demonstrated, that with increasing applied strain, new in-plane shear bands can easily intersect the existing ones, whereupon the intersected shear bands become inactive and cannot carry further plastic deformation. This mechanism can lead to effective strain hardening of metallic glasses. Not intersected shear bands are shown to be softer than the non-deformed matrix and the deformation is localized there if the sample is unloaded and re-loaded.

Presented results demonstrate that formation of shear bands of specific type in thin film metallic glasses under tensile loading does not always lead to film failure. The "only" problem is to learn how to promote formation of favorable shear bands and suppress formation of unfavorable shear bands.

[1]O. Glushko, *et al.* Exceptional fracture resistance of ultrathin metallic glass films due to an intrinsic size effect. *Sci Rep***9,** 8281 (2019)

1:40pm **F2-2-ThA2 Ultra-high Vacuum dc Magnetron Sputter-deposition and Microstructural Characterization of High Entropy Alloys Nitride Thin Films***, **Hicham Zaid (hizaid@ucla.edu)**, K. Tanaka, J.-M. Yang, S. Kodambaka, H. Kindlund,* University of California Los Angeles, USA

Over the past decades, a major goal of material has been to enhance the hardness of protective coatings. Among the transition-metal nitrides, group 4 compounds (e.g., TiN) and related alloys (e.g., TiAlN) have by far received the most attention. In search of ultra-hard coatings, early studies focused on the incorporation of smaller atoms (B, Al, and Si) into the lattices to promote stronger bonding and hence further enhance the mechanical strength of these ceramics. Recent efforts have aimed at enhancing the intrinsic plasticity of these refractory nitrides by tuning the valence electron concentration (VEC) via alloying.[[#_ENREF_1]] These studies demonstrated that the introduction of group 6 elements (e.g., Mo & W) in group 5 nitride (VN) increases the ductility, while retaining the strength. Recent theoretical calculations performed on a wider range of pseudobinary carbonitrides,[[#_ENREF_2]] predicted that: B1-structure is stable when the VEC is below 10.6, hardness decreases while ductility increases with increasing VEC, and maximal toughness is expected for compounds with VECs between 9.5 and 10.5. Furthermore, existing literature suggests that the combination of high-entropy, lattice distortion, sluggish mass transport, and the 'cocktail effects', intrinsic to high-entropy alloys, can lead to superior properties. Motivated by these studies, we focus on the structural stability and mechanical properties of multi-element alloy nitride [(VNbTaMoW)N] with VEC around 10.5.

In this talk, we report on the growth of (VNbTaMoW)N thin films on single-crystalline $Al_2O_3(0001)$ and MgO(001) substrates at 1073 K via dc magnetron sputtering of VNbTaMoW alloy target in Kr/N_2 gas mixtures. Using scanning and transmission electron microscopies coupled with energy dispersive X-ray spectroscopy, and X-ray diffraction, we determined the as-deposited film microstructures, morphologies, and composition. We find that the films are single-phase, B1-structured with a lattice constant of ~0.42 nm, and interestingly with a 111 texture, on both $Al_2O_3(0001)$ and MgO(001). The films are porous made of dendritic columns with strongly facetted surfaces. We attribute these results to kinetic limitations of sputter-deposition exacerbated by low adatom mobilities of multiple transition-metals.

[1] H. Kindlund, D.G. Sangiovanni, I. Petrov, J.E. Greene, L. Hultman, A review of the intrinsic ductility and toughness of hard transition-metal nitride alloy thin films, Thin Solid Films, (2019) 137479.

[2] D.G. Sangiovanni, L. Hultman, V. Chirita, Supertoughening in B1 transition metal nitride alloys by increased valence electron concentration, Acta Mater., 59 (2011) 2121-2134.

2:00pm **F2-2-ThA3 Kinetically Limited Phase Formation of Pt-Ir based Compositionally Complex Thin Films***, **Aparna Saksena (saksena@mch.rwth-aachen.de)**, D. Bogdanovski,* RWTH Aachen University, Germany*; H. Sahasrabuddhe,* IIT Bombay, India*; X. Chen, D. Music, J.M. Schneider,* RWTH Aachen University, Germany

The phase formation of PtIrCuAuX (X= Ag, Pd) compositionally complex thin films is investigated to critically appraise the criteria employed to predict the formation of high entropy alloys. The formation of a single phase high entropy alloy is predicted if the following requirements are fulfilled: configurational entropy ≥ 13.38 J/K mol, -10 kJ/mol ≤ enthalpy of mixing ≤ 5 kJ/mol and atomic size difference ≤ 5%. Equiatomic PtIrCuAuX (X= Ag, Pd) fulfill all of these requirements.

Based on X-ray diffraction and energy dispersive X-ray spectroscopy, near-equiatomic $Pt_{22}Ir_{23}Cu_{18}Au_{18}Pd_{19}$ thin films form a single-phase solid solution while near-equiatomic $Pt_{22}Ir_{23}Cu_{20}Au_{17}Ag_{18}$ thin films exhibit the formation of two phases. The latter observation is clearly in conflict with the design rules for high entropy alloys. However, the observed phase formation can be rationalized by considering bond strength calculations and differences in activation energies for surface diffusion. Integrated crystal orbital Hamilton population per bond showed an increase in bond strength for all the interactions when Ag is substituted by Pd in PtIrCuAuX which causes the higher activation energy required for surface diffusion. Substituting Pd with Ag decreases the activation energy barrier for each constituent by 13 to 50 % which enables the formation of two phases by surface diffusion, one rich in Au and Ag and a second phase enriched in Pt and Cu. Hence instead of configurational entropy, phase formation in these systems is identified to be a complex interplay between energetics and kinetic limitations.

2:20pm **F2-2-ThA4 High Entropy Oxide for High-Temperature Solar Selective Absorber***, **Yi Cheng Lin (chrisb03022@gmail.com)**, J.-M. Ting, Y.H. Su,* National Cheng Kung University (NCKU), Taiwan

High entropy oxide (HEO) single-layer and double layer coatings were deposited using a reactive sputter deposition technique. Silicon and stainless steel were used as the substrates. The effects of various deposition parameters, such as target power, substrate temperature, gas flow rate, and deposition time, were investigated. The obtained single-layer and double layer coatings were characterized using field emission scanning electron microscopy, X-Ray diffractometry, X-Ray photoelectron spectroscopy, and high-resolution transmission electron microscopy were used for material characterizations. The optical properties, including reflectance, emittance, and n/k values, were obtained for multilayer structures of substrate/W/single-layer HEO/HfO_2 and substrate/W/double-layer HEO/HfO_2. Selected multilayer structures were also subjected to high temperature annealing in Ar and air and then evaluated for the material characteristics and optical properties. The correlation between the material characteristics and optical properties is addressed and discussed.

2:40pm **F2-2-ThA5 High Entropy Alloy Displays Unique Strengthening and Deformation Pathways***, **Simon Tsianikas (simon.tsianikas@adelaide.edu.au)**,* The University of Adelaide, Australia*; Y. Chen,* Southwest University, China*; Z.H. Xie,* The University of Adelaide, Australia

Most of high entropy alloys (HEAs) with body centered cubic (BCC) structure suffer from limited plasticity at room temperature, which hinders their practical applications. To tackle this challenge, a $Fe_{49.5}Mn_{30}Co_{10}Cr_{10}B_{0.5}$ high entropy alloy with body centered cubic (BCC) structure was prepared by closed field unbalanced magnetron sputtering. Nanoindentation tests show a hardness of 6.2 GPa coupled with a large extent of plasticity. A two-step phase transformation; namely, BCC to hexagonal closed packed (HCP) and then to face centered cubic (FCC) structure, was identified under applied load. Transformation induced plasticity (TRIP) thus serves as the main deformation mechanism of this new alloy. On one hand, the phase transformation from BCC to HCP and then to FCC structure, along with the formation of heterogeneous, bi-modal microstructure, works to absorb the strain and mitigate the stress concentration in the alloy. On the other hand, the increased phase boundaries generated by phase transformation pose as additional barriers to dislocation movements, providing extra strain hardening. The results of this work demonstrates that the two-step phase transformation is an effective mechanism that imparts the new HEA with appreciable damage tolerance while maintaining high hardness.

New Horizons in Coatings and Thin Films
Room Pacific Salon 2 - Session F3-ThA

2D Materials: Synthesis, Characterization, and Applications

Moderators: Suneel Kodambaka, University of California Los Angeles, USA, Eli Sutter, University of Nebraska-Lincoln, USA

1:20pm **F3-ThA1 Pulsed Laser Deposition and Conversion of Atomically-Thin 2D Materials Controlled by *in situ* Diagnostics***, **David Geohegan (geohegandb@ornl.gov)**,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, USA*; Y.-C. Lin, Y. Yu,* Oak Ridge National Laboratory, USA*; C. Liu, G. Duscher,* University of Tennessee at Knoxville, USA*; A.A. Puretzky, M. Yoon, C.M. Rouleau,* Oak Ridge National Laboratory, USA*; P.D. Rack,* University of Tennessee and Oak Ridge National Laboratory, USA*; G. Eres, K. Xiao,* Oak Ridge National Laboratory, USA **INVITED**

Atomically-thin two-dimensional (2D) materials, including layered 2D transition metal dichalcogenide (TMD) semiconductors and their heterostructures, exhibit remarkable quantum properties that offer new horizons as ultrathin films for energy-efficient photovoltaics, flexible optoelectronics, catalysis, and quantum information science. However, significant synthesis and processing challenges currently limit the technologic development of these "all-surface" materials, including wafer-scale, bottom-up synthesis of uniform layers of crystalline 2D materials that are comparable in quality to exfoliated flakes of bulk materials. As-synthesized crystals of 2D TMDs display remarkable heterogeneity on both the atomistic level (e.g., vacancies, dopants, and edge terminations) and on the mesoscopic length scale (e.g., misoriented grains, layer orientations, and interactions with substrates and adsorbates) that can strongly influence their structure and electronic properties. This heterogeneity offers serious challenges for synthesis and processing of 2D materials, yet offer tremendous opportunities to tailor functionality.

To address these challenges, in addition to conventional vapor transport techniques, progress in laser-based approaches for 2D synthesis and modification, such as pulsed laser deposition (PLD) and pulsed laser processing of precursors, are described that permit control of the growth environment using time-resolved *in situ* diagnostics. First, we demonstrate the non-equilibrium advantages of PLD by revealing how tuning the kinetic energy of PLD plume species < 20 eV/atom can implant and replace chalcogens in existing 2D crystals to form novel alloys, Janus monolayers, and vertical heterojunction bilayers. Second, we show how *in situ* diagnostics can tune the size and stoichiometry of the "building blocks" deposited for synthesis, and how correlated atomic-resolution transmission electron microscopy and atomistic theory are used to understand the forces that guide their assembly into 2D crystals, comparing: (1) PLD directly on TEM grids within custom chambers; (2) conversion of PLD-deposited precursors on TEM grids using laser processing within the TEM. Coupled with *in situ* optical spectroscopy techniques to characterize the material's evolving structure and properties, these novel techniques offer the opportunity to 'close the loop' to guide synthesis for deterministic functionality of 2D materials and heterostructures.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science).

2:00pm **F3-ThA3 Transformation from Amorphous Carbon to Graphene via Nickel Catalyst***, **Hanchao Li (lihanchao@nimte.ac.cn)**, X.W. Li, P.G. Guo, A.Y. Wang,* Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, China

Nowadays, many efforts have been made to obtain high quality graphene from solid carbon source through a simple vacuum thermal annealing process, since this method has the advantage of both low cost and relatively low temperature. In this work, amorphous carbon was used as carbon reservoir and nickel was used as the metal catalyst. A sandwich structure, namely substrate/amorphous carbon/catalyst metal Ni, was designed to prepare graphene. The effect of temperature in the range of 400 °C to 900 °C, type and thickness of the amorphous carbon on the transformation process was investigated. The results showed that for tetrahedral amorphous carbon (ta-C), graphene emerged at 600 °C. Further increasing the temperature to 900 °C enhanced the quantity of graphene, but the quality was poor due to the oversaturated carbon content and the agglomeration of the Ni layer. Decreasing the thickness of ta-C to 2 nm led to graphene of 3-4 layers at 800 °C, where metal-induced layer exchange mechanism was proposed. Based on the transformation of ta-C, the graphene formation by using graphite-like carbon was also investigated. Results demonstrate that nickel/carbon ratio is the most significant factor, which directly decides the quality of graphene. In addition, cooling rate affects the quality of graphene. A medium cooling rate is beneficial to graphene formation.

2:20pm **F3-ThA4 Low-Temperature Synthesis of Vertically Standing Graphene by Microwave-Chemical Vapour Deposition***, I. Vasconcelos Joviano dos Santos,* ***Justyna Kulczyk-Malecka (J.Kulczyk-Malecka@mmu.ac.uk)****, S.J. Rowley-Neale, C.E. Banks, P.J. Kelly,* Manchester Metropolitan University, UK

Graphene is the most commonly studied 2D material due to its exceptional physical and chemical properties, originating from its atomic structure. However, the successful graphene applications are driven by the ability to synthesise it at high growth rates and low temperatures, which enable large-scale production on a variety of substrates. The synthesis of vertically standing graphene (VSG) is of particular interest due to its exposed sharp edges, non-stacking morphology and large surface-to-volume ratio, leading to advanced technological applications including sensors, flexible electronic devices and fuel cells. Plasma-enhanced chemical vapour deposition (PE-CVD) has emerged as a promising technique to synthesise graphene at lower temperatures. The plasma energy drives the CVD precursor decomposition and reaction kinetics, allowing better control over the deposition parameters that tailor graphene properties.

This study presents the growth of VSG on Si wafers in a single step process at relatively low temperatures (<300°C). The samples were synthesised in a bespoke PE-CVD reactor, using a microwave (MW) source to decompose CH_4, H_2 and Ar gas mixtures, and drive the growth process without applying an additional heating source to the substrate. Deposition conditions, such as MW power, gas ratio, and substrate-to-plasma distance were studied to determine their significance on VSG growth, morphology and electrochemical performance. Samples were characterized by SEM, Raman and XPS, which confirmed the vertical nature and sp^2 hybridisation of the deposited graphene. Cyclic voltammetry (CV) was used to determine the intrinsic electrochemical properties of VSG, such as heterogeneous electron transfer coefficient (kº) and the electroactive area (A_{active}). The VSG deposited in this study shows a large surface area, exposed sharp edges and non-stacking morphology. These characteristics are attractive for the development of energy generation and storage devices, such as fuel cells and super-capacitors.

2:40pm **F3-ThA5 Wettability, Structural and Optical Examination of Sputtered Zirconium Oxide Thin Films***,* ***Uttkarsh Patel (uttkarsh1012@gmail.com)****,* McMaster University, Canada*; P. Dave,* Gujarat Forensic Science University, India*; K. Chauhan,* Charotar University of Science and Technology (CHARUSAT), India*; S. Rawal,* McMaster University, Canada

Zirconium oxide films were deposited by reactive magnetron sputtering at different sputtering pressure values of 0.4Pa, 0.7Pa, 1.0Pa and 1.5Pa. The effect of sputtering pressure on structural, hydrophobic and optical properties of deposited zirconium oxide thin films is reported in this research work. Due to this variation during thin film growth, it is observed that zirconium oxide thin films formed have a monoclinic phase with (111) orientation. Its intensity increase with the increase in sputtering pressure from 0.4Pa to 1.5Pa. The contact angle values of 96º for water and 44º for aniline were observed at 0.4Pa. The bandgap of zirconium oxide films increases as sputtering pressure is increased from 0.4Pa to 1.5Pa.

3:00pm **F3-ThA6 Better than Homoepitaxy? van der Waals Layer Assisted Growth of Thin Films***,* ***Koichi Tanaka (koichitanaka@ucla.edu)****,* University of California Los Angeles, USA*; K. Hojo,* Nagoya University, Japan*; A. Deshpande, P. Arias, M.E. Liao, Y. Wang, H. Zaid, A. Aleman, M.S. Goorsky, S. Kodambaka,* University of California Los Angeles, USA

It is generally assumed, and often true, that homoepitaxy yields higher crystalline quality thin films than heteroepitaxy. Studies conducted nearly three decades ago have shown that layered materials, owing to weak van der Waals (vdW) bonding across the layers, can aid in heteroepitaxial growth of layered as well as non-layered materials. In the recent years, two-dimensional (2D) layered materials have been shown to promote 'remote epitaxy', where the 2D layer present at the substrate-film interface does not hinder the epitaxial registry between the film and the substrate. Here, we demonstrate that 2D hexagonal boron nitride (hBN, a = 0.250 nm and c = 0.667 nm) buffer layers improves the crystallinity of sputter-deposited thin films. We provide evidence for this phenomenon via heteroepitaxial growth of body centered cubic metal (Mo), hexagonal MoS_2, and trigonal Ta_2C thin films on hBN-covered Al_2O_3(0001) substrates. Furthermore, our studies indicate that inserting hBN layers at regular intervals results in highly-0002-orientated growth and suppression of polycrystallinity in thicker Ta_2C films.

All our experiments are carried out in an ultra-high vacuum system equipped with facilities for direct current (dc) magnetron sputtering and chemical vapor deposition. hBN layers are grown on single-crystalline Al_2O_3(0001) substrates via pyrolytic cracking of borazine. Mo and Ta_2C thin films are deposited, respectively, via sputtering of Mo and TaC targets in pure Ar discharges, while MoS_2 layers are grown by reactive sputtering of Mo target in Ar-H_2S gas mixtures. The as-deposited layers are characterized using x-ray diffraction (XRD), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS). We observe the growth of single-crystalline Mo(110), MoS_2(0001), and Ta_2C(0001) thin films with notable differences in all the layers deposited on hBN-covered Al_2O_3 (0001) compared to those grown on bare substrates: significantly stronger reflection intensities ω-2θ XRD scans with smaller full-width half maxima and observation of Laue oscillations around the primary peaks. Our results indicate that hBN layers enhance the crystallinity of sputter-deposited thin films.

3:20pm **F3-ThA7 Large Piezoelectric Response of van der Waals Layered Solids***,* ***Cristian Ciobanu (cciobanu@mines.edu)****, S. Manna, P. Gorain, G.L. Brennecka, V. Stevanovic,* Colorado School of Mines, USA **INVITED**

The piezoelectric response, as measured by the piezoelectric modulus tensor (d), is determined by a combination of charge redistribution due to strain and the amount of strain produced by the application of stress (stiffness). Motivated by the notion that less stiff materials could exhibit large piezoelectric responses, herein we investigate the piezoelectric modulus of van der Waals-bonded quasi-2D ionic compounds using first-principles calculations. From a pool of 869 known binary and ternary quasi-2D materials, we have identified 135 non-centrosymmetric crystals of which 48 systems are found to have d components larger than the longitudinal piezoelectric modulus of AlN (a common piezoelectric for resonators), and three systems with the response greater than that of PbTiO3, which is among the materials with largest known piezoelectric modulus. None of the identified materials have previously been considered for piezoelectric applications. Furthermore, we find that large d components always couple to the deformations (shearing or axial) of van der Waals "gaps" between the layers and are indeed enabled by the weak intra-layer interactions. These results have been recently published in Journal of Materials Chemistry.

Topical Symposia
Room Pacific Salon 3 - Session TS1-ThA
Anti- and De-icing Surface Engineering I

Moderators: Alina Agüero, National Institute of Aerospace Technology, Spain, Jolanta-Ewa Sapieha, Polytechnique Montreal, Canada

1:20pm **TS1-ThA1 Ice Adhesion Mechanics and Durable Icephobic Surfaces***,* ***Jianying He (jianying.he@ntnu.no)****,* Norwegian University of Science and Technology (NTNU), Norway **INVITED**

Preventing the formation and accretion of ice on exposed surfaces is of great importance for Arctic operation, renewable energy, electrical transmission cables in air and shipping. While studies on suppressing ice nucleation by surface structuring and local confinement are highly desired, a realistic roadmap to icephobicity for many practical applications is perhaps to live with ice, but with the lowest possible ice adhesion. The key to lower ice adhesion is to maximize the ice-substrate interface-crack driving forces at multiple length scales. Herein, we propose a novel macro-crack initiator mechanism in addition to the nano-crack and micro-crack initiator mechanisms, and demonstrate a new strategy to design super-low ice adhesion surfaces to fatally weaken ice-substrate interface. The results show that PDMS thin films with inner hole structure in two layers approach an ice adhesion strength well below 10 kPa. The introduction of sub-structures into PDMS thin films promotes macro-crack initiators, and is able to reduce ice adhesion strength by ~50% compared with that of PDMS thin films without sub-structures, regardless of layer thickness, curing temperature, weight ratio and the size of inner hole. The ice adhesion can be even lowered to around 1 kPa with porous sponge layer. Therefore, rationalizing the three crack-initiator mechanisms and their interactions at multi-length scales may provide an effective strategy towards designing super-low ice adhesion surfaces.

2:00pm **TS1-ThA3 Low Ice Adhesion Enhanced Electrothermal Ice Protection***, Jin Hu (jin.hu@collins.com),* Collins Aerospace, USA, United States of America*; C. Slane,* Collins Aeospace, USA*; C. Botura,* Collins Aerospace, USA

Collins Aerospace designed an electrothermal ice protection prototype enhanced with a more robust low ice adhesion coating. It was tested on the Advanced Environmental Rotary Test Stand (AERTS) and showed a power saving of 20-30% over an uncoated prototype. By combining low ice adhesion surfaces with electrothermal heaters, the power or energy required can be reduced for shedding ice accretion.

2:20pm **TS1-ThA4 Role of the Thin Coating in the Durability of Icephobic Thin-on-Thick Coating Systems***, Stephen Brown (stephen.brown@polymtl.ca), J. Lengaigne,* Polytechnique Montreal, Canada*; N. Sharifi, A. Dolatabadi,* Concordia University, Canada*; L. Martinu, J.E. Klemberg-Sapieha,* Polytechnique Montreal, Canada

In-flight aircraft icing occurs when supercooled water droplets suspended in clouds collide with exposed aircraft surfaces. The buildup of ice increases the weight of the aircraft while also changing its shape, leading to an increase in fuel consumption and a decrease in lift and thrust. In the worst case scenarios, icing can also cause the malfunction of sensors or moving parts, leading to accidents. Of the potential solutions which exist, superhydrophobic surfaces (SHS) are among the most promising, due to their ability to repel water droplets at sub-zero temperatures and reduce the adhesion strength of any formed ice. When fabricating SHS, a common methodology is to create a surface which exhibits hierarchical roughness, and to coat this surface with a thin hydrophobic topcoat. While this method of fabrication is effective, it also means that the durability of the SHS is intrinsically linked to the durability of this topcoat.

In the present study, we develop a thin-on-thick superhydrophobic coating system, focusing on the durability of the thin hydrophobic layer. The thick portion of the coating system is hierarchically rough TiO_2, deposited by suspension plasma spraying, while the thin portion is a coating stack deposited by plasma enhanced chemical vapor deposition and is based on DLC:SiO_x—diamond-like carbon networked with silicon oxide. DLC:SiO_x was selected for its improved mechanical properties compared to other hydrophobic coatings, with the deposited films having a contact angle up to 95° and a hardness up to 11 GPa, and the whole thin-on-thick system having a contact angle of 159° and a contact angle hysteresis of 3.8°. Durability of the coatings is first assessed through icing/deicing cycling, and the results are compared to TiO_2 samples coated with commonly-used hydrophobic coatings, including stearic acid and fluoropolymer, as well as a sample coated with Rustoleum NeverWet. Following this, the most interesting coatings were subjected to rain erosion tests and accelerated aging tests. The thin-on-thick coating system is shown to offer improved durability over the others, maintaining water droplet mobility after 170 icing/deicing cycles, resisting prolonged UV and high-temperature exposure, and offering a 300-times improvement over the stearic acid in rain erosion tests.

2:40pm **TS1-ThA5 Low Interfacial Toughness Materials for Effective Large-scale Deicing***, Kevin Golovin (kevin.golovin@ubc.ca),* University of Britsh Columbia, Canada **INVITED**

Reducing the interfacial adhesion between ice and a surface could be beneficial to a wide range of commercial activities. Since the 1940s, the adhesion between ice and a surface has been defined by the force, *F*, required to de-bond an area of adhered ice, *A*, typically in shear. The shear ice adhesion strength is then defined as $\tau_{ice} = F/A$, and an increasing body of literature is available delineating the various strategies for minimizing τ_{ice}. In the first part of my talk, I will briefly discuss our efforts aimed at minimizing τ_{ice}, via mechanismssuch as superhydrophobicity, interfacial cavitation, and engendering slip at the ice interface. In the second part of my part I will discuss why this definition of τ_{ice} contains an intractable scalability limit often ignored within the ice adhesion community – large areas of accreted ice will require extremely large forces to remove the ice. I then discuss our recent work understanding materials that circumvent this issue. Such materials, which exhibit Low Interfacial Toughness (LIT), offer the unique property that the force necessary to remove adhered ice becomes independent of the interfacial area – the force needed to remove a few square centimeters is the same as the force needed to remove a few square meters. We design LIT materials using a cohesive zone analysis of the ice-substrate interface mechanics. LIT materials are categorically dissimilar to traditional ice-phobic systems. For example, LIT materials become more effective with decreasing thickness and increasing shear modulus (the opposite is true for ice-phobic materials). These physical parameters make LIT systems particularly attractive for aerospace applications, which durability (requiring high modulus) and added weight (requiring low thickness) are major constraints.

3:20pm **TS1-ThA7 Collins Aerospace - Low Icing Adhesion Testing Methodology for Aerospace Application***, Galdemir Botura (galdemir.botura@collins.com),* Collins Aerospace, USA*; J. Hu,* Collins Aerospace, USA, United States of America*; N. Ching,* Collins Aerospace, USA

Collins Aerospace is leader in non-bleed air ice protection systems for aerospace application. Collins Aerospace has been developing and investigating low ice adhesion materials for many years. For quality assessment of the material / coatings capabilities, Collins Aerospace developed a methodology for testing and assessing its feasibility for aerospace applications. The paper consists of presenting the methodology developed, the reason of each step as well as the equipment used as ice adhesion test apparatus, rain erosion silo and Icing Wind Tunnel.

3:40pm **TS1-ThA8 Limitations of Anti-icing Materials for Aeronautic Applications***, Paloma Garcia (garciagp@inta.es),* National Institute of Aerospace Technology, Spain*; J. Mora,* Isdefe, Spain*; A.A. Agüero,* National Institute of Aerospace Technology, Spain

Atmospheric icing is a severe issue which affects many different sectors in different ways: energy (Eolic), communications (power lines), or transport (trains, ships, aircrafts). In aeronautic, even a thin layer of ice, accreted in a few seconds, can be a serious problem, due to the possibility losing control which imposes accident risks. Modern aircrafts are equipped with effective systems to avoid ice accretion (anti-icing), or favour its release once it accretes (de-icing mode) over the sensitive surfaces.

These systems require energy, and an objective in this field is the use of more efficient systems to decrease the energy requirements, or alternatively, the development of material systems that do not accrete ice called anti-icing materials and therefore no energy supply is required during flights.

Icing mechanisms are not completely understood, and many different surface modification strategies have been explored without sufficient success in recent decades. Most of them are based on low wetting solutions (super-hydrophobicity and high water droplet mobility), low surface energy materials, or biomimetic strategies.

There are some reported promising results, but still far from the anti-icing level, durability and reliability required for use in aeronautical applications. In addition, there are no standard for the different required testing methodologies, complicating the search for solutions which meet aeronautical regulations.

During the PHOBIC2ICE European project several types of coatings, including metallic, ceramic and polymeric materials as well as composites applied by different coating deposition technologies where tested according to a common protocol designed by the project partners. Testing included ice accretion and adhesion of samples produced in laboratory scale icing tunnels, as well as in a large scale icing tunnel in which the coated specimens were rotated at high RPMs during the test.

The results of the diverse anti-icing strategies, using common testing methodologies, indicated some partial trends, but in all studied cases, the anti-icing behaviour is too low to be considered as an alternative to actual anti-icing aeronautic systems despite the high level of super-hydrophobicity exhibited by many samples.

These results, together with many others found in bibliography, raise questions about whether the development of proposed strategies could deal to useful results, or radical changes are needed to advance in real solutions.

4:00pm **TS1-ThA9 Anti-Icing Properties of Silicon and Fluorine-doped Hydrocarbons and their Ice Adhesion Strength***, **Carol Ellis-Terrell (caellis@swri.org)**, R. Wei, M. Miller,* Southwest Research Institute, USA*; M. Zou,* University of Arkansas, USA*; S. Beckford,* Surftec, USA*; K.E. Coulter,* Southwest Research Institute, USA

Ice accumulation on surfaces exposed to cold, moist environments is a significant problem, in the aerospace, automotive, oil & gas industry. As case examples, for aircraft and automobiles, the accumulation of ice causes increased drag leading to increased fuel consumption. For off-shore oil drilling, ice adhesion along the pipe walls can trigger accretion within the pipe leading to oil blockage and consequently extended downtime. In all of the cases, a reduction in efficiency and subsequently increasing cost is experienced.

Two approaches are currently used to prevent ice accumulation; the active approach employs chemical, mechanical, or electrical techniques to remove accumulated ice. The alternative method is a passive approach using coatings and surface engineering practices to generate a water repellent surface. Hydrophobic and superhydrophobic surfaces have an apparent water contact angle of 90° or higher, thus a small water-surface contact area and potentially low ice adhesion. Hydrophobic and superhydrophobic surfaces with a combination of texturing and coating may demonstrate Cassie-Baxter wetting properties with air trapped beneath the water droplet in a particular environment. However, the same surface may switch to a Wenzel state with water in full contact with the surface profile with changing environments.

There are several different methods employed to evaluate ice adhesion to a surface, a few of the most common involves a sheet of ice freezing on the surface and shearing during centrifugation or the removal of a column of ice with a force probe. None of these techniques assess how a single droplet of ice interacts with the surface. Therefore, SwRI designed a custom-built device that allows for in-situ delineation of shear adhesion strength of a single micro-volume ice droplet adhered to the surface.

In this presentation, we will discuss the method used for evaluating the anti-icing and ice adhesion properties of the hydrophobic silicon doped hydrocarbon and superhydrophobic fluorinated hydrocarbon coatings. We will also discuss the correlation between surface roughness and surface energy and its relationship to the shear strength properties of the coatings.

4:20pm **TS1-ThA10 Improving the Efficiency of Electro-thermal De-icing Systems with Icephobic Coatings***, **Jack Brierley (jack.brierley@nottingham.ac.uk)**, X.H. Hou, B. Turnbull, W. Sun,* University of Nottingham, UK

Helicopters operate in a wide range of extreme environments, including low altitude flight through harsh weather conditions that make them susceptible to ice formation on the leading edge of the rotor blades. Electro-thermal heating systems, typically used for rotor blade de-icing, are power-intensive reducing the helicopter operating envelope and flight duration. Durable and repairable icephobic coatings may offer a cost-effective improvement to the efficiency and safety when operating in icing conditions. Stiff and hard filler particles have been implemented to improve the durability of an icephobic polymer coating while increasing the thermal conductivity. Whilst this increases the ability to remove latent heat of freezing it also improves the heat transfer from electro-thermal de-icing systems to the ice-coating interface. Combined with a low ice adhesion strength that aids interfacial cracking and ice shedding, this results in net energy savings of the de-icing system. This energy-saving is shown through laboratory experiments presented in this paper.

Coatings for Use at High Temperatures
Room Grand Hall & Foyer - Session AP-ThP

Coatings for Use at High Temperatures (Symposium A) Poster Session

**AP-ThP1 Effect of Different Addition of Fluoride on Wear Behavior of TC_4 Alloys at Elevated Temperature as Hard Phase and Lubricating Phase*, Zikun Xie (1102729399@qq.com),* *X.F. Cui, G. Jin, E. Liu, W. Su,* Harbin Engineering University, China

In this study, TC4-10CaF_2 (CaF_2 coating) and TC4-10CaF@Ni (CaF_2@Ni coating) coatings were successfully fabricated on the TC4 substrate by plasma cladding technology. The formation and evolution of wear surface was confirmed by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive X-Ray Spectroscopy (EDS). The maximum microhardness of CaF_2 coating and CaF_2@Ni coating were 525.5HV and 417.5HV, respectively. Compared with substrate and CaF_2 coating, CaF_2@Ni coating presented brilliant wear performance from 25 ℃to 600 ℃. The wear loss of CaF_2@Ni coating decreased 75.4% compared to substrate at 600 ℃. The wear mechanism of tribo-layer transited from abrasive wear to oxide wear and adhesive wear with temperature increased. The excellent wear performance depends on the stable and consecutive oxide layer. No accumulation of fluoride was found. Through the analysis of the wear loss and the SEM images of the wear surface, the tribological behavior of CaF_2 coating was subjected by the softening of CaF_2. Meanwhile, the soft Ni@CaF_2 promoted the formation of dense oxide layers at high temperature.

Keywords: TC4/CaF_2 and TC4/CaF_2@Ni coatings; Plasma cladding; Friction and wear

Acknowledgements

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**AP-ThP2 Anodic Plasma Electrolytic Deposition of Composite Coating on Ferrous Alloys with Low Thermal Conductivity and Excellent Thermal Stability*, Chen Zhao (zhao15e@uwindsor.ca),* *J. Sun, X.Y. Nie,* University of Windsor, Canada

To improve the thermal efficiency of automotive engines, this work is to prepare a ceramic coating as thermal barrier coating (TBC) on ferrous alloys with excellent adhesion by plasma electrolytic aluminating (PEA) process [1], an anodic plasma electrolytic deposition process. The PEA process was conducted in an aluminate-contained aqueous electrolyte under a high voltage. The coating has superior adhesion (>60MPa) and low thermal conductivity (~1W/mK) measured by the pull-off test and steady-state heat flow method, respectively. Scanning electron microscope (SEM) observation reveals that the coating has numerous micropores. X-ray diffraction (XRD) analysis shows that the coating mainly consists of α-Al_2O_3 and hercynite ($FeAl_2O_4$), which indicated that the substrate involved in the plasma oxidation reaction and the coating had a metallurgical bonding to the ferrous substrate. The α-Al_2O_3 phase with numerous micropores contributed to the low thermal conductivity of the coating. The hercynite phase was considered critical for enhanced adhesion properties of the coating. After thermal shock tests quenching from 425 °C to 20 °C water for 10 times, the coating's microstructure, phase composition, thermal conductivity, and coating adhesion did not show obvious changes. The results demonstrate that the ceramic composite coating may prove useful for thermal management of automotive engines.

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AP-ThP3 Oxidation of NiCrAlY Coating Deposited by Selective Laser Melting for Thermal Barrier Coating Application*, E. Copin,* ***Damien Texier (damien.texier@mines-albi.fr)****, A. Flores, J. Lee,* ICA, France*; M. Terner, H.-U. Hong,* Changwon National University, Republic of Korea*; P. Lours,* ICA, France

Designing high temperature jet and power plant turbine components is more and more complex in terms of geometry and in multi-layered microstructure, including thermal barrier and/or environmental coating systems, to satisfy both structural and environmental specifications. Selective laser melting (SLM) technique is particularly appropriate for manufacturing such components. In the present investigation, the environmental integrity, *i.e.* the high temperature oxidation, of fully SLM-processed NiCrAlY overlaying In625 parts was investigated between 800°C and 1000°C. Freestanding bulk NiCrAlY, In625 and bi-materials were fabricated using SLM. To be representative of coated components, solely three thin layers of NiCrAlY powder were lasered at the surface of In625 to form the bi-materials. Thin samples were then extracted using a gentle mechanical polishing technique in order to ensure repeatable thickness and surface finishing of the specimens [1]. It is worth noting that the fabrication of SLM NiCrAlY was particularly difficult and results in extensive cracking within NiCrAlY specimens in both bulk and coating fabrication routes. As expected, bulk NiCrAlY and bi-materials demonstrated an improved oxidation behavior compared to In625. However, the formation of oxides at the surface of the bi-layer material differs from that of the bulky freestanding NiCrAlY. Indeed, the oxidation of the bi-layer material results in regions with a dense and continuous Al_2O_3 layer and regions composed of a mixture of external Cr_2O_3 and internal Al_2O_3. As a comparison, the oxidation of bulky freestanding NiCrAlY results in a dense and continuous Al_2O_3 layer in this temperature range. Extended EDS maps at the surface of the bi-material highlighted a heterogenous distribution of constitutive elements of the NiCrAlY coating, resulting in some regions to an Al activity lower than the one required for the formation of a continuous and dense Al_2O_3 layer [2]. Low Al activity and high Al activity regions were related to the topography of the SLMed surface and correspond to peak and valley regions, respectively. Furthermore, cracks were mainly found in high Al activity regions, where the brittle β-NiAl phase is present. The fabrication of coated but small components with a brittle coating by SLM is not trivial and need further investigations.

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AP-ThP4 Development of Aerospace Turbine Blade Thermal Barrier Coating*, Yu-Ming Liu (gbabs26785@gmail.com),* National Taipei University of Technology, Taiwan

This study uses suspension plasma spraying(SPS),developed a thermal barrier coating(TBC) with high life and good thermal insulation. Because aircraft gas turbine engines operate in harsh high temperature environments, The use of a thermal barrier coating allows the superalloy under the coating to be internally cooled, and also reduces the surface temperature of the superalloy, allowing the gas engine to operate at gas temperatures well above the melting temperature of the superalloy, thereby improving engine performance and efficiency, making the engine more durable.The use of suspension spraying can obtain top layers of different microstructures at relatively low cost, thereby increasing the life of the thermal barrier coating.In this experiment, isopropanol and commercial yttrium stabilized zirconia (8YSZ) powder were used to prepare the suspension, and then the prepared suspension was externally connected to atmospheric plasma spraying (APS) and then melted and deposited on the substrate. The effect on the coating was investigated by adjusting the working distance of the plasma gun tip and the amount of air pressure flow of the suspension atomization.After spraying the samples will go to x-ray diffraction analysis, scanning electron microscope, tensile tester, high-temperature heat cycle furnace and computer software to observe the composition, surface morphology and cross-section microstructure of the coating. The strength of the coating and the effect of porosity on the life of the coating were analyzed.

AP-ThP5 Preparation of Solid Oxide Fuel Cell Electrolyte by Thermal Spraying*, Yu-Cheng Lai (semaj84726ma@gmail.com),* National Taipei University of Technology, Taiwan

Solids oxide fuel cells (SOFCs) have a wide range of applications because of it has an efficient energy chemical energy conversion system, high power density, and environmentally friendly, besides, the operation needs at high temperature so it doesn't require expensive catalyst. In this study is to create a method for measuring tubular SOFC. Tubular SOFC is better than flat SOFC because the sealing in high temperature for measuring battery. Because the metal is conductor, it uses glass or ceramic materials stick the components that need to sealed.This study the full cell was prepared using a porous nickel tubular as a substrate, and a Ni-8YSZ cermet anode were prepared by flame spraying. A high-density electrolyte were prepared by suspension flame spraying. A 8 mol% of yttria-stabilized zirconia (8YSZ) nano powder was dispersed in isopropanol. A high-density electrolyte can prepared by spraying isopropanol using atomized feed. The last step a Lanthanum Strontium Manganite (LSM) were prepared in electrolyte by flame spraying.

AP-ThP6 Aging Behavior of Ag-Pt Alloy Thick Film on AlN at High Temperature by Joule Heating, ***Jae-Seong Jeong (jjseicp@keti.re.kr)***, *An An,* Korea Electronics Technology Institute (KETI), Republic of Korea*; Sa Sa,* SEMES CO., LTD, Republic of Korea

A ceramic heater by joule heating has the structure of Ag75Pt20(wt%) alloy thick film on AlN(aluminun nitride). Metallization layer for heater was created by screen printing and then firing AgPt alloy to thermal annealed AlN substrate. AlN substrate has the size of 120mm x 40mm x 4mm (XYZ). AgPt alloy has the thickness of approximately 20µm, the pattern width is 160µm, and the pattern space is 340 µm. Electrical resistance was 10 ohm. Heat temperature was controlled using AC power in a zero-crossing method.

In this paper, the changes in electrical characteristics and thermodynamic properties of AgPt alloy on AlN were analyzed according to aging as heating temperature varied. Heater DUT (AgPt alloy on AlN, AgPt/AlN) was created to be 30 ohm by connecting three in a series. Input power was adjusted within the range of 10~50%, and the temperature was set between 200°C ~ 700°C. AgPt/AlN heater was aged for approximately 3,000 hours per input power to measure the changes in electrical characteristics. Input power and heat temperatures were 10%(~200°C), 20%(~300°C), 40%(~500°C), and 50%(~600°C). The changes in resistance increased first with aging at each heat temperature and then decreased afterwards. As the heat temperature increased, the maximum time which decreases after the resistance increase was reduced. The resistance decreased from the electrode of AgPt metallization to which bias is applied and proceeded toward the inner part. The physical analysis of AgPt/AlN coupon, which the resistance has lowered to 20% or less, shows that AgPt alloy, which has been manufactured in a flat shape through screen printing, was changed to a random shape through thermal aging. The phase of AgPt alloy changed and then separated into Ag-rich and Pt-rich phases. Separated phases decreased the resistance and increased the capacitance, thus inducing the changes in electrical characteristics. Electrical characteristics and material thermodynamic characteristics were analyzed through high-temperature aging of Ag-Pt/AlN heater. Through such analysis, prognostic health monitoring factors of Ag-Pt/AlN heater were deduced, thus enabling service lifetime predictive maintenance period prediction.

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AP-ThP8 Corrosion Behavior of Volcanic Ash on Sintered Gd_2SiO_5 for Environmental Barrier Coatings, ***Kim Seung-Hyeon (kim.seung-hyeon@kyudai.jp)***, Kyushu University, Japan*; K. Byung-Nam,* National Institute for Materials Science (NIMS), Japan*; J. Byung-Koog,* Kyushu University, Japan

High temperature corrosion behavior was evaluated by gadolinium monosilicate (Gd_2SiO_5) with volcanic ash. Gd_2SiO_5 specimens were fabricated by spark plasma sintering (SPS) method at 1400°C for 20 min. The volcanic ash sprinkled sintered Gd_2SiO_5 specimens were exposed at 1400°C for 2, 12, and 48 h by heat treatment. The result of heat treatment at 1400°C. Represents volcanic ash that is not completely melted. In addition, it was confirmed through X-ray diffraction measurement (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectrometry (EDS) analysis that Gd_2SiO_5 specimens was stacked on the surface. At the cross-section of sintered Gd_2SiO_5 specimens volcanic ash, sintered Gd_2SiO_5 specimens were partially dissolved in the molten volcanic ash. The largely reacted region covered the top surface of the sintered Gd_2SiO_5 specimens which was mainly form volcanic ash. Therefore, the degradation of surface under volcanic ash deposits became to be severe in longer heat treatment time condition.

AP-ThP9 Lowering Costs by Improving Efficiencies in Biomass Fueled Boilers: New Materials and Coatings to Reduce Corrosion (BELENUS), *A. Illana, V. Encinas-Sánchez, M.T. de Miguel, M.I. Lasanta, G. García-Martín,* ***Francisco Javier Pérez (fjperez@ucm.es)***, Universidad Complutense de Madrid, Spain

The primary objective of BELENUS is to lower bioenergy CAPEX and OPEX by an average of 5 and 60% respectively. This will be addressed by preventing or mitigating corrosion as the main limiting factor through a holistic approach to prevent corrosion in the boiler, in particular in superheater (SH) tubes: a) new surface engineering: biomass corrosion highly resistant coatings on creep resistance materials; b) new strategies of welding and bending for coated tubes improving the quality and efficiency of boiler components; and c) new online corrosion monitoring system specifically designed for biomass CHP plants. In addition, the BELENUS solution will impact on other LCOE parameters by improving efficiency in the conversion (up to 42%), increasing a 5% the operational hours of the plant and plant life time (5 years) and reducing the fuel expenditure of the plant by optimising its use and providing flexibility by allowing the use of different types of biomass. Improved performance for high temperature material systems through the technological breakthroughs, will be evaluated and validated an innovative test protocol. Finally, modelling and lifetime prediction tools will be developed and cost analysis and Life Cycle Analysis (LCA) undertaken so the optimum materials and coatings are chosen from the durability, economic and environmental perspectives, maximising the sustainability in economic and environmental terms. BELENUS brings together a multidisciplinary consortium comprising the main stakeholders with leading utilities, steel and tube developers, boiler designer and specialized research institutions from across Europe. This synergy allows a direct transfer of results in TRL5 to be obtained in BELENUS as technical base to go further to higher TRL into commercial biomass electric power plants within less than 5 years.

AP-ThP10 Microstructural Growth and Oxidation Performance of Ti_xSi_y on ɣ -TiAl, *J. Crespo Villegas, S. Brown, E. Bousser,* Polytechnique Montreal, Canada*; M. Cavarroc,* Safran Tech, France*; S. Knittel,* Safran Aircraft Engines, France*; L. Martinu,* ***Jolanta-Ewa Klemberg-Sapieha (jsapieha@polymtl.ca)***, Polytechnique Montreal, Canada

For several decades now Ti-Al intermetallic compounds have been considered attractive materials for structural applications because of their low density and good mechanical characteristics. One area of particular interest is the use of γ-TiAl for low pressure turbine components of aircraft engines, as a replacement for much heavier Ni-based superalloys. Despite this advantage in terms of density, the usage of γ-TiAl is currently limited to the coldest low pressure turbine stages of the engine, due to its oxidation susceptibility above 750°C.

In the current work, we explore the oxidation protection of γ-TiAl using titanium silicide (Ti_xSi_y) coatings which have been shown to have strong temperature stability (melting point > 2000°C), and a relatively good oxidation resistance due to the growth of a protective SiO_2 oxide scale. The Ti_xSi_y coatings are synthesized in a two-step process: silicon is first deposited on γ-TiAl substrates by RF magnetron sputtering, and the coated substrates are then thermally annealed at 950°C in vacuum. The influence of (i) silicon thickness and (ii) thermal annealing time on the growth and the microstructure of the titanium silicides is investigated, with tested values ranging from 3–9.5 µm of silicon and 2-24 hours of thermal annealing. Both of these parameters are shown to directly affect the thickness and composition of the different zones in the γ- TiAl/Ti_xSi_y coating system. In particular, it is noted that beginning with a thicker silicon layer results in more varied compositions of Ti_xSi_y, and that increasing the annealing time improves the uniformity of each individual zone as well as increasing the total thickness of the coating system.

Following annealing, the oxidation performance of the coatings is tested by exposing them to a temperature of 900°C in air for 100 hours. The mass gains during oxidation are recorded, and changes to the chemistry and microstructure of the samples are analyzed. Oxidation of the coated samples is estimated to be parabolic, and all samples show a marked improvement in oxidation resistance, with mass gains 2-3 times lower than those observed for the bare γ-TiAl.

AP-ThP11 An Ab Initio Guided Approach for Enhancing the Oxidation Resistance of Period Vi Carbides and Borides, ***Thomas Glechner (thomas.glechner@tuwien.ac.at)***, *E. Aschauer, R. Hahn,* TU Wien, CDL-SEC, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; J. Ramm, H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* TU Wien, CDL-SEC, Austria

Period six transition metal carbides and borides, i.e. binaries such as WB_2 and TaB_2 or ternaries like $W_{1-x}Ta_xB_2$, exhibit extraordinary phase stability and mechanical properties imposing them as highly interesting coating materials for UHT applications. However, they are limited by their relatively poor oxidation resistance obtaining linear scale growth kinetics and the formation of partly volatile oxides already in the range of 0.1 to 0.2 T_m. To gain an in-depth knowledge on the scale formation of period VI ceramic coating materials in oxidative environments, we apply an ab initio guided approach (Density Functional Theory) to link initial steps of the oxidation process with experimental observations.

We used ab initio Molecular Dynamics applying VASP to model oxidation of period VI transition metal carbides and diborides at different temperatures (in the range of 400 to 1200 °C). The simulations were then compared with the formed oxides of the corresponding coating materials. The coating materials were synthesized using PVD based deposition techniques and oxidized using a DSC/TG system. Furthermore, the as deposited thin films and the formed scales were in depth analysed by HR-TEM, APT, as well as XRD.

AP-ThP12 High-temperature Oxidation and Tribological Properties of Al–Cr–Si–N Nanocomposite Coatings Deposited by Filtered Arc Ion Plating Process*, **In-Wook Park (ipark@kitech.re.kr)**, S. Heo, J.-H. Kim, W.R. Kim,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

High-temperature oxidation behavior and tribological property of nanocomposite coatings is very important characteristics for application of machining and cutting tools. Quaternary Al–Cr–Si–N nanocomposite films with various compositions were deposited onto WC-Co and Si wafer substrates using a filtered arc ion plating technique. The composition of the films were controlled by different combinations of $CrAl_2$ and Cr_4Si composite target power in a reactive gas mixture of high purity Ar and N_2 during depositions. The instrumental analyses revealed that the synthesized Al–Cr–Si–N films with Si content of 2.78 at.% were nanocomposites consisting of nano-sized crystallites (3-7nm in dia.) and a thin layer of amorphous Si_3N_4 phases. The nanohardness of the Al–Cr–Si–N films exhibited the maximum values of ~42 GPa at a Si content of ~2.78 at.% due to the microstructural change to nanocomposite as well as solid-solution hardening. The Al–Cr–Si–N film shows superior result of oxidation resistance at 1050ºC for 30 min in air. Based on the XRD and GDOES analyses on the oxidized films, it could be revealed that the enrichment of Al (17.94at.%) and Cr (26.24at.%) elements in the film leads to form an Al_2O_3 and Cr_2O_3 layer on the Al–Cr–Si–N film surface. Furthermore, high-temperature tribological properties were evaluated by ball-on-disc tribometer with Inconel testing balls in the temperature range 25 to 750 ºC. The testing parameters were as follows: normal load of 3 N, linear sling speed of 20 cm/s, and wear track radius of 3.3 mm. In this study, the microstructural changes on the mechanical properties and oxidation behavior and high temperature tribological properties with various compositions in the Al–Cr–Si–N nanocomposite films were discussed and correlated with the deposition parameters for cutting and milling performance of the tools.

AP-ThP13 Modeling of Coating Thickness in Electrostatic Spray Deposition using Response Surface Methodology and Artificial Neural Network*, **Uma Maheshwera Paturi (maheshpaturi@gmail.com)**,* CVR College of Engineering, Hyderabad, India*; N.S. Reddy,* Gyeongsang National University, South Korea*; R.K. Gunda, S.K.R. Narala,* BITS Pilani Hyderabad Campus, India

To improve the quality and productivity of costly and time-consuming electrostatic spray deposition (ESD) coating process, it is necessary to model and predict the process performance with respect to its operational parameters. In this aspect, predictive modeling through artificial neural network (ANN) is one of the most popular soft computing techniques, an alternative to conventional statistical response surface method (RSM) technique. The current study attempts to model the coating thickness in complex electrostatic spray deposition (ESD) coating process using RSM technique and relate its prediction capability with the ANN model. For this task, RSM and ANN models were developed for the real-time ESD experiments conducted according to Taguchi's L27 (3^{13}) orthogonal array-based design of experiments (DOE). The optimum ANN model with 3-6-6-1 architecture consists of 0.6 momentum term and 0.3 learning rate with attained mean squared error (MSE), absolute error in prediction (AEP) of trained and test data are 0.000334, 0.197 and 0.54365 respectively. From the results presented, the Pearson's correlation coefficient (*R*) value with ANN model for the training and testing data were determined as 0.993, 0.921 respectively; whereas, with RSM model, *R*value for corresponding data was estimated to be 0.949 and 0.882 respectively. The outcome of this study conclude that the use of ANN modeling approach can endow a possible substitute to ESD process optimization as well as curtailing time-consuming and expensive experimental investigations.

Hard Coatings and Vapor Deposition Technologies
Room Grand Hall & Foyer - Session BP-ThP

Hard Coatings and Vapor Deposition Technologies (Symposium B) Poster Session

BP-ThP1 Behavior of Partially Oxidized Metal Targets*, **Jiri Houska (jhouska@kfy.zcu.cz)**, T. Kozak,* University of West Bohemia, Czech Republic

We investigate the oxidation of a wide range of metal surfaces by ab-initio calculations. The metals of interest span from transition metals (Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) through noble and post-transition metals (Cu, Ag, Au, Zn, Cd) to the main group (Al) [1,2]. We go through a wide range (up to 329 per metal) of distributions of O atoms on a partially oxidized metal surface. First, we focus on the qualitative information whether the preferred distribution of O atoms is heterogeneous (stoichiometric oxide + metal; e.g. Al or La), homogeneous (substoichiometric oxide; e.g. Ti or Zr), homogeneous at low surface oxygen coverage and heterogeneous at high surface oxygen coverage (e.g. Sc or Y), etc. This is of crucial importance for the quantities such as secondary electron emission coefficient, which correspond to a weighted average of those of stoichiometric oxide and metal only in the case of heterogeneous oxygen atom distribution. Second, we correlate these qualitative results with the known formation enthalpies of oxides of various compositions. Third, we provide the quantitative values of adsorption energies corresponding to the energetically preferred O atom distribution for various partial coverages of various metals by O. We find that the dependence of adsorption energy on the surface oxygen coverage can be decreasing (e.g. Al or La), increasing (e.g. Ti or Zr), concave (e.g. Sc or Y), etc. These data also include the information about the maximum stable surface oxygen coverage (nonzero but lower than 100% for Cu, Ag, Zn, Cd). Fourth, we demonstrate one use of these results by presenting Monte Carlo simulations of sputtering. Fifth, we utilize the theoretical results in order to explain the experimental results, such as the time dependence of the magnetron voltage during sputter cleaning of oxidized metal targets (monotonic e.g. for Al but non-monotonic e.g. for Ti).

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BP-ThP2 Effects of Cu Metal Barrier on Electrical Stability and Reliability of Porous Low-dielectric-constant Materials*, **Chih-Yen Lee (ck7766@gmail.com)**, Y.L. Cheng,* National Chi-Nan University, Taiwan

Porous carbon-doped oxide (CDO) film is a promising low-dielectric-constant (low-*k*) material used as inter-metal-dielectric (IMD) for Cu interconnects in advanced technological nodes. To prevent Cu from diffusing into the low-*k* dielectric film and induces the electrical instability and reliability degradation, a metal Cu barrier layer is needed to insert between Cu and low-*k* films. This study compares the effects of Co and Ru barriers deposited by physical vapor deposition (PVD) on the electrical characteristics and reliability of the CDO film. Experimental results indicated that Co barrier has better ability against Cu diffusion, enhanced adhesion, and less trap generation rate induced by electric stress. Both Co and Ru barriers caused damage to the underlying CDO film during PVD process. Co barrier induced more damage due to a less deposition rate, resulting in longer VUV light irradiation emitted by Ar plasma. Consequently, Co metal is the promising Cu barrier, but an issue of severe damage on the porous CDO film during deposition is required to be solved.

BP-ThP3 Nanolayer Ti-Al-O-N Hard Coatings for Corrosion Protection in Electrolytes Simulating Polycarbonate Melt Processing Conditions*, T. Brögelmann, K. Bobzin,* Surface Engineering Institute - RWTH Aachen University, Germany*; G. Grundmeier, T. de los Arcos,* Technical and Macromolecular Chemistry - University of Paderborn, Germany*; N.C. Kruppe,* Surface Engineering Institute - RWTH Aachen University, Germany*; S. Schwiderek,* Technical and Macromolecular Chemistry - University of Paderborn*; **Marco Carlet (carlet@iot.rwth-aachen.de)**,* Surface Engineering Institute - RWTH Aachen University, Germany

To protect forming tools and components from abrasion, adhesion and corrosion, the application of thin hard coatings by physical vapor deposition is state of the art. The use of a hybrid coating technology, consisting of High Power Pulse Magnetron Sputtering (HPPMS) and direct current Magnetron Sputtering (dcMS), allows a combination of the advantageous properties of HPPMS, such as a dense morphology, high hardness and smooth surface, with the high deposition rates of dcMS. Within the scope of this work, a new multilayer coating of the system Ti-Al-O-N was developed. The coatings were deposited using an industrial coating unit. Cold work steel AISI 420 (X42Cr13, 1.2083) was used as substrate material. The coatings consist of a metallic titanium bond coat and a nitride nanolayer TiN/AlN interlayer was deposited. The nanolayer coating architecture leads to a dense, compact and fine crystalline morphology with smooth surfaces. Finally, an oxynitride toplayer with two different oxygen contents was applied. The morphology, chemical and phase composition of the coatings were examined by scanning electron microscope, electron probe micro analysis and X-ray diffraction. The chemical composition of the surface was measured by X-ray photoelectron spectroscopy. In order to investigate the corrosion protection relevant for polycarbonate melt processing, electrochemical impedance spectroscopy and linear sweep voltammetry were carried out in borate buffer, $NaClO_4$ as well as carboxylic acid containing electrolytes. In addition to the corrosion tests, a comprehensive failure analysis of the samples was conducted by scanning electron microscope and atomic force microscopy. The multilayer coating with increased oxygen content in the oxynitride top layer shows the best corrosion resistance of the investigated coatings. The results indicate that aluminum was selectively dissolved from the coating during the corrosion tests and that an increased titanium content in the outer surface region promotes the corrosion resistance.

BP-ThP4 Mechanical and Tribological Performance of V-C-N Coatings Deposited by RF Magnetron Sputtering*, L. Aissani,* Larbi Ben M'Hidi University, Algeria*; **Akram Alhussein (akram.alhussein@utt.fr)**,* University of Technology of Troyes (UTT), France*; C. Nouveau,* ENSAM Cluny, France

Vanadium nitrides are known as hard and wear resistant materials widely used for cutting tools and other components. Vanadium carbides present excellent properties at high temperature, such as good wear resistance and high hardness, due to the very fine grain dispersion in the films. This work aims to show the influence of the following deposition parameters on the structure, mechanical and tribological properties of V-C-N thin films deposited by RF magnetron sputtering: nitrogen partial pressure, Ar-N_2 deposition atmosphere and film thickness. VN, V–C-N coatings were deposited on silicon wafers and XC100 steel substrates and characterized with X-ray diffraction, XPS, EDS, SEM, nanoindentation and tribological tests.

Controlling the gas pressure in the deposition chamber is important to elaborate desirable coatings (good adhesion, structure and performance). It has been found that compared to the VN system, the V–C-N films presented a smooth surface based on pyramidal morphology. Films deposited at 0.06 Pa presented the best properties: highest hardness of 26.1 GPa and lowest friction coefficient of 0.42 [1].

The Variation of nitrogen percentage in the deposition camber (10 - 20%) and the film thickness (0.26 – 2.5 µm) influenced significantly the film structure, hardness and wear resistance. Multi phases of V2N and VN were formed and the thick films containing more nitrogen were slightly dense compared to the thinner ones [2].

Keywords: *Vanadium carbonitride thin films, PVD, microstructure, mechanical properties, tribological performance.*

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BP-ThP5 Correlation Between the Plasma Analysis and Properties of the Films of ZnO-Au Deposited by the Hybrid Technique Combining Pulsed Laser Ablation and Magnetron Sputtering*,* ***Osmary Depablos-Rivera (osmarydep@yahoo.com)**, R. Álvarez-Mendoza, M. Martínez-Fuentes, C. Sánchez-Aké,* Universidad Nacional Autónoma de México, México*; T. García-Fernández,* Universidad Autónoma de Ciudad de México, México, Mexico*; S. Muhl, M. Villagrán-Muniz,* Universidad Nacional Autónoma de México, México

The hybrid technique that combines pulsed laser deposition (PLD) and magnetron sputtering (MS) was implemented to prepare films of ZnO-Au. Individual ZnO and Au films were also deposited by the individual techniques MS and PLD, respectively. The individual deposits and their plasmas were studied as a reference to understand the effects of the combination of the plasma. The plasmas were diagnosed by optical emission spectroscopy (OES) during all of the deposition processes. The aim of this work is to correlate the plasma analysis with the properties of the films. The processes that involved MS were carried out applying 150 W, while the processes with PLD were done varying the pulse laser fluence at 4.5, 13.6 and 20.9 J cm^{-2}. All of the deposition processes were done under Ar atmosphere (0.67 Pa), the substrates were heated at 400 °C, and the time deposition was 20 min. The films were characterized by profilometry, scanning electron microscopy, atomic force spectroscopy and X-ray photoelectron spectroscopy. The thicknesses of the Au films decreased as the laser fluence increased, this revealed the loss of material from the films. However, the decrease of the thicknesses was not observed in the ZnO-Au films. Even, the thicknesses of the combined films were larger than the sum of the thicknesses of the individual films. This suggests that the combination of plasmas enhanced the deposition rate. The morphology and topology results revealed that the combined films were different and less rough than the ZnO films due probably to the incidence of energetic species from PLD. The composition data showed that Au content increased with the laser fluence in the combined films and it was incorporated as a secondary phase homogeneously distributed throughout the thickness. The OES results allowed to identify and to study the emission evolution of neutral atoms of Au, Ar and Zn, and single-ionized Au atoms. The loss of material during the individual deposition of Au films was evidenced by the increase of the emission of Au atoms in front of the substrates. However, the Au emission was not strong in front of the substrates during the hybrid deposition, while the Zn emission was. The Zn excitation reveals the energy loss of the Au species by the collisions, and their final energy was not enough to cause the removal of material from the films, hence the deposition rate improved.

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BP-ThP6 Pulse Synchronized Substrate Bias for the HPPMS Deposition of (Cr,Al)N*,* *K. Bobzin, T. Brögelmann, N.C. Kruppe, M. Engels, **Dennis Christopher Hoffmann (hoffmann@iot.rwth-aachen.de)**, C. Schulze,* Surface Engineering Institute - RWTH Aachen University, Germany

In a high power pulse magnetron sputtering (HPPMS) process a substrate bias is applied to affect the ions in the coating chamber and therefore the coating properties. For industrial coating processes there are two main modes to apply the substrate bias. While the influence of a continuous bias and its effect on plasma and coating properties were the subject of many previous studies, the effect of a pulsed and synchronized substrate bias on a HPPMS process is more complex. For this reason the present experiments on an industrial scale coating unit are focusing on the identification of correlations between plasma and coating properties for a (Cr,Al)N process while using pulsed substrate bias. The measurements regarding the plasma properties were carried out on the substrate side. These investigations should point out the significant potential of plasma diagnostics for measuring plasma properties to contribute to improved coating processes using pulsed substrate bias U_B. For this purpose a substrate bias synchronized to the HPPMS pulse is used. As part of the plasma characterization the Debye sheath thickness s_D was determined by langmuir probe (LP), the ion flux and mean ion energy by retarding field energy analyzer (RFEA) and the relative line intensities and ratios by optical emission spectroscopy (OES). The values of the pulsed substrate bias were varied from U_B = 0 V to U_B = –250 V. Both, the pulse-on-time of the substrate bias $t_{on,B}$ and the pulse-on-time of the cathode t_{on} were 40 µs. The delay between the HPPMS pulse and substrate bias pulse was chosen to zero. The power P and frequency f were hold constant during each measurement. As part of the coating characterization the chemical composition was analyzed by glow discharge optical emission spectroscopy (GDOES), the indentation modulus E_{IT} and the indentation hardness H_{IT} by nanoindentation (NI), the phase composition by means of X-ray diffraction (XRD) and the coating thickness and morphology by scanning electron microscope (SEM). The correlations of different plasma and layer properties are discussed and compared with investigations using continuous substrate bias. For the present measurements it was found that with increasing pulsed substrate bias U_B the Debye sheath thickness s_D and the mean ion energy E_i are increasing significantly. An impact of the Debye sheath thickness s_D and the mean ion energy E_i on the coating thickness was proven by SEM.

BP-ThP7 Fracture-related Characteristics of TiN Films at Elevated Temperatures*,* ***Julian Buchinger (julian.buchinger@tuwien.ac.at)**,* TU Wien, Austria*; L. Löfler,* Montanuniversität Leoben, Austria*; J. Ast, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P.H. Mayrhofer,* TU Wien, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; M. Bartosik,* TU Wien, Austria

Providing experimental and theoretical viewpoints on widely uncharted territory, we examine the fracture toughness and its related properties of TiN films at high, i.e. application-relevant, temperatures. For the experimental side, we conduct in situ micromechanical bending tests on freestanding cantilevers of a reactively sputtered TiN film at temperatures ranging from room temperature (298 K) to 773 K. In doing so, we register a marginal decrease of the fracture toughness K_{IC} up until the deposition temperature of 653 K. Once this temperature is exceeded, the fracture toughness is irreversibly reduced from 2.9 ± 0.1 to 2.5 ± 0.1 MPa√m.

Our theoretical groundwork, constituted by molecular dynamics (MD) & density functional theory (DFT) calculations, shows an insignificant decrease of the (100), (110), and (111) surface energies over a temperature range spanning from 0 K to 1000 K. Based on these results, we predict a theoretical decrease of K_{IC} of 4 to 7 %, depending on the orientation.

In tandem with X-ray diffraction, and nanoindentation data, we identify the recovery of growth defects (i.e. point defects, and dislocations) as the main contributing factor to the experimentally observed decrease in toughness. Furthermore, we observe no substantial influence of temperature on the fracture behaviour of TiN films, neither experimentally (up to 773 K), nor theoretically (up to 1000 K).

BP-ThP8 High Photoresponsivity Sensor with Stannic Oxide Thin Film Transistor based Architecture, ***Yu-Chuan Chiu (w4204ww@gmail.com)****, P.-T. Liu, D.-B. Ruan, K.-J. Gan, C.-C. Hsu, S.M. Sze,* National Chiao Tung University, Taiwan

With the rapid progress and continuing improvements of thin film transistor (TFT) technologies over the past few years, TFT display panels have been demanded not only for screens but also for other optical input functions. In order to develop the sensing application, a high photoresponsivity and ambient-stable material is needed. In this report, a p-type stannic oxide (SnO) thin film is applied as the active layer of TFT for its high optical sensitive characteristic. As a result, the photo sensor TFT exhibits a high optical responsivity and excellent signal to noise ratio under the light illumination. It may provide a new choice for the future embedded optical photosensor with advanced touch function.

BP-ThP9 Incorporation Of Metallic Nanoparticles On Diamond-Like Carbon Films For Combustion Engine Components Using Dc Pulsed Pe-Cvd With Additional Cathode., ***Marco Ramos (marco.macrol@hotmail.com)****,* Universidade do Vale do Paraiba - UNIVAP- Brazil, Brasil*; F.O. Kolawole, L.B. Varela,* University of São Paulo, Brazil*; V.J. Trava-Airoldi,* National Institute for Space Research - INPE, Brazil*; A. Tschiptchin,* University of São Paulo, Brazil

1. Introduction

Diamond-like carbon (DLC) coatings has become very attractive for various industrial applications, such as cutting tools, automotive engines, biomedical implants, micro-electromechanical devices (MEMS). Due to their surface energies and ability to interact with lubricants to form surface protective films, good adhesion with substrate, increased wear resistance, improved electrical conductivity, decreased internal compressive stresses during deposition and thermal stability there are used in automobile components.

In the automobile industry, DLC coatings are usually applied on combustion engine components such as piston, tappet, camshaft, piston rings and gudgeon pin, valve stem and head and rocker arm. DLC coating helps in reducing friction and wear of the moving parts. However, there are challenges facing the use of DLC coated components during service, which are; internal compressive stresses, low adhesion and low thermal stability leading to failures such as rolling contact fatigue, micro-pitting, delamination, oxidation and scuffing.

Hardness and internal compressive stress increase with increasing sp^3 content (sp^3/sp^2) ratio in DLCs. Internal compressive stress for DLC coatings in tribological applications is not good, due to the elastic strain energy that drives fractures along the coating/substrate interface, leading to delamination through blistering. The addition of non-metals (Si, N, F or O) or metals (W, Cr, Ta, Ti, Mo or Cu) can improve thermal stability of DLC up to about 500 o C. Above, 500 o C transformation of sp^3 to sp^2 begins to occur leading to graphitization.

2. Experimental or **Theory**

This paper analyzes the morphological and structural characterization using SEM, and Raman spectroscopy to analyze atomic arrangement. The roughness analyze was made using optical profile. Tribological behavior was analyzed by linearly reciprocating wear tests in high temperature around 500˚C. Adhesion was tested according to the VDI3198 standard. The hardness was measured using nanoindentation.

3. Results and Discussions

This work will discuss the microstructure in their different deposition conditions, and the incorporation of different metallic nanoparticles on the DLC films an their effect with high temperature exposure. The elevated coating hardness (higher than 25 GPa) promoted good wear resistance. These results suggest that the PECVD-DC Pulsed with additional cathode and methane as a precursor gas to grow DLC films on metallic substrates with incorporation of metallic nanoparticles may represent a new alternative to improve the mechanical behavior in automotive applications.

BP-ThP10 e-Poster Presentation: Bipolar HiPIMS for Tailoring Ion Energies in Thin Film Deposition, ***Daniel Lundin (daniel.lundin@liu.se)****, R.P.B. Viloan,* Linköping University, Sweden*; M. Zanáška,* Linköping University*; H. Du,* Guizhou University, China*; R. Boyd,* Linköping University, Sweden*; T. Shimizu,* Tokyo Metropolitan University, Japan*; U. Helmersson,* Linköping University, Sweden

Bipolar HiPIMS, where a reversed positive pulse is applied to the target following the negative pulse, has promised great potential to solve challenges in growth of insulating thin films or when insulating substrates are used. In this mode of operation, a significant fraction of the ion energy distribution functions (IEDFs) can be shifted with an energy proportional to the magnitude of the applied reversed potential, U_{rev}. This is a consequence of the fact that a limited region of the plasma, near the cathode, experiences an increased plasma potential with a value close to U_{rev}. However, the ion energy gain and the distribution of energy in the accelerated populations can be affected by the magnetic field arrangement, the anode position and shape as well as the HiPIMS pulse configuration. These aspects are of great interest in the present contribution, where time- and energy-resolved ion mass spectrometry was performed in different discharge configurations to further understand the physics in bipolar HiPIMS discharges. Based on the features of the recorded IEDFs, optimized bipolar HiPIMS deposition processes for relevant material systems, such as aluminum oxide, were investigated to observe the effect of ion acceleration on the tailoring of the phase constitution during film growth.

BP-ThP11 Influence of Deposition Parameters on the Corrosion Resistance and Wear Resistance of Iron-Based Coatings Produced with Electric Wire Arc Spraying Technique for Application in Shipbuilding Industry, ***Hector Rojas (hectorf.rojasm@unilibrebog.edu.co)****,* Universidad Libre, Colombia

In this research, 140MXC-530AS and 140MXC-560AS coatings were produced using electric wire arc-spraying on an AISI / SAE 4340 steel, in order to evaluate the effect of the deposit parameters on corrosion resistance and wear in the shipbuilding industry, using the experimental method of fractional factorial orthogonal Taguchi arrays L_9 (3^{4-2}).

The characterization techniques used for chemical, morphological and microstructural identification were EDX, AES, XPS, COM, SEM, CLM and XRD; to establish the mechanical behavior and the abrasive and adhesive wear (*Pin on disc*) Vickers microhardness (HV) and adhesion (tension) tests were performed and to evaluate the corrosion resistance, the saline chamber and potentiodynamic TAFEL and EIS tests were carried out.

The computational modeling carried out allowed analyzing the pressure and velocity profiles of the air flow in the projection hood, estimating the shearing efforts at the tips of the wires and predicting the thermal and dynamic behavior of the particles in the transport phase in function of the sizes assumed for this purpose. These sizes were approximate to those obtained experimentally by exerting influence on the final properties of the coatings. The microhardness and particle size were selected as attributes for the approach of the optimization model of the electric wire arc-spraying technique using the NSGA-II genetic algorithm against wear resistance and corrosion.

The results obtained showed that the 140MXC-560AS coatings performed better regarding the properties evaluated. It is considered the best option, with the finalrecovery of a naval component.

BP-ThP12 In-situ Analysis of B-doped Diamond Synthesis using Hot Filament CVD, ***Ryo Tanaka (s16a3083gp@s.chibakoudai.jp)****, M. Takuya,* Chiba Institute of Technology Graduate School, Japan*; Y. Sakamoto,* Chiba Institute of Technology, Japan

B-doped diamond (BDD) has excellent electrochemical properties, and its application for electrochemical electrodes is progressing. BDD is prepared in substrates such as Si by hot-filament chemical vapor deposition (HFCVD), microwave plasma CVD, etc. BDD synthesis using HFCVD apparatus, source gases are decomposed by filaments heated to 2273㉃K] in pressure of between molecular flow and viscous flow. Therefore, complicated convection occurs between filament-substrate, it's difficult to control the B source flow between filaments and the substrate. In addition to control the flow of gases supplied into the chamber, it is necessary to feedback control based on measurements of reaction gas states.

In this study, reaction gas states were measured with quadrupole mass spectrometer (QMS) during BDD synthesis, it was explored relationship of electrical resistance to peak intensity of fragments.

BDD films were synthesized on Si substrates using HFCVD apparatus. CH_4-H_2-$B(OCH_3)_3$ gas mixture was used, with CH_4/H_2 flow rate: 1/50 [SCCM], $B(OCH_3)_3$ flow rate: 0.025 to 0.150 [SCyCM]. Pressure was 4.0 [kPa]. Filament temperature was 2273≦[K]. Synthesis time was 1 [h]. Reaction gas states were measured with QMS. Deposits were evaluated by Raman Spectroscopy. Electrical resistances were measured by four-probe method.

As a result of measuring reaction gas states with QMS, it was confirmed that $B(OCH_3)_3$ fragments of $(OCH_3)^+$, $BH(OCH_3)^+$ and $B(OCH_3)_2^+$. These peak intensities decreased during synthesis, so, it was recognized that can be measured the $B(OCH_3)_3$ with QMS. There was correlation between decreased electrical resistance and increased peak intensity of $(OCH_3)^+$ up to $B(OCH_3)_3$ flow rate 0.100 [SCCM]. In the case of $B(OCH_3)_3$ flow rate exceeded 0.100 [SCCM], electrical resistance indicated constant value. Supersaturated of B and O occurred on the surface of the substrate and electrical resistance of CVD diamond became constant value.

In conclusion, it was confirmed that controlling electrical resistance of BDD was suggested by in-situ analysis of reaction gas states with QMS.

BP-ThP13 Relationship between Electrical Resistivity and Emission Species in Plasma during Boron Doped Diamond Synthesis*, Jun Adegawa (s16a3005qa@s.chibakoudai.jp),* Chiba Institute of Technology, Japan*; A. Suzuki,* Chiba Institute of Technologyl, Japan*; Y. Sakamoto,* Chiba Institute of Technology, Japan

Boron doped diamond (BDD) has semiconductor properties. BDD is expected to be applied to electrodes and sensors. Many researches have been conducted on the relationship between BDD synthesis conditions and electrical properties. However, there are many unclear points about the mechanism. In particular, many researches on the electrical resistance of BDD are conducted. However, these researches attempts to control the resistivity, there is no uniformity in resistivity. In this research, plasma during BDD synthesis was measured by Optical Emission Spectroscopy (OES). Relationship between emission species and electrical resistivity verified.

BDD films were synthesized on Si substrates using mode-conversion type microwave plasma CVD apparatus. Si substrates were scratched with diamond powders and cleaned ultrasonically in acetone solution. Trimethyl borate solution with concentration of 0.01 g / ml in which boric acid was dissolved in methanol was used. Flow rate of reaction gases were used H_2;100 SCCM,CH_4;15 SCCM and H_2 carrier gas;1 -- 5 SCCM, respectively. Trimethyl borate solution was supplied to the chamber by hydrogen bubbling. Pressure was 20.0 kPa and microwave power was 1.0 kW. Film thickness was unified to 16 ± 4 µm. Plasma during synthesis was measured by OES. Deposits were evaluated by SEM and Raman spectroscopy. Deposits resistivity were measured by the four probe method.

OES spectra of B source derived B (249.7 nm), BH (433.1 nm), BO (436.3 nm) and C_2, CH, H_α and H_β were observed. Different OES spectra were observed in 4 groups (a -- d). Under any conditions, cross sectional SEM images of the deposits showed 16 ± 4 µm thickness. In addition, peaks of BDD were observed in the Raman spectra. The resistivity groups were (a) 0.2 -- 0.3 Ω, (b) 0.2 -- 0.4 Ω, (c) 0.8 -- 2.4 Ω, and (d) 20.4 -- 37.3 Ω. The resistivity decreased as the emission intensity of B-type emission species increased. In the case of the emission intensity ratio (BH / H_β) exceeded 0.8, the resistivity indicated constant value regardless of the conditions.

Relationship between electrical resistivity and emission species in plasma during BDD synthesis was verified using mode conversion microwave plasma CVD apparatus. As a conclusion, relationship between B-type emission species in OES spectra during BDD synthesis and resistivity of BDD were implied by experiments.

BP-ThP14 Development of a Multilayer Ti/TiN/TiAlN/ReN Coating System and Evaluation of their Microstructural, Mechanical and Tribological Properties*, Hernán Darìo Mejía Vásquez (hdario.mejia@udea.edu.co), G. Bejarano Gaitan,* University of Antioquia, Medellín, Colombia*; M. Arroyave Franco,* University EAFIT, Colombia

The need to improve the wear resistance of hot work steels in applications such as injection and extrusion of aluminum alloys, and high-speed steels for machining different parts in manufacturing processes, have led to the development of new materials in the form of coatings. With the purpose of improving the wear resistance of the M2 high-speed steel, a multilayer coating system consisting of 1, 10, 20, 30 and 40 Ti / TiN bilayers was developed, followed by a TiAlN monolayer and an outer layer of ReN. The selection of the ReN is because this nitride is one of those considered super hard, with hardness around 40 GPa and also has a high chemical and thermal stability. The (Ti/TiN)n/TiAlN/ReN multilayer coatings were co-deposited onto AISI M2 steel by the DC and R.F. magnetron sputtering techniques with a total thickness of 2000 nm. For the deposition of the coatings, Ti, Al and Re targets were used, as well as argon for the deposition of titanium and a mixture of Ar / N2 for the TiN, TiAlN and ReN layers. The SEM images of the cross section revealed a dense and homogeneous columnar growth structure, whose roughness and grain size decreases with the increase in Ti / TiN bilayers, as evidenced by the AFM measurements. The X-ray patterns showed peaks of the fcc cubic phases of ReN, TiAlN and TiN with preferential growth in directions (111) and (110), while only a single peak (110) was observed for Ti with bcc structure. The critical load, determined by the scratch test, increased from 25 N to 40N with the increase in the number of bilayers of the coating. This behavior is associated with the growing compressive residual stresses of the multilayer system as the number of bilayers increases, which was determined by measuring the radius of curvature of selected samples before and after coating them. The hardness of the coatings increased from 22 GPa to 35 GPa and the wear volume decreased substantially with the increase in the period of the Ti / TiN bilayers. The greater resistance to wear is associated with the higher hardness, less roughness and greater adhesion of the coatings as the number of bilayers increases. All deposited coatings showed greater performance in wear tests than uncoated steel.

BP-ThP15 Pulsed Laser Deposition of Nitride and Carbide Single- and Multi-Layered Coatings*, Jahn Falko (Jahn@hs-mittweida.de), S. Weißmantel,* University of Applied Sciences Mittweida, Germany

Nitride and carbide compounds belong to the most versatile materials in the world. Their extraordinary properties such as high hardness or chemical and thermal resistance lead to various industrial applications, e.g. in the fields of wear protection or sensor technology.

A method of universally producing such films both as single and multilayers using pulsed laser deposition is presented. As an example for the carbide compounds the results of the deposition of B_4C are given. Showing a hardness of up to 40 GPa these coatings could be suitable in many applications concerning wear protection.

The deposition results of AlN and BN, representing examples of the nitride compounds, are given. The influences of various deposition parameters such as laser fluence, substrate temperature and atmospheric conditions on film growth, microstructure and film properties are discussed.

The ability of producing multilayers consisting of different film materials in order to obtain specific and optimized film properties is demonstrated, furthermore. The selection criteria of the film material combinations are presented. Finally, the film properties such as hardness and adhesive strength are discussed according to the combination of film materials and the thickness of the sublayers.

BP-ThP16 Hybrid LACS Coatings: Industrial Use*, Mojmir Jilek (m.jilek.jr@platit.com),* PLATIT a.s., Czech Republic*; A. Luemkemann,* PLATIT AG, Switzerland*; B. Torp,* PLATIT Inc., USA*; D. Bloesch,* PLATIT AG, Switzerland

In today's tooling applications PVD coatings are exposed to a challenging combination of wear factors such as mechanical impact and abrasion. This poster will show how hybrid LACS coatings can assist to withstand these challenges.

Properties and cutting test results of structurally optimized LACS hard coatings are shown. The coatings were produced by the π411+ coating unit, featuring a combination of arc and sputtering cathodes. The Lateral Arc & Central Sputtering technology (LACS®) implements the simultaneous use of arc and sputter cathodes.

BP-ThP17 Plasma Analyses and Microstructure Characterization of Multicomponent AlTi(X)N Series Coatings Synthesized by Cathodic Arc Evaporation*, Y.Y. Chang,* ***Yen-Chen Chao (yinyu@nfu.edu.tw),*** National Formosa University, Taiwan

AlTiN coatings are widely used as protective coatings in various industrial applications of cutting tools, die casting molds and automobile parts, due to their excellent properties including their high hardness, wear and erosion resistance, and excellent thermal stability. In order to meet the increasing requirements of modern tools in high-speed yet dry cutting applications, such as higher hardness, excellent resistance against wear and oxidation. Recently, different elements, such as Si, Cr, B and Mo, has been added to form different multilayered structure and solid solution multicomponent AlTi(X)N using cathodic arc evaporation (CAE) technique. In this study, AlTiBN, AlTiCrSiN and AlTiCrMoN coatings were produced via CAE, while the plasma dynamics were studied non-destructively by optical emission spectroscopy (OES). Spectra obtained by analyzing the plasma optical emission under controlled cathode current of the alloy targets showed how the composition and structure of the deposited coatings vary within the plasma plume. Plasma ionization degree and kinetic energies are enough to grow the high quality multicomponent nitride coatings. From emission spectra obtained ionic and atomic species were observed. The electron temperature dependence on Ar and nitrogen gas pressure by using some specific metal, Ar and N emission line intensities were studied. The surface morphologies, chemical composition and microstructures of the prepared coatings was investigated by field emission scanning electron microscope (FESEM), equipped with an energy-dispersive x-ray analysis spectrometer (EDS) and X-ray diffraction (XRD). The optical emission spectra supply information about the reactive chemical species present in the plasma, and the densities of these species can be correlated with the structure and composition of the deposited AlTi(X)N. On the basis of the results obtained, we are developing OES as non-intrusive and in situ diagnostic of the plasma reactive species for controlling and optimizing the multicomponent AlTi(X)N deposition process in CAE.

Keywords: Coatings; optical emission spectroscopy; plasma analyses; microstructure

BP-ThP18 Carbon PVD Deposition with Doped Targets, ***Christian Kirchner (christiankirchner@mail.de)***, *M. Thomalla,* Vitesco Technologies, Germany; *P. Polcik,* Plansee Composite Materials GmbH, Germany

Diamond like carbon (DLC) coatings are more and more used for tools and sliding components in tribological and wear resistant applications. The advantages of these coatings are high hardness accompanied by extremely low friction coefficients. Typically, DLC-coatings are grown by plasma-enhanced chemical vapor deposition (PECVD) processes, which are characterized by high deposition rates but also rough surfaces due to high defect densities. Furthermore, high hydrogen contents limit the hardness of PECVD DLC coatings up to 25 GPa. In general, a reduction of hydrogen while increasing sp^3 hybridization (hence mechanical properties) can be realized by physical vapor deposited (PVD) coatings. The disadvantage of these sputtered DLC coatings is a very low deposition rate compared to PECVD or CVD.

Thus, the aim of this work is to improve the growth rate of sputter deposited DLC coatings using doped carbon targets. Based on diverse studies in the field of transition metal nitrides [1,2] are heavy as well as strong secondary electron emitting elements, e.g. Cerium or Lanthanum, highly beneficial for increasing deposition rates. The positive effect is related to the high electron emissivity as well as enhanced collision cascade, as heavy atoms reflect more energy to the target surface. In a first step, the bias voltage as well as coil current have been optimized for a pure carbon target to achieve highest deposition rates, high hardness as well as good adhesion. Subsequently, these conditions were used to sputter deposit a DLC coating utilizing a Cerium doped carbon target – about 2 at. % Ce within the target material. The sputter time was kept constant for all coatings. In addition, the weight was evaluated before and after the deposition process, respectively. Cross sectional micrographs using a focused ion beam (FIB) system reveal a 40 % increase in thickness from 827 to 1176 nm by applying the Ce doped target. These results fit well to the increase of weight reduction of the targets by 33 % correspondingly. The characterization of the coatings shows that there is a content of 6,3 wt% Cerium in the coating and that the hardness decreases up to 18%.

In summary, the deposition rate of physical vapor deposited DLC coatings was increased up to 40 % by doping the pure carbon target with cerium. The on-going research is focused on further improved process parameters aiming for higher coating hardness and even higher deposition rates.

BP-ThP19 High-power Cathodic Arc Evaporation for High-rate Deposition of Hard Stress-free TiN Coatings, ***Michal Zítek (michal.zitek@unileoben.ac.at)***, *N. Jäger, M. Meindlhumer,* Montanuniversität Leoben, Austria; *H. Hrubý, F. Nahif,* voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany; *C. Mitterer, R. Daniel,* Montanuniversität Leoben, Austria

TiN coatings are widely used as protective coatings for machining and tooling applications for several decades. They are favored especially due to high controllability of their microstructure and properties and their golden-yellow color. Despite of that, the coatings may suffer from high compressive stresses originating from high-energy deposition processes, which limits their performance in some applications. Moreover, it is beneficial to shorten deposition times for each batch to make deposition runs more effective. The focus of this work was thus to deposit nanocrystalline TiN coatings at high deposition rates with high hardness and controllable residual stress state.

The TiN coatings were synthesized in an industrial-sized coating system (alpha400P, voestalpine eifeler Vacotec GmbH) in pure N_2 atmosphere at a total pressure of 4 Pa and bias voltages of -50 V and -100 V. The effect of these deposition parameters on the coating microstructure and properties was then systematically investigated. An increase of the substrate temperature and current during deposition at cathode currents up to 200 A led to the formation of well crystalline coatings with a gradual change of texture from (100) towards (111). The high-energy deposition furthermore promoted annealing of structural defects accompanied by a significant reduction of compressive residual stress and increased density while the hardness of the coatings remained unchanged with values of about 29 GPa. The evaluation of droplet surface coverage revealed that the coating deposited at high cathode currents and substrate bias voltage of -100V exhibited about a half the coverage of the coatings deposited at low incident particle energies. High-energy high-rate depositions thus represent a promising way for growth of hard, nanocrystalline stress-free TiN coatings with enhanced adhesion and reduced droplet surface coverage.

BP-ThP20 Fracture Mechanisms in Superlattices: A Case Study of TiN/TaN, ***Nikola Koutná (nikola.koutna@tuwien.ac.at)***, *J. Buchinger, H. Hazeu, M. Bartosik,* TU Wien, Austria; *D. Holec,* Montanuniversität Leoben, Austria; *D.G. Sangiovanni,* Linköping University, Sweden; *P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Superlattice architecture has been identified as a promising concept to control hardness as well as fracture resistance of thin films by optimising thicknesses of the film-forming nanolayers. However, mechanisms behind the remarkable hardness and/or fracture toughness enhancement in superlattices—experimentally showcased by e.g. TiN/CrN and TiN/WN—are yet to be understood. This work focuses on the TiN/TaN superlattice system with (001)-oriented interfaces and cubic rocksalt structure. To shed light on atomistic processes driving strength, plasticity, and fracture subject to tensile loading at finite temperatures, we employ density-functional ab initio molecular dynamics. Our structural models allow for addressing not only the trends conditioned by changes of the bilayer period but also the impact of point defects, namely N and Ta vacancies. Vacancies, energetically favoured by TaN and highly expectable in real superlattice films, lead to effective redistribution of stresses via local structural transformations upon tensile deformation. To further support our theoretical findings, magnetron sputtered TiN/TaN superlattices are carefully analysed.

BP-ThP21 The State of Coating – Substrate Interfacial Region formed during the Coating Deposition by Gas Injection Magnetron Sputtering Technique, *R. Chodun,* Warsaw University of Technology, Poland; *K. Nowakowska-Langier,* National Centre for Nuclear Research, Poland; ***Bartosz Wicher (Bartosz.Wicher.dokt@pw.edu.pl)***, Warsaw University of Technology, Poland; *S. Okrasa,* National Centre for Nuclear Research, Poland; *R. Minikayev,* Institute of Physics, Polish Academy of Sciences, Poland; *M. Dypa, K. Zdunek,* Warsaw University of Technology, Poland

This work presents the magnetron sputtering technique: Gas Injection Magnetron Sputtering (GIMS), operating in the pressure oscillations, controlled by a pulse gas valve. In this technique plasma lifetime is controlled by small gas portions, creating a pressure between the threshold values: initiating the discharge and extincting the discharge. For the experiment we have used an own – designed controller which electronically couples the gas valves with the power supply, so we were able to operate those devices independently on their time scale. In presented experiment we have used different time shift of power pulses respectively with the gas pulses. For that purpose, we provided a gas conditions creating the 2.5s long discharges. It gave us a possibility to generate the plasma in various phase of pressure pulse. In this experiment we have divided the plasma formative 2.5s gas pulse for a five 500 ms phases of power working on. Plasma formed in each phase were studied by means of the Optical Emission Spectroscopy. Additionally the TiO_2 coating were deposited in each phase of a gas pulse, and studied by means of experimental techniques revealing their structure (SEM, TEM) and phase – chemical (Raman spectroscopy, XRD) content. Our experiment showed that the material state of a deposited coating is strongly dependent from the phase of deposition process. Depending of the phase of deposition we could obtained: nanocrystalline or amorphous structures, Ti, TiO phase or rutile TiO_2 phase, single layer structure or double layer structure, thin coating or thick coating, etc. OES measurements provided us with information of the particular groups of plasma species evolution during the gas pulse and helped to give explanation for observed differences in the state of a coating material.

BP-ThP22 Integral and Time-Resolved Ion Distribution Functions in a Reactive Ti-Al HiPIMS Discharge, ***Lukas Zauner (lukas.zauner@tuwien.ac.at)***, TU Wien, CDL-SEC, Austria; *T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria; *T. Kozák, J. Čapek,* University of West Bohemia, Czech Republic; *H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria; *H. Riedl,* TU Wien, CDL-SEC, Austria

Within the everlasting scientific topic of pushing the boundaries for Al solubility limits (x_{max}) in Ti-Al-N based coatings, reactive high-power impulse magnetron sputtering (R-HiPIMS) has been established as one key-technology. The introduction of enhanced ionization rates allows for additional pathways in tuning the structural and chemical evolution by surface-diffusion driven growth. Hence, especially depending upon the charge state and mass-ratio of the metal-ions incident on the growing film, metastable thin films are decisively influenced in their overall growth characteristics.

Here, we review in detail the dependence of the phase-stability, and hence x_{max}, on varying deposition parameters during R-HiPIMS of Ti-Al-N thin films using $Ti_{1-x}Al_x$ composite targets (x = 0.40, 0.50 and 0.60). The influence of HiPIMS pulse parameters such as frequency, pulse length, or peak power density, but also of deposition parameters including N_2 partial pressure, substrate bias voltage, or target compositions were investigated methodically. The so obtained coating structures were analysed with respect to phase-stability, thermomechanical properties, and morphology applying nanoindentation, X-ray diffraction combined with electron imaging techniques. The systematic studies revealed an Al solubility limit of x_{max}~0.55, obtained for a duty cycle of 3.75 % (peak power density of ~1 kW/cm^2) and a N_2-to-Ar flow-rate ratio of 0.3. Moreover, sufficient intermixing of the arriving film species controlled via bias potentials (DC as well as discharge synchronised) was observed as decisive for the deposition of high Al containing *fcc*-structured coatings. To gain a further insight in the growth kinetics of selected coatings, time- and energy resolved mass-spectroscopy measurements have been conducted. Based on these analyses, the ratio and energy of simultaneously arriving Ti^{n+}- and Al^{n+}-ions at the substrate surface, are highly influential for stabilising the preferred cubic modification with respect to the prevailing deposition conditions.

BP-ThP23 Increasing Oxidation Resistance of Reactive Magnetron Sputtered ($Al_vCr_wNb_xTa_yTi_z$)N Thin Films by Si-alloying, ***Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at)***, TU Wien, Institute of Materials Science and Technology, Austria; *K. Yalamanchili, H. Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloyed nitrides are promising materials for hard coatings. One major drawback is a lack of oxidation resistance in most coatings, which limits high-temperature applications in ambient conditions. In this work we report a method to increase the oxidation resistance of these materials.

($Al_vCr_wNb_xTa_yTi_z$)N coatings were formed in a cubic (c) solid solution in thin film form by reactive magnetron sputtering in N_2-atmosphere using a powder metallurgically prepared metal target (Plansee) with nominal composition of 20 at% of each element. Si was alloyed by placing different numbers of pieces (about 2x2x0.4 mm^3 each) of Si on the cathode racetrack during deposition.

We measured the oxidation resistance of the coatings by placing the samples in a furnace in ambient air at 850 °C for 0.5, 1, 5, 10, 30, and 100 h. After these durations we extracted the samples from the hot zone and analysed them with X-ray diffraction, Energy-Dispersive-X-Ray-Analysis, and Transmission Electron Microscopy (TEM). After 100 h the oxide scales on coatings without and with Si were 2800 and 300 nm thick, respectively. Plotting the oxide scale thickness against the oxidation time reveals a parabolic oxide growth behaviour without Si, which changes to logarithmic growth with Si in the solid solution. This different behaviour can be explained with the oxide morphology, visible in TEM. Without Si, the oxide is porous, whereas with Si the oxide is separated into a dense inner region and a porous outer region.

Therefore, we can conclude that Si-alloying improves the oxidation resistance tremendously and may be applicable to increase the performance of other high-entropy nitride coatings in oxidative environments.

BP-ThP24 Phase Stability and Mechanical Properties of (Re,Ti)B_2 Thin Films, ***Vincent Moraes (vincent.moraes@tuwien.ac.at)***, *S. Maric, P.H. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

The development of protective coatings with outstanding properties is a highly important topic, challenging industry as well as academia. In recent research history, nitrides have therefore served as a fruitful playground but are gently reaching their physical limits. Recently, transition metal diborides (TMB_2) have pushed into focus, due to their exceptional properties, such as high melting points or their excellent hardness. Especially in highly specialized industrial machining applications, where commonly used superhard materials (e.g., diamond or BC_2N) cannot be applied, this material class is highly promising.

One outstanding representative, because of its theoretical predicted superior mechanical properties (hardness > 40 GPa), is ReB_2. Whereas theoretical studies have dealt with this material combination, experimental studies are rather rare. The reported weak oxidation resistance of ReB_2, draws the challenge to combine its superior properties and simultaneously reduce its drawbacks in chemical stability.

In this study, we theoretically (by means of density functional theory) and experimentally investigate the phase stability and mechanical properties of ternary Re alloyed Ti(Re)B_2 thin films. Therefore we applied ab-initio calculations and physical vapour deposition (PVD - magnetron sputtering) to explore their preferred structure type and the subsequent influence on their mechanical properties. The different possible polymorphs, which appear as different stacking sequences of hexagonal boron planes and transition metal layers, and their stability makes this an excellent material system for the beneficial combination of theoretical predicitions and PVD thin film experiments.

Keywords: TMB2; multinary borides; mechanical properties; magnetron sputtering;

BP-ThP25 *In Silico* Nanoindentation of TiN/AlN Superlattices: A Molecular Dynamics Study, ***Lukas Löfler (lukas.loefler@unileoben.ac.at)***, Montanuniversität Leoben, Austria; *P.H. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria; *M. Bartosik,* TU Wien, Austria; *D. Holec,* Montanuniversität Leoben, Austria

Nitride thin films are commonly used to protect components against the harsh conditions they are exposed to in modern applications. An effective way to improve the mechanical properties of such coatings is to carefully design their micro- and especially nanostructure. Developing multilayers with incoherent, semicoherent or coherent interfaces between the constituting layers (sometimes even only nm-thin) is an elegant method to realize that. Such superlattice coatings (with coherent interfaces and nm-thin constituents) often exhibit higher hardness and fracture toughness, two often mutual exclusive material properties, than their individual components.

Utilizing molecular dynamics (MD) both indentation and tensile loading simulations were performed to investigate AlN/TiN superlattices. For the indentation a spherical object was gradually moved into the coating displacing atoms, as for the tensile loading the atoms at the top and bottom of the coating were moved to put it under axial tension. For both setups the forces, stresses and the nucleation of dislocations were analyzed. To gain more insight into the nucleation process of the dislocations, different cores and their structures were calculated for the most common slip systems.

BP-ThP26 Influence of Intermetallic TiAlNbMoY Target Material on the Thermomechanical Properties and Oxidation Resistance of Ti-Al-N Films, ***Stefan Kagerer (stefan.kagerer@tuwien.ac.at)***, TU Wien, Institute of Materials Science and Technology, Austria; *P. Polcik,* Plansee Composite Materials GmbH, Germany; *P.H. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Oxidation resistance in combination with excellent thermomechanical properties is nowadays the fundamental prerequisite for thin film materials. The widespread industrial usage of Ti-Al-N coatings proves this harsh requirements for cuttings tools and also for high precision components in automotive and aviation sector.

Recently, we showed the good oxidation resistance of intermetallic γ-TiAl coatings which are alloyed with Mo, Nb and Y. In this work we combined the oxidation resistance of this aluminum rich intermetallic coating with the excellent hardness of common Ti-Al-N coatings.

Therefore, we used an intermetallic TiAl target (containing 61.5 at.% Al and 33.2 at.% Ti) which was alloyed with 4 at.% Nb, 1.2at.% Mo and 0.2at.% Y [1]. The γ-TiAl based Ti-Al-N coatings were grown onto well-established TNM bulk alloys and on chemical inert sapphire substrates ((0001)-oriented) using a semi-industrial scaled unbalanced magnetron sputtering system [2]. The oxide scale formation of coating and the diffusion between coating and the TNM alloy substrate material was induced by annealing treatments for 100 h at 850°C in ambient air. The thermally driven influence of the bulk TNM alloy compared to the coating properties itself was investigated optically and chemically by secondary electron microscopy techniques (SEM) and energy dispersive x-ray spectroscopy (EDS). The influence of the thermally grown oxide (TGO) on the hardness was compared to vacuum annealed samples and measured by nanoindentaion.

[1] US 10,465,264 B2 (Smarsly et al.), 5.11.2019

[2] US 2018/0163291 A1 (Schloffer et al.), 14.6.2018

BP-ThP27 Radiation Stability of nc- ZrN/a-ZrCu Multilayered Films after He Implantation*, Grégory Abadias (gregory.abadias@univ-poitiers.fr),* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; V. Uglov, S. Zlotski, I.A. Saladukhin,* Belarusian State University, Belarus

The development of a new generation of nuclear reactors requires the use of materials and coatings with high radiation resistance. It's necessary to create materials with a large number of sinks for point defects, such as dislocations, grain boundaries, and interphase boundaries to achieve this goal [1-2]. One of the most promising materials with the large number of grain boundaries are nanocrystalline coatings, for example nc-ZrN, formed by vacuum arc deposition [3]. Nanocrystalline coatings with crystalline/amorphous interfaces (such as nanocomposite and multilayered nc-MeN/a-Si_3N_4 systems) exhibit a high radiation tolerance along with crystalline/crystalline systems, due to amorphous nanolayers associated with excellent defects absorption capability [4-5]. In this paper, the idea of replacing amorphous a-Si_3N_4 layers with amorphous a-ZrCu metal layers is proposed.

The work is devoted to the study of the elemental and phase composition, surface morphology and microstructure of the nc-ZrN/a-ZrCu multilayer systems and their evolution after He implantation. Nanoscale nc-ZrN/a-ZrCu multilayers with elementary layer thickness of 5 nm/5 nm and 5 nm/10 nm with different Cu concentration in a-ZrCu layer were grown by reactive magnetron sputter-deposition from Zr and Cu targets at substrate temperature of 300°C. XRD, EDX, SEM and AFM investigation of as-deposited and after He ion irradiation (40 keV and doses up to 1E17 cm^{-2}) of nc-ZrN/a-ZrCu multilayer systems were conducted.

XRD analysis confirms that multilayered films consist of nanocrystalline ZrN and amorphous ZrCu. It was found formation amorphous ZrCu in a wide range of Cu concentrations (up to 80 at.%).

The influence of the Cu composition (in the range of 20-80 at.%) in the ZrCu layers and thickness of individual layers (5 nm/5 nm and 5 nm/10 nm) of nc-ZrN/a-ZrCu multilayer on radiation stability of elemental and phase composition, surface morphology (blistering) and microstructure of films after He ion irradiation is discussed.

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BP-ThP28 BCl_3 Gas Boriding and Simultaneous Precipitation Hardening of Nickel-Based Superalloy 718*, Alexander Nienhaus (alexander.nienhaus@ist-extern.fraunhofer.de), P. Kaestner, J. Vogtmann,* IOT TU Braunschweig, Germany*; H. Paschke,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany*; G. Braeuer,* IOT TU Braunschweig, Germany*; A. Hunger,* BorTec GmbH & Co. KG, Germany*; R. Berger,* BorTec GmbH & Co. KG*; M. Paulus, C. Sternemann,* Technical University Dortmund, Germany

Hot forming applications, e.g. hot extrusion molding or die forging, demand tool surfaces with excellent tribological properties under thermal load conditions to reduce wear and increase tool lifetime. For high temperature applications, Nickel-based superalloys as Alloy 718 (DIN 2.4668) with their high corrosion and oxidation resistance and low coefficient of thermal expansion represent an interesting choice, but low hardness and wear resistance are a huge drawback. Boriding the surface increases the surface-near hardness, which leads to increased wear resistance. The innovative approach of this work is the combination of precipitation hardening of the Alloy 718 bulk material with simultaneous boriding. The tool surface is modified by boron diffusion, using a gaseous BCl_3 precursor at low pressure of p = 7 mbar. In detail, the exposure time at T = 720 °C is separated into two parts: 4 h without surface treatment (H_2 atmosphere), followed by 4 h of boriding (BCl_3-containing atmosphere). The hardness of the bulk material increased from 22 HRC to 42 HRC and a 12 µm thick, dense, homogeneous boride layer is formed at the surface. The boriding of similar Nickel-based coatings showed hardness values up to 3,000 HV. In contrast to often-used solid boron donors, there are no remaining, hard-to-remove pastes, which simplifies the finishing process before use. X-ray diffraction (XRD) measurements were carried out to investigate the phase composition of the boride layer. Alloy 718 contains 17-21% Chromium, but no CrB_x phases were detected. A comparison between gas and paste borided Alloy 718 shows that the XRD-diffractograms differ, presumably mainly because of the higher process temperatures and not because of the different medium. The paste borided Alloy 718 were precipitation hardened later on. From investigations on borided AISI H11 it is known, that CrB_x forms at temperatures above 900 °C. The simultaneous precipitation hardening limits the temperature to T = 720 °C, which makes the formation of hard and wear resistant CrB_x unlikely with this duplex treatment.

BP-ThP29 A Continuum Mechanical Study Towards Understanding Fracture Resistance of Superlattice Thin Films*, Antonia Wagner (antonia.wagner@tuwien.ac.at),* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; P.H. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; M. Bartosik,* TU Wien, Austria

It has been shown that a careful multilayer design at the nanoscale is an effective strategy to improve the performance of ceramic thin films. Depending on the lattice mismatch of the film building blocks and the layer thicknesses, the nanometer thin materials grow either in a coherent, semi-coherent or incoherent manner on each other. The (semi-)coherent growth is accompanied by the formation of residual stresses in the range of a few GPa.

The stress state is of particular salience when it comes to fracture behavior of ceramic thin films. A microcrack at the surface can experience either shielding or anti-shielding depending on the type of residual stress in the layer, compressive or tensile. Hence, the applied mechanical load required for crack growth is increased in the presence of compressive residual stresses leading to an enhanced 'apparent' fracture toughness.

Here we propose a model based on continuum elasticity theory to estimate the energetically favored dislocation density in a superlattice thin film deposited on an elastically anisotropic substrate. The significance of various parameters considered in this analysis, i.e. elastic properties, lattice parameters, interface width, and architecture of the system, for the dislocation density is investigated. The resulting stress state in the thin film is analyzed regarding its potential to improve the resistance of the system against brittle fracture.

BP-ThP30 Mechanical Properties of Reactively Magnetron Sputtered Cr-rich Cr-Zr-O Thin Films*, Stefanie Spitz (stefanie.spitz@helmut-fischer.com), T. Haas,* Helmut Fischer GmbH, Institut für Elektronik und Messtechnik, Germany*; M. Stüber, S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany

Chromium zirconium oxide thin films with different chemical compositions could be obtained during reactive magnetron sputtering with an Ar/O_2 gas mixture according to their position below a segmented Cr-Zr target. This combinatorial approach also implies that each individual sample exhibits a lateral gradient. It has been shown earlier that depending on the position below the target the chemical compositions of the samples vary and therefore different microstructures and properties evolved. The Cr-rich samples grew in a Cr_2O_3-like structure where Zr was incorporated. The formation of a second phase, an amorphous Zr-rich $(Zr,Cr)O_x$ phase, has been shown elsewhere. In this study, Cr-rich Cr-Zr-O thin films with the above specified microstructural features were investigated regarding their mechanical properties with different indenter geometries and measuring modes over the lateral compositional gradient. Such experiments can provide further information about the influence of small changes in composition on the properties of these new types of oxide thin films in comparison to the classic indentation mode. The indentation hardness and the plain strain indentation modulus $E_{IT}/(1-\nu_s^2)$ was determined e.g. with a Vickers indenter over the lateral concentration gradient of the films. The hardness increased for the Cr-richest film from 13.5 GPa ± 1.4 GPa to 18.6 GPa ± 1.9 GPa with increasing Zr content. The plane strain indentation modulus increased slightly from 246 GPa ± 15 GPa to 274 GPa ± 17 GPa. For the sample with a higher Zr content the hardness remains constant at an average value of 19.6 GPa ± 1.8 GPa with an average value of the plane strain indentation modulus of 276 GPa ± 16 GPa despite the compositional gradient. Load-partial unload measurements were conducted in order to achieve depth-based information. The results with a Vickers indenter showed that e.g. for the Cr-richest sample the hardness almost remains unchanged with increasing indentation depth. The average value is about 17.7 GPa ± 2.2 GPa. The plane strain indentation modulus increased from 232 GPa to about 270 GPa.

BP-ThP31 Study of the Plasma used to Deposit Ti and TiN Films by HIPIMS Technique*, José Omar Berumen (berpel1995@gmail.com),* Universidad de Guadalajara, México*; E.D. García,* Universidad de Guadalajara, Mexico, México, Mexico*; J. Pérez,* Universidad de Guadalajara, Mexico, México*; M. Flores,* Universidad de Guadalajara, México, Mexico

The plasma characteristics as ion energy and electron temperature depend on parameters used in the technique called high-power impulse magnetron sputtering (HIPIMS). This work studied the evolution of the plasma characteristics (density, electron temperature, etc.) as a function of pulse length of (50- 150 µs) and the Ar/N2 gas fluxes ratio. A frequency of 500 Hz was used in a non-reactive and reactive atmosphere. The reactions of particles and the ion energy distribution in the plasmas were studied using optical emission spectroscopy (OES) and mass spectrometry, respectively. The OES technique was performed using Horiba iHR320, and for the ion energy and particle mass measurements was used an Electrostatic Quadrupole Plasma (Hiden EQP 300). The plasma density, plasma voltage, and electron temperature were studied with a cylindrical Langmuir probe. These studies showed the plasma characteristic at different duty cycles, making a distinction between reactive and non-reactive modes. The deposit rate was determined by mechanical contact profilometry, the crystalline phases present were determined with XRD and the morphology of the films through of SEM.

BP-ThP32 HIPIMS Plasma Diagnostic for TiAlN Films Growth: Ion Energy Distribution, Mass Spectrometry, and Optical Emission Spectroscopy*, **Sebastián Gascón (gasconsebas95@gmail.com)**, E.D. García, M.F. Flores, J. Perez, M. Flores,* Universidad de Guadalajara, Mexico

In contrast to dcMS, High Power Impulse Magnetron Sputtering (HIPIMS) provides higher ionization of sputtered atoms increasing the ion flux towards the growing film. Due to its excellent mechanical properties and thermal stability, TiAlN has applicability as a protective coating against oxidation and corrosion. The main objective of this work was the study of the plasma conditions when sputtering a metal TiAl target, at different duty cycles of 9, 5 and 2.5% in pure Ar and Ar/N_2 atmospheres and the constant pressure of 0.8 and 1.4 Pa (6 and 10.5 mTorr), respectively. The plasma diagnostics, major emission lines, and ion energy distribution for Al^{2+}, Al^{1+}, Ti^{2+}, Ti^{1+}, Ar^{2+}, Ar^{1+}, N^{2+}, N^{1+}, were investigated by optical emission spectroscopy (OES) and mass spectrometry, respectively. It was found that a decrease in the duty cycle produces an increase in the peak target current. Therefore, a higher number of Al^{1+} and Ti^{1+} ions were observed, and its energy tail extended toward higher energies, either the metallic or reactive mode. The OES spectral intensities for the atomic, first and second ionization of Al and Ti in the plasma were studied as a function of the frequency and the pulse width. Using the plasma condition at 2.5% duty cycle, a TiAlN monolayer with a thickness of 1.3 µm was deposited on Si and AISI 52100 steel. The film growth was analyzed by SEM at the cross-section of the coatings, and X-ray diffraction was used to identify its crystalline structure.

BP-ThP33 Properties of Hafnium Nitride Coatings Deposited by Direct Current, Mid-Frequency, and Inductively Coupled Plasma Assisted Magnetron Sputtering*, **Sung-Yong Chun (sunnyonj@hotmail.com)**,* Mokpo National University, South Korea

Properties of hafnium nitride coatings are mainly influenced by the deposition conditions, which are affected by the sputtering technique. A suitable use of the different sputtering modes allows to control the structural development of the films and thus to adjust the profile of the properties. hafnium nitride coatings were deposited using direct current magnetron sputtering (dcMS), mid-frequency magnetron sputtering (mfMS), and inductively coupled plasma assisted magnetron sputtering (ICPMS). dcMS produces films with a columnar microstructure, where as a fully-dense morphology is achieved by mfMS and ICPMS. X-ray diffraction patterns show that the films sputtered in dcMS have both δ-HfN and HfN0.4 structures, whereas mfMS and ICPMS modes have a cubic δ-HfN rocksalt structure. Mechanical properties of hafnium nitride coatings were also investigated and strongly affected by the sputtering modes.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Grand Hall & Foyer - Session CP-ThP
Fundamentals and Technology of Multifunctional Materials and Devices (Symposium C) Poster Session

CP-ThP1 Preparation and Photocatalytic Properties of Heterostructured Ceria/Polyaniline Core-Shell Nanoparticles*, **Chin-Yi Chen (chencyi@fcu.edu.tw)**, Y.-S. Li, G.-J. Lee, J.-J. Wu, Y.-C. Chang, C.-Y. Tsay, J.-H. Chen, T.-L. Horng,* Feng Chia University, Taiwan*; A. Fang,* Texas A&M University, USA

Cerium dioxide (CeO_2, ceria), a promising catalytic material with high-efficiency, nontoxicity, abundant, photochemical stability and low-cost, can be used as a photocatalyst to photocatalytically degrade organics and split water for hydrogen production under the ultraviolet (UV) irradiation (about 5% of solar energy). However, the applications of the CeO_2 photocatalyst are limited due to low photocatalytic efficiency under sunlight irradiation. In this study, a nanosized CeO_2 powder was prepared by precipitation method; and subsequently, various amounts of polyaniline (PANI) nanoparticles were deposited onto the surface of CeO_2 nanoparticles to form a core-shell heterostructure by polymerization method. The crystal structure, morphology, surface and optical properties of the core-shell CeO_2/PANI nanoparticles were investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), UV–visible absorption spectroscopy (UV-Vis) and photoluminescence (PL). Experimental results demonstrated that PANI deposition improved the light absorption of CeO_2 nanoparticle in the visible light region. The separation of photogenerated electron-hole pairs was effectively enhanced due to the formation of a heterostructure, so-called *p-n* junction, at the interface between *n*-type CeO_2 and *p*-type PANI. The heterostructured CeO_2/PANI core-shell nanoparticle with 4 wt% PANI deposition exhibited the optimized photocatalytic activities in a methyl orange (MO) degradation rate of 45% within 4 h and a H_2 production rate of 462.8 μmol^{-1} within 6 h, respectively, under visible light irradiation.

CP-ThP2 Investigation of Nanostructured Thin Films based on Water Soluble Precursors for Perovskite Solar Cells*, **Gwomei Wu (wu@mail.cgu.edu.tw)**,* Chang Gung University, Taiwan

The objective of this study has been to develop water soluble processes for high efficiency perovskite solar cell s . Fluorine-tin oxide -coated g lass substrate w as cleaned , then surface-treated with plasma and UV light irradiation to increase its hydrophilicity. The electron-transport layer, composed of titanium dioxide dense layer and a mesoporous layer , w as spin-coated and further annealed. A precursor solution of l ead nitr ate wa s used to deposit lead dioxide film , which was then immersed in MAI to create the $MAPbI_3$ perovskite nanostructured thin film. Spiro-OMeTAD was used as the hole - transport layer, and silver was applied as the cathode. T he contact angle analysis suggest ed that 20 min under the UV-ozone treatment was enough to provide a good surface condition for coating. In addition, t he solar cell C-V performance s under the various lead nitrate precursor concentrations have been studied . The conversion efficiency was a chieved at higher than 10.0%. Since the develo pment of less toxic, water- based precur sor formulation , it has been encouraging to find better deposition method for lead precursor, thus the perovskite nanostructure. After the parameters have been optimized, long time stability characterization c ould be carried out for the new high efficient perovskite solar cells. The new results will be presented and discussed in greater details.

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CP-ThP4 Sonochemical Synthesis of $BiVO_4$ composite photocatalysts for Photocatalytic Degradation of Bisphenol A under Simulated Sunlight Irradiation*, **Jing-Heng Chen (jhchen@fcu.edu.tw)**, G.-J. Lee, H.-Y. Lee, J.-J. Wu,* Feng Chia University, Taiwan

Copper doped $BiVO_4$/g-C_3N_4 composite photocatalysts were successfully synthesized using a sonochemical approach. Copper can trap the charge carriers, which resulted in the charge separation and photocatalytic activity enhancement. In addition, the composite semiconductors can improve the stability, and light harvesting efficiency of photocatalyst. Cu doped $BiVO_4$/g-C_3N_4 composite photocatalysts exhibited a significant enhancement of the photocatalytic degradation performance. The optimal condition is the BPA concentration of 20 mg L^{-1}, pH value of 10, and 10Cu/$BiVO_4$/g-C_3N_4

photocatalyst amount of 0.4 g L^{-1}. The removal of BPA could degrade about 100% after 90 min at the optimal condition (Figure 1). Moreover, the excessive doping of copper cannot synthesize the monoclinic scheelite phase, which resulted in the decrease of the photocatalytic activity.

CP-ThP6 Synthesis of Copper-doped CdS/COF Composite Photocatalysts for Efficient Visible Light Photocatalytic Production of Solar Fuels, *G.-J. Lee, H.-J. Yang,* ***Jerry J. Wu (jjwu@mail.fcu.edu.tw)***, Feng Chia University, Taiwan

The plate-like covalent-organic frame (COF)was synthesized by the molecular organization approach (Figure 1a). Meanwhile, a novel visible-light-driven CdS/COF composite photocatalyst was successfully synthesized by the ultrasound irradiation method. The CdS/COF samples presented a sea urchin-like morphology (Figure 1b). COFs, a new class of porous crystalline materials, have attracted tremendous attention considering their broad applications due to a lot of activity sites, resulting in the enhancement of the photocatalytic activity.In this study, the result has revealed that the appropriate modification of COF and copper could significantly improve the hydrogen evolution. The optimal conditions, such as the concentration of 10% v/v formic acid and the 2Cu/CdS/0.5COF compositephotocatalyst dose at 0.3g L^{-1}, could completethe excellent photocatalytic activity for water splitting.

CP-ThP7 Characterization of Phosphor Layer for Perovskite Solar Cell with Enhanced Stability, *S.G. Shin, C.W. Bark,* ***Hyung Wook Choi (chw@gachon.ac.kr)***, Gachon University, Republic of Korea

Recently, organo-halide metal perovskites have shown great potential to be used in next-generation solar cells and have become a substitute for silicon in solar cells. Perovskite materials have been investigated as potential semiconductors and ferroelectrics due to their wide band gaps. Currently, organic materials and halogens are used, which have a band gap of 1–1.5 eV, which is ideal for use in solar cells. Perovskites have gradually been used in solar cells since 2009, and the number of studies in this area has considerably increased since 2012. However, ultraviolet rays destroy perovskite and consequently degrade perovskite solar cells. In order to prevent such a problem, the stability of the solar cell can be improved by introducing a phosphor layer at each interface to form a tandem structure that effectively converts light.

In this study, we analyzed perovskite solar cells coated with phosphors at each interface to solve the stability problem of perovskite solar cells. The introduction of phosphors that excite ultraviolet light and emit visible light can be a promising approach for high stability, high efficiency perovskite solar cells.

CP-ThP8 An Algorithm for Fast Diagnostics of the Sensitivity of Localized Surface Plasmon Resonance Sensors Based on Thin Films, ***Marco Rodrigues (marcopsr@gmail.com)***, *R.M.S. Pereira, M.I. Vasilevskiy, J. Borges, F. Vaz,* University of Minho, Portugal

Plasmonic thin films with gold and silver nanoparticles are known to be important platforms for sensing devices. Their optical response related to the Localized Surface Plasmon Resonance (LSPR) phenomenon in the visible range gives them unique optical sensing properties. Several strategies have been used in recent research works to study the optical sensitivity of plasmonic thin films by using straightforward optical transmittance measurements. These works have focused in monitoring: i) the LSPR peak position (either wavelength shifts or transmittance intensity variations), ii) the transmittance intensity at specific wavelengths, or iii) just by calculating the area below the transmittance spectra. In the present work, an algorithm was developed to extract all these features, and to perform a statistical analysis with the central moments of the normalized spectral distribution. For each monitored parameter a signal-to-noise ratio is also calculated. The algorithm was tested with several plasmonic thin film systems and for different conditions, in a controlled atmosphere chamber with real-time Transmittance-LSPR (T-LSPR) monitoring. The results showed that the algorithm can be a powerful tool to have a real-time analysis of the response of LSPR sensors and perform a fast diagnostic of the sensitivity of LSPR sensors to different analytes (either gas molecules or biomolecules).

CP-ThP9 Electron Fluence Dependency on Synthesis of Ru-rGO and its Specific Capacitance, *M. Iqbal,* Central University of Punjab, India*; A. Ambadas,* University of Pune, India*; N. Saykar,* Central University of Punjab, India*; I. Banerjee,* Central University of Gujarat, India*; V.N. Bhoraskar,* University of Pune, India*;* ***Santosh Kumar Mahapatra (skmahapatra741973@gmail.com)***, Central University of Punjab, India

Ruthenium-reduced Graphene Oxide (Ru-rGO) is synthesized using 6 MeV electron beam assisted radiolytic reduction method. The solution of $RuCl_3$ and dispersed GO is exposed to four electron fluencies of 1×10^{14}, 5×10^{14} ,1×10^{15} and 2×10^{15} e^{-}/cm^2. Structural and morphological properties of Ru-rGO are studied using XRD, Raman spectroscopy, FESEM and TEM. The size of Ru nanoparticles in the range of 2 nm to 5 nm, defect density of rGO in the range of 1.9 to 2.05 $\times10^{6}cm^2$, inter defect distance of Ru-rGO in the range of 1.5 to 1.65 nm are obtained with increase in electron fluency. Specific capacitance and time constant of Ru-rGO are obtained using CV and charging discharging plot. It is seen that specific capacitance of Ru-rGO prepared at electron fluence of 1×10^{14} e^{-}/cm^2 has more specific capacitance as compared to Ru-rGO prepared at electron fluence of 2×10^{15} e^{-}/cm^2. Decrement in specific capacitance may be due to increase in crystallinity and porosity of Ru-rGO prepared at higher fluence. The dependency of bulk resistance, charge transfer resistance, energy and power density of synthesized Ru-rGO on the electron fluence are also studied.

CP-ThP10 Atmospheric Plasma Oxidative Polymerization of Ethylene Dioxythiophene (EDOT) for the Large-Scale Preparation of Highly Transparent Conducting Thin Films, ***Dominique Abessolo Ondo (dominique.abessolo@list.lu)***, Luxembourg Institute of science and Technology, Luxembourg*; F. Loyer,* Luxembourg Institute of Science and Technology, Luxembourg*; J.B. CHEMIN, S. Bulou, P. Choquet,* Luxembourg Institute of science and Technology, Luxembourg*; N.D. Boscher,* Luxembourg Institute of Science and Technology, Luxembourg

The lightweight and flexibility of polymeric conductors are important asset appealing to the new generation of microelectronic. Among the various existing conducting polymers, the poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted a lot of interest for applications involving energy conversion. To overcome the poorly solubility of PEDOT encounter in wet chemistry, the plasma-enhanced chemical vapour deposition (PECVD) processes is shown to be an excellent alternatives for the formation such material. However, numerous side reactions occurring in PECVD obstruct the formation of regular polymer chains, leading to the formation of highly cross-linked materials called “plasma-polymers.” As a result, the PECVD attempts to form conductive polymers only formed thin films with rather low conductivity.

In an attempt to increase the conductivity of plasma polymerised EDOT (ppEDOT) thin films, the present study is reporting on for the first time the atmospheric pressure -PECVD (AP-PECVD) reaction of EDOT using an ultra-short square-pulsed dielectric barrier discharge. The AP-PECVD is a simple and easily scalable approach operating at room-temperature where the formation of the ppEDOT thin films does not involve the use of oxidants other than the reactive oxygen species (ROS) formed by the open air Ar/O2 dielectric barrier discharge. The oxidative polymerisation of EDOT is confirmed using UV-visible (UV-vis), Raman, and Fourier-transform infrared (FTIR) spectroscopy. The highly transparent (i.e., 98% transmittance) and durable conducting thin films are deposited on polyethylenenaphthalate (PEN) foils, demonstrating the scalability of the process on any substrates.

CP-ThP11 A Comparative Microstructure and Wear Morphology Study of Various Uncoated Cermet Tools for the High-Speed Dry Turning of AISI 304, ***Uttkarsh Patel (uttkarsh1012@gmail.com)***, *S. Rawal, A.F. Arif, S.C. Veldhuis,* McMaster University, Canada

This research work aims to investigate wear morphology of Ti(C, N)-based cermet tool for the high-speed dry turning of austenitic stainless steel 304 (AISI 304) specifically for finish turning operation. The different grades of cermet tools from the various manufacturers were used for comparative study. Various elements presence influence the microstructure of the cermet tool, which impacts on the cermet tool wear mechanism. A progressive wear study was performed at a fixed interval of cutting length to measure the tool wear of different cermet tools. The tool wear and structure of cermet tools were examined by Scanning Electron Microscope (SEM). Tool material compositions and phases were determined using Energy-Dispersive X-ray Spectrometry (EDS) and X-ray diffraction (XRD), respectively. The results show that different cermet grades significantly affect the tool life and microstructure of cermet tools.

CP-ThP12 Characterization of Flexible Transparent Electrodes Fabricated by Etching-Free Patterning of Silver Nanowire-Conductive Polymer Composites, ***Tae-Gon Park (ppxorhs@naver.com)***, *J.S. Park, J.S. Park,* Hanyang University, Republic of Korea

With the development of electronic devices, researches on deformable devices that bend or stretch are being actively studied. Indium tin oxide (ITO), the most widely used transparent electrode material, has low sheet resistance and high transmittance. However, ITO is fragile due to structural problems and it requires a high process temperature in order to maintain crystallinity, which makes it difficult for ITO to be used in deformable devices. For this reason, many studies are being conducted on the development of new transparent electrode materials, such as metal nanowire, metal mesh, graphene, carbon nanotube (CNT), and conductive polymers, to replace ITO. Among these materials, metal nanowires are expected to be commercialized first because they are evaluated to have advantages in terms of optical and electrical properties as well as flexible characteristics. In particular, research is focused on silver nanowires (AgNWs) having excellent electrical properties as the most representative electrode material of metal nanowires. In addition, a study has been reported on coating PEDOT: PSS, a kind of conductive polymer, on AgNWs to reduce contact resistance between nanowires and further improve flexibility. However, in this case, since PEDOT: PSS is coated on the entire AgNWs, there is a problem in that the transmittance of the electrode is significantly reduced.

In this study, we propose an effective method to improve the electrical properties and flexibility of AgNWs transparent electrodes as well as to improve the visible light transmittance of these electrodes. To achieve this, a transparent electrode was fabricated using AgNWs solution mixed with PEDOT:PSS and formed to have a mesh-like pattern through an etching-free method. Dispersed solution with AgNWs, PEDOT:PSS, and diacetylene glycol(2,4-Hexadiyne-1,6-diol) was spin-coated on PET substrate. Diacetylene glycol is photo-sensitive material which is used for developing AgNWs and PEDOT:PSS pattern by polymerizing. The coated sample was irradiated with UV (254 nm) under a photomask, then washed with DI water to develop the pattern. For the manufactured AgNWs electrodes, the surface morphology, sheet resistance and visible-light transmittance were measured via FESEM (Field Emission Scanning Electron Microscope), non-contact sheet resistance measuring system and spectrophotometer, respectively. In addition, the flexibility characteristics of these AgNWs electrodes were analyzed through bending and twist tests.

CP-ThP13 Mesh-like Patterning of Silver Nanowires through Selective Heat Treatment for Application to Flexible Transparent Electrodes*, Jong-Seol* ***Park (jongseol89@hanyang.ac.kr)****, T.G. Park, J.S. Park,* Hanyang University, Republic of Korea

Recently, as applications such as display and touch panels of flexible electronic devices have been expanded, transparent electrode materials are required to be flexible in addition to having excellent electrical and optical properties. Examples of such materials include carbon nanotubes, metal meshes, metal nanowires, and graphene. Among them, metal nanowires are evaluated to be advantageous in terms of commercialization because of superior electrical conductivity and high flexibility. In addition, metal nanowires can be prepared by inexpensive solution-based processes such as spin-coating, bar-coating, and spray-coating. However, metal nanowires have relatively high reflectance and high haze, as is commonly found in metal meshes. In addition, metal nanowires are generally used by coating them on the entire substrate, which causes a problem that the visible-light transmittance of the nanowire electrodes is lowered. To increase the transmittance, there is a need to manufacture a nanowire electrode having a pattern such as a mesh. Furthermore, metal nanowires have a relatively large electrical sheet resistance due to the large contact resistance between wires. To improve the sheet resistance of nanowires, post-treatment methods have been proposed by welding wire-wire contacts via heating. Such a post-treatment process can be easily carried out using a simple heat treatment device, but the nanowire will break if prolonged heating occurs.

In this study, a flexible transparent electrode of silver nanowires (AgNWs) with mesh-like pattern was manufactured using solution processes. Surface modification of the flexible substrate was performed using corona plasma. Using a bar-coating method, AgNWs were deposited on the flexible substrate. The mesh-like pattern of the AgNW electrode was successfully obtained by selective heat treatment without using lithography. For the mesh-type AgNW electrodes produced, surface morphology, transmittance and reflectance, electrical sheet resistance, and flexibility were measured and characterized as a function of the heat conditions used.

CP-ThP14 Optical and Electrical Properties of ZnO/Ag/ZnO and AZO/Ag/AZO Multilayers Deposited on Flexible Substrate Using High Power Impulse Magnetron Sputtering*, Yu-Hsuan Hsu* ***(tina0524@gmail.com)****, H.-W. Liu,* National Chung Hsing University, Taiwan*; W.-Y. Wu,* Da-Yeh University, Taiwan

As indium (In) becomes less and less, alternative transparent conducting oxide (TCO) coatings, especially for applications that need flexible or soft substrates, are being intensively investigated. Zinc-oxide (ZnO) is recognized as the most promising alternative material. Most of the studies show that substrate heating during the deposition or post annealing is required for ZnO or doped-ZnO coatings to exhibit high transmittance and low electrical resistivity. However, the required heating severely limits the use of flexible substrate. In this study, the ZnO/Ag/ZnO and AZO/Ag/AZO multilayers were deposited on polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) flexible substrates using high power impulse magnetron sputtering (HiPIMS) technique. During the deposition process, there is no additional heating and bias was applied to the substrates. The results show that multilayered coating on flexible substrate exhibiting excellent 96% transmittance and $3.4*10^{-5}$ Ωcm electrical resistivity has been obtained without any heating during the deposition or post annealing.

CP-ThP15 In-situ Observation of Low Temperature Crystallization Process of Germanium Thin Film by Gold Induced Layer Exchange*, Narin* ***Sunthornpan (nb19506@shibaura-it.ac.jp)****, K. Tauchi, N. Tezuka, K. Kyuno,* Shibaura Institute of Technology, Japan

Recently, crystallizing semiconductor thin films at low temperature using metal catalyst is becoming an increasingly active research field. The technique is important in realizing electronic circuits on flexible substrates which utilizes the low-temperature aspect of the process. Especially, the process to crystallize germanium (Ge) by gold (Au) is very popular both in the fabrication of nanowire and thin films. In this study, to clarify the crystallization mechanism in detail, an in-situ x-ray diffraction experiment during the crystallization reaction has been performed. It is found that an explosive crystallization of Ge takes place at a temperature as low as ~150°C, which is much lower than the eutectic temperature of AuGe alloys (~360°C) and is low enough for fabrication of electronic devices on plastic substrates such as polyimide.

Au films ranging from 1 to 10 nm were prepared by RF magnetron sputtering process on Si wafer with 100 nm thermally grown oxide (SiO_2) layer. Subsequently, Ge films (30 nm) were sputter-deposited on these Au films. The in-situ crystallization process was observed by x-ray diffraction (XRD) using a built-in heating chamber under N_2 ambient with temperatures ranging from 100 to 200°C. It is found that a rapid crystallization process of Ge takes place at a temperature as low as ~150°C, which decreases slightly as the Au thickness decreases. The Ge (111) diffraction intensity was also higher for thinner Au films, which suggests higher crystallinity. This was also confirmed by ex-situ Raman spectroscopy. By ex-situ SEM-EDS observation, it was also found that the density of crystalline grains was higher for Ge films crystallized with thinner Au films, which implies higher nucleation rate and therefore lower crystallization temperature by reducing the Au layer thickness. These new findings will open up the possibility to apply metal-induced crystallization methods to fabricate electronic devices on plastic substrates.

CP-ThP16 Role of Rare Earth Metal Ions Substitution on Structural, Electrical, Magnetic and Dielectric Behavior of Magnetic Nanomaterials*,* ***Salma Ikram (salmaikram@gcuf.edu.pk)****,* GC University Faisalabad, Pakistan

In this research work, we have investigated the influence of rare earth metal ions (RE^{3+}) substitution on various properties of Spinel ferrites. Four different series of spinel ferrites were prepared by wet chemical route. X-Ray Diffraction (XRD) analysis had confirmed the cubic spinel structure for all the synthesized nanoferrites having preferred (311) plane. Average particle size lies in the range 21.9- 46.4 nm. Both x-ray density and bulk density found to be increased by the substitution of RE^{3+} ions with Fe^{3+} ions but porosity of material decreases for all the prepared nanoferrites. FTIR spectra further confirmed the formation of spinel structure by showing two strong absorption bands ~ 480 cm^{-1} and 550 cm^{-1} that corresponds to octahedral and tetrahedral sites. Grain size obtained from SEM results lied in the range 54.05-38.69 nm. Crystallite size, grain size and lattice constant are found significantly affected by concentration of RE^{3+} ions. The temperature and composition dependent electrical resistivity and activation energy were calculated by current-voltage characteristics in the temperature range 423 to 823K by two probe method. It was observed that DC Resistivity and activation energy ranges between 10^9 to ~10^{10} Ωcm and ~ 2.85 eV respectively. Dielectric results showed that by decreasing frequency both dielectric loss and dielectric constant decreases. At low frequency region ac conductivity increases while at high frequencies it decreases with increasing frequency. MH curves of synthesized samples showed with the increase in RE^{3+} ion concentration saturation magnetization and remanence both found to be decreased. The reported characteristics made these prepared nanoferrites suitable candidates for high frequency and microwave absorber devices.

Coatings for Biomedical and Healthcare Applications
Room Grand Hall & Foyer - Session DP-ThP

Coatings for Biomedical and Healthcare Applications (Symposium D) Poster Session

DP-ThP1 Analysis of NO Radicals Generation by Extended Atmospheric Pressure Plasma Jet through Machine Learning and its use in Bactericide*, J.H. Hsieh,* ***Chun Yi Lee (M08188007@mail2.mcut.edu.tw)****,* Ming Chi University of Technology, Taiwan

NO radicals generated by atmospheric pressure plasma have been known to have great contribution on wound healing and other medical treatment. In this study, an extended APPJ was used to study how frequency, gas flow rate, type of gas influenced the NO density. For the extension of the plasma plume, silicone tubes of 20 and 50 cm were attached to the tip of quartz tube which served as the plasma generator. Then, varied frequency (5-10 KHz), He flow rate (5-15 slm), nitrogen flow rate (0-5 sccm), and oxygen 1 sccm were adopted to generate data of NO, OH, and O emission density. Optimization and prediction of the outcome for the processes are the aim of this study. In order to achieve this goal, a methodology involved BIG DATA analysis was adopted by using the software of STATISTICA. Totally, 20,000 sets of data were obtained for analysis. These results were compared with focus on the generation of OH and O radicals. The results of neural network analysis show that it is possible to predict the production NO, OH and O radicals when a combination of certain process parameters was used. It is also shown that the proportional NO intensity increases with O intensity, in general. In the experiment, three conditions which can produce mainly NO radicals were predicted and used to study their bactericidal effects, as a function of distance. The result is compared with conditions where OH or O was the major radical.

DP-ThP2 Characterization of Hierarchical TiO_2 Nanowires-Calcium Phosphate Composite for Biomedical Application*,* ***Kyung Hee Park (see0936@jnu.ac.kr)****, H.J. Song, Y.J. Park,* Chonnam National University, Republic of Korea

The deposition of TiO_2 thin films on dental implants is a way to improve the biological properties of implant materials by controlling the structure, morphology and thickness of the TiO_2 layer on the implant surface. Hierarchical rutile TiO_2 nanowires were successfully fabricated on titanium substrate via hydrothermal reactions of titanium tetraisopropoxide and hydrochloric acid at 180ºC for 3 h. These TiO_2 nanowire films were soaked in modified simulated body fluid (m-SBF) for 1 to 7 days to encourage the formation of calcium phosphate (CaP). The crystalline structure, shape and size of the prepared composites were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The nucleation and growth of CaP coating on TiO_2 nanowires (NW) in m-SBF solution was investigated using SEM, XPS, and FT-IR surface analytical techniques. Their density increased as the soaking time in m-SBF increased. These crystallites were aggregated with nano-sized particles which had sphere-like shape and low crystallinity of calcium phosphate. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2019R1A5A2027521 and No. 2017R1A2B1012074).

DP-ThP3 Light-activated High Efficiency Antimicrobial Coatings*,* ***Victor Bellido-Gonzalez (victor@gencoa.com)****, P. Killen, T. Sgrilli, D. Monaghan,* Gencoa Ltd, UK*; O. Hernandez-Rodriguez,* IK4-TEKNIKER, Spain

Antimicrobial resistance (AMR) is one of the major global challenges facing healthcare. Prevention of infections acquired in hospitals is the most effective way to fight AMR. Bacteria and other pathogens could be transferred via shared touch surfaces and instrumentation, and unfortunately health centres like hospitals present a breathing ground opportunity for some of the more resistant strains of pathogens. Maintaining an sterile environment is not always easy. Some of the complex instrumentation and equipment in hospitals, like robotics surgery instrumentation, are difficult to undergo through regular complete sterile conditioning protocols as they require complex and expensive cleaning procedure. In some cases the standard sterilasition autoclaving is not possible due to the nature of the instrumentation itself.

An approach which would offer a lower risk of cross contamination in such environments is the use of surfaces which can be “activated” and rapidly kill pathogens. In this paper we will present solutions based on surface coating technology which by light-activation becomes a very effective self-sanitizing surface, able to kill to levels of >99.99% of bacteria.

Recent developments by the authors have provided new analytical techniques for quantifying the ligh-activated antimicrobial efficiency of these coatings. Some of the coatings developed have been able to achieve high sterilisation performance even under “standard office”visible light conditions. Results will be presented.

DP-ThP4 e-Poster Presentation: Metallization of Polymers for Medical Applications using HiPIMS*,* ***Aarati Chacko (aarati.chacko@empa.ch)****, K. Thorwarth, R. Crockett, U. Müller, H.J. Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

In contrast to wet processes, which require toxic precursors, High Power Impulse Magnetron Sputtering (HiPIMS) is a relatively clean method to achieve polymer metallization. This makes it especially interesting for medical applications such as coating polymer implants. The large proportion of metal ions in the coating discharge, characteristic of HiPIMS, allows a high level of control over film-forming species. This physical vapor deposition method is therefore our method of choice to tailor and study the substrate-film interphase region responsible for adherent and durable coatings.

This study aims to understand the effect of oxygen plasma activation on the surface of a polymer using AFM and XPS. We then relate this to HiPIMS-metallized surfaces and interfaces using ATR-FTIR. The metal-polymer system for this study is titanium on PEEK (Polyetheretherketone), which has shown exemplary adhesion in the case of orthopedic implants for use in spinal fusion surgery. We aim to understand the interactions that lead to this good adhesion to bring further improvements, and also, translate our understanding to other metal-polymer systems.

DP-ThP5 Preparation and Properties of Ag Doped DLC Coating for Total Hip Joint Replacement*,* ***Jaykumar Patel (jay915795@gmail.com)****,* University of Saskatchewan, Canada

The silver (Ag) doped diamond-like carbon (DLC) coatings are prepared on the CoCrMo alloy using DC magnetron sputtering for biomedical implants. The silver concentration is varied from 0 at% to 10 at% in DLC matrix by varying the DC power to the silver target. Raman spectroscopy is carried out to evaluate the structural changes in carbon matrix. X-ray photoelectron spectroscopy (XPS) is done to measure the percentage of sp^3 carbon hybridization in coating with various percentages of silver. Secondary electron microscopy (SEM) is used with backscattered imaging (BSI) to check the uniformity and the size of silver particles. Mechanical and tribological properties are measured using nano-indentation, wear test and Rockwell C indentation. The hardness values show that initially with low percentage of silver, the residual stresses decrease drastically whereas the hardness values decrease slightly. But, after 7 at% of silver decreases the hardness drastically. Also, the reduced wear rate is measured with 5 at% of silver. The Rockwell C indentation indicates the improved adhesion of Ag-DLC coating on CoCrMo alloy.

DP-ThP6 Superamphiphobic Stainless Steel Surface Prepared by Femtosecond Laser Patterning and Pulsed Plasma-Polymerization*, C.W. Lin,* Central Taiwan University of Science and Technology; Feng Chia University, Taiwan*; C.M. Chou,* Taichung Veterans General Hospital; National Yang-Ming Universit, Taiwan*;* ***Chi-Jen Chung (cjchung@seed.net.tw)****,* Central Taiwan University of Science and Technology, Taiwan*; J.L. He,* Feng Chia University, Taiwan

Superamphiphobic surfaces, being super-repellent either water or oil, show various applications in self-cleaning, antifouling, non-staining surfaces, spill-resistant, corrosion prevention, and liquid separation. By employing femtosecond laser patterning and pulsed plasma polymerization, this study developed a dual-technique of surface modification to obtain superamphiphobic surfaces on the AISI 304 stainless steel substrates, usually made into dental archwires in orthodontics and dentofacial orthopedics. The characteristics of the superamphiphobic surfaces and *in vitro* wear tests in artificial saliva that mimicked tooth brushing, peanut-chewing, and nougat-chewing modes were performed to determine the durability of the superamphiphobic layer.

The experimental results showed that the water and oil contact angle (WCA and OCA) for bare stainless steel is 65° and 18°, respectively. After dual-technique treatment, the WCA and OCA were 160° and 146°, respectively; namely, both hydrophobicity and oleophobicity were enhanced significantly. It remains WCA and OCA to be 137° and 120°, respectively after 500 times toothbrush wear test. On the other hand, for simulating the food chewing circumstances, the WCA and OCA were, respectively, 129° and 26° for peanut, and 133° and 80° for nougat after 500 times. The peanut-chewing causes much disappearing superamphiphobic behavior than nougat-chewing because the carbohydrate, protein and oil ingredients in peanut transferred onto the surface. This has been verified by SEM, EDS, and FTIR analyses. As a whole, the superamphiphobic surface prepared on the dental stainless steel substrate exhibits good durability, demonstrating the promising applications in dental archwires for orthodontics and dentofacial orthopedics.

DP-ThP7 Low Temperature Plasma Oxidation Capability and Bactericidal Effectiveness of the Transparent Diffusive Coplanar Surface Barrier Discharge*, **Shi-Wei Huang (yax0915123876@gmail.com)**,* Ming Chi University of Technology, Taiwan*; C. Li,* National Yang Ming University, Taiwan*; J.H. Hsieh,* Ming Chi University of Technology, Taiwan

In this study, transparent IZO thin films were used as the embedded electrodes in diffusive coplanar surface barrier discharge (DCSBD). These films were deposited using RF sputtering at 140 W. The thickness was set at 200 nm. The electrodes were then patterned using photolithographic process. The plasma characteristics were investigated as a function of electrode gap by optical emission spectroscopy. The gap was set within the range of 0.8 to 1.2 mm. The width was maintained at 1.5 mm. Then, the device was applied in bactericide and low temperature oxidation. It is found the plasma intensity as well as radical density of the DCSBD was affected by the electrode gap. The shorter the gap was, the more significant the bactericidal effect would be. The DCSBD was also used to oxidize medical-grade titanium at the temperature of 35 ^{o}C. According to the results obtained from electrochemical testing in 3.5% NaCl solution, the samples could be more corrosion resisting, depending on the intensity of OH and O. Overall, the transparent DCSBD can be applied in bio-related fields efficiently that include bactericide and surface modification.

DP-ThP8 Improved Biocompatibility of Materials for Medical Applications via Coating Revealed by Studies of Nanoparticle-Cell Interactions*, **Natalia Abrikossova (natalia.abrikossova@liu.se)**, G. Pozina,* Linköping University, IFM, Thin Film Physics Division, Sweden

Progress in coating technologies and advances in fundamental understanding of materials with low dimensionality open exciting opportunities for their safe and efficient biomedical applications. For example, magnetic resonance imaging (MRI) contrast agents based on magnetic nanoparticles represent an efficient tool to improve image quality by enhancing the contrast between normal and diseased tissue, thereby increasing the utility of MRI [1]. In the optimization of the performance of the agent the improvement of the MRI signal contrast must be combined with its biocompatibility. Coating of the nanoparticles used as MRI contrast agents is an efficient tool to achieve this goal. Moreover, functionalization of the implant surface, e.g. via incorporation of nanoparticles of an average size of 500 nm or less containing an oxide of a non-toxic post-transition metal such as gallium can reduce the risk of a harmful infection caused by microbes when medical implants are in contact with living cells or tissues [2]. However, multiple preclinical and clinical studies are required to proof the biocompatibility of the newly designed materials. Thus, the development of methodologies for efficient evaluation and improvement of biomedical performance of novel coatings at the initial stages of their design is of primary importance. This is a complex process. A promising path presented in this work is to start with studies of nanoparticle interactions with isolated blood cells [3]. In particular, the effect of coating Gd-oxide nanoparticles (GdNPs) with sorbitol on their performance as MRI contrast agents has been investigated. The results show that the presence of sorbitol as capping layer on GdNPs clearly improves the nanoparticle performance and biocompatibility [3]. At present, we are investigating the effect of the Ga_2O_3 nanoparticles on the viability of neutrophils with more conventional cytotoxicity assays.

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DP-ThP9 Parameter Analysis of Flame Spraying Biomedical Ceramic Coatings*, **Pei-Jia Lai (ap414507@gmail.com)**,* National Taipei University of Technology, Taiwan

This study shows that hydroxyapatite coatings are formed by slurry flame spraying (SFS) under different spray conditions. Modern biomedical materials are typically coated with hydroxyapatite on metal surfaces for long service life and high biocompatibility, and most of these materials are sprayed with plasma spray, which is fast and can be applied on large areas. However, it is more expensive than flame spraying. Thus, in this experiment, hydroxyapatite powder (nano/micron/nano and micron) was used as a solute, solvent syllable for ethanol and deionized water, and with different proportions. Mix the slurry and spray it with flame on a 304 stainless steel surface. The effect of various parameters on the coating structure, the size of the powder, the surface roughness of the substrate, and the change of the spray distance through the robotic arm during spraying, and the air pressure flow rate of the atomized slurry are adjusted by changing the proportion of the slurry composition. We use X-ray diffraction analysis, scanning electron microscopes, surface roughness gauges, stretch testers and water contact angle gauges to measure the composition, surface and cross-section of the specimen. The structure of the coating as well as roughness, bondstrength and hydrophilicity. The contact angle gauge with water measures the composition, surface and cross-section of the test piece. The structure of the coating as well as roughness, bondstrength and hydrophilicity. The contact angle gauge with water measures the composition, surface and cross-section of the test piece. The structure of the coating as well as roughness, bondstrength and hydrophilicity.

DP-ThP10 Multi-functional Ta-Ga-O Thin Films Prepared by Codeposition of Gallium Oxide and Tantalum*, J.H. Hsieh,* ***Yi-Hsuan Hsiao (U04187145@mail2.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

Gallium oxide is a highly transparent semiconducting oxide material with good thermal stability and chemical inertness, while tantalum is a corrosion resistant material with excellent biocompatibility. Gallium has no known function in human physiology. However, the chemical properties that it shares with iron allow it to bind to iron-containing proteins (Trojan Horse effect), including the iron transport protein transferrin. Thus, malignant cells and microorganisms may be tricked into incorporating gallium in place of iron for iron-dependent processes which are critical to bacterial viability and growth. Hence, gallium ions can cause the death of bacteria. Accordingly, it is of great interest to know how Ga can function in Ta-Ga-O coatings, particularly. In this study, the targets of Ga_2O_3 and Ta were used in co-sputtering processes with Ar plasma. The binding states were also studied using XPS and Raman spectroscopy. The results show all the properties could varied according to the atomic ratios of three elements. When Ga_2O_3 :Ta = 1:3, the hardness is at the highest while the resistivity is at the lowest. In this condition, the antibacterial efficiency is not significant. When the percentage of Ga_2O_3 increased, the films transformed into amorphous state. When Ga_2O_3:Ta = 3:1, the antibacterial efficiency and optical transmission were improved.In addition to their antibacterial behaviors, the films’ mechanical and optical properties may be varied. The multi-functionality of the Ta-Ga-O films may be adjusted.

DP-ThP11 The Correlation and Machine Learning of O and OH Radical Generation with Process Parameters in an Atmospheric Pressure Plasma Jet and its Use in the Enhancement of Biocompatibility*, J.H. Hsieh,* ***Yu Wei Liu (U04187040@mail2.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan*; C. Li,* National Yang Ming University, Taiwan

Radical density is known to be critical in many of the applications involved low temperature atmospheric pressure plasma. In this study, an APPJ system was used to study how frequency, gas flow rate, type of gas influenced the densities of OH and O radicals produced in the APPJ. Overall, 50,000 set of data were generated. Then, the data were analyzed using the concept of neural network for machine learning. Eventually, the result shows that a developed algorithm was possible to predict the production of OH,and O radicals when a combination of certain process parameters was used. Following this, various ratios of OH and O radical intensities predicted by machine learning was used to treat polyurethane (PU) films in order to understand the improvement of biocompatibility. It was found that higher OH density may be more effective in culturing 3T3 cells, while O radicals may affect the surface roughness significantly.

DP-ThP12 Surface Modification of 3D Printed Polycaprolactone (PCL) Scaffold with Polydopamine Coating to Improve Bone Regeneration*, **Park Jisun (owner5306@kbiohealth.kr)**, J. Taegon, J. Yonghoon,* Osong Medical Innovation Foundation, Republic of Korea

Three-dimensional (3D) printing that can free-form fabrication of bone like scaffolds with controllable features and interconnected pores is noted for tissue engineering and drug-screening applications. For tissue engineering, a porous 3D scaffold which is applied to bone tissue regeneration should offer the hydrophilicity for favorable cellular interaction as well as bioactive molecule such as a growth factor owing to improve cell differentiation. In this study, we designed a bio-active scaffold using a very simple and direct method to manufacture polydopamine (DOPA) coated 3D polycaprolactone(PCL) pRHorous scaffold grafted with recombinant human bone morphogenic protein-2 (rhBMP2) as a means to create bone-tissue regenerative scaffolds. Moreover, 3D PCLSD exhibited an improved retention of bone morphogenetic protein 2 to evaluate osteoblastic proliferation and differentiation in vitro analysis in 3D DOPA coated scaffolds. To our knowledge, our approach can allow for the generation of scaffolds which possessed good properties for use as bone-tissue scaffolds.

DP-ThP13 Micro- and Nanoscale Antibacterial Sacrificial Anode Structures*,* ***Nadine Ziegler (nadine.ziegler@rub.de),*** Ruhr University Bochum, Germany*; A. Abuayyash, C. Sengstock, M. Köller,* Berufsgenossenschaftliches Universitätsklinikum Bergmannsheil, Germany*; A. Ludwig,* Ruhr University Bochum, Germany

Implant associated infections often lead to serious and difficult to treat clinical complications caused by bacteria adhering to implant surfaces and medical devices. To reduce implant associated infections, implant materials with antibacterial properties as well as good tissue compatibility are needed. Their development is guided by strategies that inhibit initial bacterial colonization and reduce biofilm formation, e.g. by surface functionalization with antibacterial elements like Cu or Ag. The antibacterial effect of those elements is based on the release of their ions. Since on an implant material the antibacterial agent is just needed directly after the implantation, the goal of this study was to use the sacrificial anode concept to achieve a fast but time-limited ion release of Ag^+. Therefore, Ag has been combined with more noble elements like Pt, Pd or Ir. In the first approach Ag microstructures were fabricated on top of a dense thin film of the noble element (Ag, Pd or Ir) using a combination of magnetron sputtering and photolithography. Although the total amount of Ag has been reduced compared to a dense Ag thin film this material combination leads to an increased ion release rate as well as an increased antibacterial activity against gram-negative (*E. coli*) and gram-positive *(S. aureus*) bacteria. The antibacterial activity of the microstructured samples has been tested under cell culture conditions as well as in an in vitro tissue-like infection model. The Ag amount was further decreased in the second approach. Using short time co- and sequential magnetron sputtering of Pt and Ag within the range of a few 10 s it was possible to generate bi-metallic nanoislands which are highly antibacterial against *E. coli* as well *S. aureus*. In summary, highly antibacterial sacrificial anode structures have been successfully realized on the micro- and nanoscale with a minimum of the used materials.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Grand Hall & Foyer - Session EP-ThP

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces (Symposium E) Poster Session

EP-ThP1 Effect of Molybdenum Disulfide nanoparticles addition on the Structure and Wear Resistance of Micro-arc Oxidation Self-lubricant Ceramic Layer on the 2A50 Aluminum Alloy*,* *X.-J. Li,* ***Min Zhang (m.zhang@live.com),*** *S. Wen, X. Mao,* Liaoning Normal University, China*; Y. Guo,* Liaoning University of Science & Technology, China

In this work, self-lubricant ceramic coatings with antifriction and lubrication properties were prepared on 2A50 aluminum alloy by micro-arc oxidation technique in silicate electrolyte containing nano molybdenum disulfide (0 g/l-8 g/l) of different concentration. The effects of MoS_2 concentration on the microstructure, phase structure, composition and wear resistance of self-lubricating Ceramic coatings were investigated by means of SEM, XRD, EDS, profiler and ball-disk friction and wear tester. The results show that the addition of molybdenum disulfide improves the critical breakdown voltage of micro-arc oxidation. Self-lubricating ceramic coatings are mainly composed of α-Al_2O_3, γ-Al_2O_3 and MoS_2. MoS_2 nanoparticles were evenly distributed in the MAO ceramic coatings. MoS_2 concentration has a great influence on the microstructure and wear resistance of micro-arc oxidation self-lubricating coatings on 2A50 aluminum alloy. The protective lubricating film formed between the ceramic coatings and the friction pair is the largest when the particle content is 4g/l, and MoS_2 can play a better role in reducing friction and lubrication, optimizing the microstructure of the ceramic layer, and improving the wear resistance of the ceramic layer.

EP-ThP2 e-Poster Presentation: Triboactive and Tribocatalytic Effects of Mo, W and Cu in (Cr,Al)N based PVD Coatings*,* *K. Bobzin, T. Brögelmann,* ***Christian Kalscheuer (kalscheuer@iot.rwth-aachen.de),*** *M. Welters,* Surface Engineering Institute - RWTH Aachen University, Germany

The efficient and sustainable use of energy and the associated reduction of greenhouse gas emissions are two of the major issues of our time. Therefore, the formation of friction and wear reducing tribochemical reaction layers in technical applications is induced by the interaction of steel surface and additives of the lubricant. Since the sweeping application of physical vapor deposition (PVD) hard coatings in order to meet the increasing demands concerning efficiency and reliability, the original steel surface is no longer available for steel/additive interactions. An alternative approach to enable the formation of tribochemical reaction layers is the deposition of triboactive and tribocatalytic PVD coatings on components. Thereby, the incorporated triboactive and tribocatalytic elements such as Mo, W and Cu can interact with lubricants. In prior studies the interaction of Mo and W with additives of the lubricants was already confirmed by the in situ formation of MoS_2. However, only a local restricted formation of MoS_2 was revealed. Therefore, the influence of Cu as triboactive and tribocatalytic element was investigated in order to enhance the amount and distribution of reaction layers in tribological contact.

Within this study, triboactive (Cr,Al,Mo,Cu)N and (Cr,Al,W,Cu)N coatings were deposited on AISI 5115 (16MnCr5E) in an industrial scale coating unit by means of PVD hybrid technology, consisting of direct current and high power pulse magnetron sputtering (dcMS/HPPMS). The influence of Mo, W and Cu on the phase formation were investigated using X-ray diffraction (XRD). Analysis of the mechanical properties was conducted by nanoindentation (NI) measurements. Tribological behavior of the coatings was analyzed under continuous sliding conditions in a pin on disc (PoD) tribometer at temperatures of T = (23±5) °C and T = (90±5) °C. Conventional additive free and additive enhanced mineral oils were used as lubricants. The initial Hertzian contact pressure was set to $p_H \approx 1{,}600$ MPa. In order to investigate the influence of the counterpart material on the tribological behavior, inert Si_3N_4 balls and 100Cr6 steel balls were used. The resulting wear was analyzed by confocal laserscanning microscopy (CLSM). Tribochemical and tribocatalytic interactions between the coatings and lubricants were studied by Raman spectroscopy. It was found that tribochemical interactions between the coatings and the lubricants can be determined. The results confirmed, that triboactive and tribocatalytic (Cr,Al,Mo,Cu)N and (Cr,Al,W,Cu)N coatings are a promising approach to achieve reduced friction and wear in tribological systems.

EP-ThP3 Influence of Gaseous Environment on the Tribological Behavior of TMD-based MS Coatings*,* ***Andrey Bondarev (bondaan2@fel.cvut.cz),*** *T. Polcar,* Czech Technical University in Prague, Czech Republic

The TMD coatings have been widely used in tribological applications where low friction coefficient is highly desirable, meanwhile presence of oxygen or/and water vapors in the ambient environment significantly reduce their tribological performance. By tailoring composition and structure, it is possible to achieve enhanced mechanical properties of TMD-based coatings and decrease the sensitivity to environment. For tribotesting in controlled environment air with different humidity, dry argon, dry nitrogen or vacuum were utilized mostly. But published results indicate that still there are splits in over leading factor affects degradation of TMDs lubricity, is it ambient moisture-sulfur bonding or oxidation process. Behind this discussion about reasons of TMDs degradation exposed to different environment one more curious observation was misplayed - it was found that friction behavior of Mo-Se-C coatings in even oxygen and moisture free environments can be influenced by inert atmosphere. This phenomenon was also detected for carbon-based coatings and, moreover, it was reported that friction coefficient in vacuum was higher in comparison with inert gas atmosphere, which means physisorption and chemisorption processes, changes in surface energy or even intercalation of gas atoms in material structure have measurable impact on friction processes. Another point is that gas atoms can be located in cages in the amorphous TMD coatings and their release in molecular form during friction test also influence on tribological properties. But gas-involved tribological processes are still almost fully under-explored field of material science and goal of present work is to uncover phenomena occurred in different environments during friction of TMD-based coatings using advanced characterization and simulation methods.

EP-ThP4 Tribological Behavior of DLC Films with Niobium Nanolayers of Several Thicknesses*, Adedayo Adeniyi (sherifadeniyi@gmail.com), J. Corona, J. Patel, Q. Yang,* University of Saskatchewan, Canada

To enhance the adhesion of diamond-like carbon (DLC) films unto implant biomaterials, interlayers are often used. In this investigation, different thickness of Nb nanolayer films was applied as an interlayer, to investigate their effect on the tribological behavior of the top layer DLC films. These Nb films which varied between 20 and 150 nm were deposited by RF magnetron sputtering, while the DLC films were deposited by DC magnetron sputtering. Using a profilometer, it was observed that the surface roughness of the several Nb nanolayer varied with thickness. The microstructure and bonding states of the DLC films were obtained with scanning electron microscopy and Raman spectrometry respectively. Tribological behavior of the DLC films was studied by nanoindentation, friction and wear tests. Improved adhesion was observed for all deposited DLC film with the best observed between 80 and 120 nm Nb interlayer. DLC films deposited within this range also showed improved wear resistance.

EP-ThP5 Preparation and Tribological Research of the Electrodeposited Ni–W Coatings for Piston Ring Application*, Pao-Chang Huang (abow213@gmail.com), C.C. Chou,* National Defense University, Taoyuan, Taiwan*; H.C. Wang,* National Chung-Shan Institute of Science & Technology, Taoyuan, Taiwan

Ni-W alloy displayed excellent mechanical strength, superior corrosion resistance and wear resistance by process of electrodeposition. Furthermore, it had potential to substitute for hard chrome because of fewer environmental hazards than conventional chromium bath processes. This study investigated to compare the Ni-W coatings with different processing parameters and their effects on mechanical properties and wear resistance. Then the optimal parameter was applied to piston ring. Results indicated that the content of tungsten (W) in the coatings of Ni-W alloy were between 23.8 wt.% and 42.2 wt.% by altering the DC current density and the concentration of the main salt. The best mechanical properties were obtained under the conditions of 40.6 wt.% W and a temperature of 600 °C for 1 hour. The friction and wear of the coating were performed by using a ball-on-disk abrader tester under SAE 10W40 lubricated conditions. The Ni-W coatings were compared with hard chrome plating which was widely used on piston rings. It was shown that the Ni-40.6 W coating had lower friction coefficient and better anti-wear characteristics than the hard chrome plating when heat treatment was at 600 °C for 1 hour. Then the Ni-40.6 W coatings were applied on pistion ring and operated in a 125cc, Single-cylinder, Air-cooled engine. Results shown that the Ni-40.6 W coating has good wear resistance and scratch resistance.

Keywords:Ni-W alloy, Electrodeposition, Tribology, Lubrication, Piston ring

EP-ThP6 Research on Thermal Lying Cu-Ni-Ti Three-element Alloy Coating*, Pei-Cih Jhan (bigeis188@yahoo.com.tw),* National Taipei University of Technology, Taipei Tech, Taiwan

This study mainly discusses the preparation of CuNiTi ternary alloy powder by mechanical alloying. The basic principle of thermal melting is a technique in which a material (powder or wire) is heated and melted, and then conveyed by high-pressure air to form a coating on a substrate. And using three different thermal spray coating methods, Flame Spray, High Velocity Oxygen Fuel (HVOF), and Air Plasma Spraying (APS) to prepare the coating. Comparison of coating microstructure and phase composition. The results show that X-ray diffraction analysis (XRD) of pure metal powders (Copper, Nickel and Titanium) with a single face-centered cubic solid solution phase (FCC). As the ball milling time increases, the powder begins to crack due to the strain hardening caused by the repeated impact of the grinding ball, and the powder particle size was decreases, and the intensity and width of the diffraction peak are continuously reduced. The powder particle size has not changed significantly during the three to six hours period of ball milling, and a ternary alloy is formed during mechanical alloying. The powder samples synthesized were characterized by scanning electron microscope (SEM). The three spraying methods are layered, and the layered structure of the coating is wide by flame spray coating, and there are obvious holes and oxide layers. As the ball milling time increases, the spray coating gradually thickens, and the layered structure of the coating is relatively dense for 36 hours.

In addition, during the spraying process, it was found that the HVOF unmelted large particle powder phenomenon was obvious, which was presumed to be caused by the powder not being preheated, so the powder preheating spray was compared. It is obvious from the SEM cross-section analysis that the cross section of the powder by flame spraying and HVOF unpreheated has obvious phenomenon of unmelted particles. After the powder is preheated to 60 degrees in a high temperature furnace, the large powder particles of the coating by flame spraying are melted.

EP-ThP7 Crack Behaviors and Optimization of Residual Stresses in L aser Cladding Based on HVOF Sprayed WC-Co C lad s*, M.D. Jean,* ***Cheng-Wu Liu (767962605@qq.com)****,* Fujian University of Technology, China

A comprehensive experimental study on the high-velocity oxygen-fuel (HVOF) sprayed tungsten carbide/cobalt (WC/Co) deposits using laser cladding was conducted. A response surface methodology based on a central composite design was used to analyze, predict and optimize the WC/Co deposits of the laser-based HVOF sprayed coatings. The morphologies and microstructures of the laser clads were characterized using optical microscope, scanning electron microscope and X-ray diffraction techniques. The crack behavior and residual stress-based fractures were explored. In addition, the relationships between the residual stress of the laser clads and three factors: laser power, scanning speed and stand-off distance were examined. Further, optimization of the control factors: laser power, scanning speed and stand-off distance to minimize the residual stress was attained using a response surface methodology. The resulting lower residual stress has decreased the fracture crack activities and did not easily induce delamination in the laser clads. Findings from this study would greatly contribute to optimizing the experiments and achieve an enhanced structural evolution in laser cladding.

EP-ThP8 The Effect of Interlayer on the Mechanical and Tribological Properties of TiSiN/CrAlN Multilayered Coatings Deposited by Cathodic Arc Deposition*, Wei-Yu Ho (weiyuho@mdu.edu.tw),* MingDao University, Taiwan*; J. Hung, L.C. Hsu,* Aurora Scientific Corp., Canada*; D.Y. Wang,* MingDao University, Taiwan

In this research, TiSiN/CrAlN multilayer coatings was deposited by cathodic arc deposition (CAD), controlling the different interfaces in order to evaluate their effect on mechanical and tribological properties. FE-SEM images showed multilayer architecture of coatings with different interface and the bilayer period. Mechanical properties exhibited a behavior that Hardness and Young's modulus depend on the different interface of multilayer coatings. Regarding to the residual stresses, a significant variation of residual stress was observed for multilayer coatings compare to each other. By scratch test, it was possible to study the deformed tracks in scratch tests to observe and to determine the main deformation mechanisms. The increase in critical load of coatings was obtained by changing the different interface in the investigation. With Regard to tribological properties, it was clearly observe the influence of multilayer architecture and the bilayer period. TiSiN/AlCrN coatings with different interlayer exhibited lower friction coefficients and wear rates than the monolayered coatings.

EP-ThP9 Fabrication and Characteristics of La-doped CoCrFeMnNi High-Entropy Alloy Films*, Chia-Lin Li (chialinli@ntu.edu.tw),* National Taiwan University of Science and Technology, Taiwan

A series of La-doped CoCrFeMnNi high-entropy alloy films (HEAFs) were deposited by using RF magnetron co-sputtering deposition system. Two CoCrFeMnNi high-entropy alloy (HEA) targets with identical chemical compositions were prepared, and one of the targets was then decorated with La ingots. La concentrations in CoCrFeMnNi-based thin films were controlled by various sputtering powers applied on a CoCrFeMnNi HEA target and a fix sputtering power on a La-decorated CoCrFeMnNi HEA target. Thereby, CoCrFeMnNi HEAFs with different La contents ranging from 0 to 19.4 at.% were acquired. The influences of La contents on the microstructure of HEAFs were studied by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Meanwhile, mechanical properties were examined by a nanoindentation. When La concentration was increased to 19.4 at.%, elastic modulus decreased to 139 GPa from 192 GPa of CoCrFeMnNi film. A discussion on the phase structure and precipitation mechanisms will be given further in this study based on the experimental results.

EP-ThP10 Influence of Nitrogen Flow Variation on The Structural, Mechanical and Tribological Properties of TiAlVN Coatings Deposited By DC Magnetron Sputtering*, Francisco Giraldo (francisco.giraldom@udea.edu.co), G. Bejarano,* Universidad de Antioquia, Colombia

AISI 420 stainless steel has become one of the most commonly used materials for the manufacture of cutting tools, injection molds, and surgical instruments in which high hardness, high corrosion resistance, and high wear resistance are required. However, this material barely reaches the minimum properties to have optimal performance in these applications. On the other hand, quaternary nitride hard coatings have been widely studied in the last decade due to their elevated mechanical and tribological properties which may be even superior to those exhibited by other hard coatings such as TiN, TiAlN, and TaN which have been widely studied in the literature. TiAlVN coatings were deposited from Ti-6Al-4V target at a working pressure of 0,4 Pa, rotation speed of 12 rpm, discharge power of 2 kW, temperature of 200 °C, an Ar gas flow of 16 sccm and fixed bias of -70 V with N2 gas flow of 0, 6, 7, 8 and 9 sccm in order to evaluate the effect of this on the microstructural, mechanical, and tribological properties of the coating. As shown in the analysis by SEM microscopy, a significant change in the structure of the coating is observed with the addition of nitrogen, where the densification of the columnar structure, commonly seen in these coatings, is observed with the increase in the flow of nitrogen. In the microstructural analysis performed by x-ray diffraction (XDR), evidence was found of the formation of α-Ti and b-Ti, as well as of the TiN phase with FCC structure, which are characteristics for this type of coatings, and there is no evidence of the formation of phases such as VN, AlN. These results were confirmed in the evaluations carried out by TEM. AFM analysis showed a decrease in roughness and grain size with an increase in nitrogen flow from 24.2 to 11.6 nm and 220.5 to 172.8 nm, respectively. The hardness of the TiAlV coated steel increased from 4.5 GPa to 19.5 GPa with the incorporation of nitrogen and the wear volume decreased by an order of magnitude. On the other hand, the incorporation of nitrogen into the TiAlV structure induced compressive residual stresses, which increased the adhesion of the coating to the substrate, as determined by the scratch test method. All coatings showed greater hardness and wear resistance compared to uncoated steel. These results suggest that TiAlVN coatings have potential for applications in the biomedical field and manufactures processes, particularly for the coating of surgical and dental instrumentation, as well as in the coating of injections and extrusion molds and dies of polymeric materials, among others.

EP-ThP11 Novel Spatially Coordinated In-situ Raman and Nanoscale Wear Analysis of DLC Film*, M. Rouhani,* ***Yeau-Ren Jeng (imeyrj@gs.ncku.edu.tw),*** National Chung Cheng University, Taiwan

The wear induced transformation on the microstructure of diamond-like carbon (DLC) film was analyzed using a novel combined in-situ system, integrating Raman spectroscopy and depth-sensing techniques. The DLC film was deposited on Si substrates using a filtered cathodic arc vacuum (FCVA) deposition system. Analysis using this synchronized characterization technique demonstrated that upon wear-induced removal of upper surface layers, the intensity ratio (I_D/I_G) for the area inside wear tracks decreases. It was also demonstrated that the peak position for the *D* line (P_D) shifts to higher wavenumbers, while the peak position for the *G* line (P_G) shifts to lower wavenumbers. Significant reduction in the coefficient of friction was noticed upon increasing the depth of the wear tracks. These results confirm our previous preliminary report on the possible existence of layers rich in sp^2 in the surface region. It was also shown that the wear debris is more graphitized.

EP-ThP12 Solid Lubricant Coatings Based on WS_2 Inorganic Fullerene*,* ***Svetlana Barseghyan (sbarseghyan@genioinc.com),*** Genio Inc., USA*; G. Diloyan,* NIS Inc., USA

Solid lubricants are solid materials that provide low friction between sliding and rolling surfaces. Most of them have lamella type structure and provide low friction thanks to low shear forces between their crystalline lattices. These materials can be used independently or in continuous matrix of binder to achieve the desired results such as high load and temperature, corrosion rand abrasion resistance etc. In the last few decades, nanoparticles have been widely studied and used to reduce both friction and wear. Inorganic nanoparticles with lamellar anisotropic structure are good candidates for lubrication. They provide high compression strength and low shear strength. In current research we describe a series of novel solid lubricant coatings, based on the modified nanostructured tungsten disulfide particles.

Inorganic fullerene like tungsten disulfide (IF-WS_2) has been selected as a main ingredient for the below described solid lubricant films. IF-WS_2 particles have spherical morphology that allows them to roll between the contacting surfaces and withstand considerably high loads compare to their classical analogues. The nanosize dimensions of those particles allows them to penetrate into the grooves between two rough surfaces, while their distinctive spherical morphology allows them to roll between the sliding surfaces by lowering friction between them up to 10 times in some applications. Decreased friction leads to reduced operating temperatures, metal wear, and overall production cost. In addition it provides non-failure service of many important mechanisms under extreme conditions of exploration.

The coating to the stainless steel and aluminum test samples have been applied by pressurized gas spraying at an ambient temperature with and without polymer binders. As polymer additives polyethylene and polyurethane have been applied and investigated. As pin on disk experiments have shown all solid lubricant have good adhesion to metal substrates with the thickness at about 0.5-2. µm and with the coefficient of friction less than 0.15. Some basic characteristics of the suggested coatings are described in Table I.

Table I. Some Basic Characteristics of the Suggested IF-WS2 based Coatings

Material	Coating	Thickness(µm)	Micro – Hardness(HV)	Coefficient of Friction
SS	IF- WS_2	0.5 -1.0	800-1000	0.05 - 0.1
SS	Polyethylene /IF- WS_2	1.0 -2.0	600-800	0.1 - 0.15
SS	polyurethane /IF- WS_2	1.5 -2.0	600-800	0.1 - 0.15
Al	IF- WS_2	0.5 -1.0	200 -250	0.05 - 0.1
Al	Polyethylene /IF- WS_2	1.0 -2.0	150 -200	0.1 - 0.15
Al	Polyethylene /IF- WS_2	1.5 -2.0	150-200	0.1 - 0.15

EP-ThP13 Effects of Sputtering Gas Systems on the Preparation of a-BN Films using RF Sputtering*,* ***Yuki Yamada (s16A3132FM@s.chibakoudai.jp),*** *T. Markuko,* Chiba Institute of Technology Graduate School, Japan*; M. Imamiya,* Hana Saidan, Japan*; Y. Sakamoto,* Chiba Institute of Technology, Japan

Mechanical properties and the structure of boron nitride (BN) are similar to carbon materials. In particular, chemical inertness of BN such as excellent oxidation resistance and reaction with iron-based materials is better than carbon. In addition, structure of a-BN (amorphous BN) is similar to amorphous carbon such as Diamond-like carbon. a-BN is considered to have excellent tribological properties. However, little has been reported on tribological property of a-BN films. So, in this research, preparation of a-BN films by sputtering method and evaluation of the tribological property were investigated.

BN films were prepared by RF sputtering using Ar, Ar-N_2, and Ar-N_2-H_2 as sputtering gas systems. h-BN was used as a target. RF power and pressure were 500W and 0.5Pa, respectively. Deposits were evaluated using Raman spectroscopy. The tribology properties were investigated using a ball on disk friction test.

The peaks of sp^2-BN (near 1370 cm^{-1}) and a-BN (near 1600 cm^{-1}) were recognized in the Raman spectra prepared under all conditions. In addition, peak of sp3-BN (near 1310 cm^{-1}) was recognized in the Raman spectrum of Ar-N_2-H_2.

As a result of the friction test, it was confirmed that a low friction coefficient of 0.1 was exhibited at sputter gas Ar-N_2-H_2. In contrast, high friction coefficient was exhibited at sputter gas Ar and Ar-N_2. From the wear depth of the sample after the friction test, it was confirmed that the wear depth was the deepest in Ar and the shallowest in Ar-N_2. The difference in the wear depth is considered to be caused by the difference in the wear mechanism.

As a result of Raman spectroscopy of the adhesion to the ball after friction test, the peak of H_3BO_3 was recognized under conditions exhibiting high friction coefficient (sputtering gas; Ar, Ar-N_2). Conversely, no peak of H_3BO_3 was recognized under the condition exhibiting low friction coefficient (sputtering gas; Ar-N_2-H_2). Therefore, the high friction coefficient exhibited in Ar and Ar-N_2 are considered to be due to the formation of H_3BO_3 during the friction test. Furthermore, low friction coefficient exhibiting in Ar-N_2-H_2 is caused by no formation of H_3BO_3 during the friction test.

In conclusion, tribology properties of a-BN were varied on the structure by using of different sputtering gas systems, and low friction coefficient was exhibited at Ar-N_2-H_2 sputter gas.

EP-ThP15 Development of Hydroxyapatite (HA) - Si Multi-layer Coatings Deposited on Ti-6Al-4V by Magnetron Sputtering*,* ***Julian Lenis (julian.lenis@udea.edu.co),*** *K. Pérez, F.J. Bolívar,* University of Antioquia, Medellín, Colombia

Hydroxyapatite (HA) is a calcium phosphate with the molecular formula $Ca_5(PO_4)_3OH$, which has a high osteointegration due to its chemical similarity with bone mineral. For this reason, it has been widely used as a component for implant manufacture. Its mechanical resistance is low, so it is normally used for filling small cavities or prosthetic replacement in zones subject to low loads. Nevertheless, for some years it has been used to coat metal surfaces which provide greater mechanical support, which extends its range of applications in the biomedical field. Besides, it has been found that silicon can enhance the biological response of this coatings. Among the techniques commonly used to obtain HA coatings, magnetron sputtering (MS) has been found to give these films high homogeneity, compaction and purity. In addition, the highest adhesion values between this biomaterial and, for example, the Ti-6Al-4V alloy, have been obtained by this technique. In the present work, a multilayer HA-Si coating was deposited on a Ti-6Al-4V alloy. The morphology, structure, phases, mechanical properties and the biological response were studied by means of field emission scanning microscopy, atomic force microscopy, Raman spectroscopy, X-ray diffraction, nano indentation and cell viability and adhesion.

Keywords: Magnetron sputtering**,** Hydroxyapatite, Structure, Roughness, Hardness, Cell viability, Cell adhesion.

EP-ThP16 Corrosion Resistance of Plasma Nitrided 410S Ferritic-Martensitic Stainless Steels*, **Luis Varela (luisvarelajimenez@usp.br)**,* University of São Paulo, Brasil*; M.T. Umemura, J.C. Calderón-Hernández,* University of São Paulo*; C.E. Pinedo,* Heat Tech Technology for Heat Treatment and Surface Engineering Ltd,*; A.P. Tschiptschin,* University of São Paulo

Low Temperature Plasma Nitriding of 410S ferritic-martensitic stainless steel was carried out in a 75%N_2 - 25%H_2 gas mixture, at 400°C, for 20 hours. Conventional Plasma Nitriding (CPN), was also carried out in the same atmosphere but at 500 °C. Structural and mechanical properties of the plasma nitrided 410S ferritic-martensitic stainless steel were examined using X-ray diffraction, scanning electron microscopy and microhardness testing. The corrosion resistance was asessed by potentiodynamic polarization testing in a 3.5% NaCl solution. Measuring of the mass loss was carried out after immersion of the specimens in a 3% $FeCl_3$ solution during 88 hours. The degree of sensitization (DOS) was conducted using the Double-Loop Electrochemical Potentiodynamic Polarization Technique (DL-EPR).T he results show that the 400 °C plasma nitrided surface consisted mainly of α'_N expanded martensite, ε-Fe_3N iron nitride and small quantities of γ'-Fe_4N nitride. At the higher temperature (530 °C) a white layer formed on top of the specimen's surface accompanied by an adjacent nitrogen diffusion layer, consisting of ε-$Fe_{2-3}N$, γ'-Fe_4N and CrN. The potentiodynamic polarization measurements showed that the pitting corrosion resistance of nitrided 410S steel was improved in comparison with the non-nitrided specimens. On the other hand, the mass loss results show that the LTPN samples presented a corrosion resistance equivalent to the non-nitrided samples. In contrast, the CPN sample showed the worst corrosion resistance, presenting a much higher mass loss. The DOS results showed that the non-nitrided specimens were less resistant to intergranular corrosion in comparison with the LTPN specimens. On the contrary, the CPN specimens exhibited a typical general corrosion curve without any passivation.

EP-ThP17 Mechanical Behavior of Boriding Microalloyed Steels Immersed in Diesel*, **Noe Lopez Perrrusquia (noeperrusquia@hotmail.com)**,* Universidad Politécnica del Valle de México, México*; M.A. Donu-Ruiz,* Universidad Politécnica del Valle de Mexico, México*; E.D. Garcia Bustos,* Universidad de Guadalajara, Mexico*; C.R. Torres San Miguel,* Instituto Politécnico Nacional - ESIME, Mexico*; G.J. Perez Mendoza,* Universidad Politecnica del Valle de Mexico, México*; J.V. Cortes Suarez,* Universidad Autonoma Metropolitana Azcapotzalco, Mexico, México

In this work is examined, the mechanical behavior of boriding microalloyed steels subjected to diesel immersion. The growth of the iron boride layers was obtained by the boron dehydrated paste process using the temperature of 1273 K for 6 h. the first part consisted in the determination of FeB/Fe_2B phases obtained by boron dehydrated paste, identified by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and microhardness (Hv). The second part; the boriding specimens are immersed for one year, after tensile test to observe the effect of mechanical behavior of each study material. This work contributes mechanical characteristics of innovative coatings for potential applications in the storage of fuels, oils and biofuels.

EP-ThP18 Substrate Influence on the Adhesion of Metallic Films*, **Megan J. Cordill (megan.cordill@oeaw.ac.at)**,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; P. Kreiml,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria

Flexible and foldable electronics are becoming more visible for consumers. These devices are often manufactured with metallic films or islands deposited onto compliant polymer substrates. More research is needed to fully understand how to control the metal-polymer interface of the vital interconnecting metal lines found in flexible electronics to improve reliability. While the methods to quantify the interface adhesion are available, a direct comparison of the adhesion of a standard metallic films on different substrates has not been performed. Our results demonstrate that a sputtered Ti adhesion interlayer does not improve the adhesion of Ag films to polyimide (PI) or polyethylene naphthalene (PEN). In addition, the Ag-PI interface had a higher adhesion energy relative to the Ag-PEN interface due to the different polymer substrate chemistries which influence the interface structure and chemistry.

EP-ThP19 Tribocorrosion Behavior of Boride Coating on Cocrmo Alloy Produced by Thermochemical Process in 0.35% NaCl Solution*, A. Rentería,* Universidad de Guadalajara, México*; **Marco Antonio Doñu-Ruiz (marckdr_69@hotmail.com)**,* Universidad Politecnica del Valle de Mexico, México*; M. Flores-Martinez,* Universidad de Guadalajara, México*; S. Muhl,* Universidad Nacional Autónoma de México, México*; N. Lopez-Perrusquia,* Universidad Politecnica del Valle de México, México*; E.D. García,* CONACYT - Universidad de Guadalajara, México, Mexico

This work presents the corrosion and tribocorrosion studies of the CoB and Co_2B layer on CoCrMo alloy surfaces, produces by the thermochemical process. The boriding process was carried out at 850°C per 2 hrs, using dehydrated boron past such as boron source. The boride layers were characterized with XRD, SEM and optical profilometry in order to determine the structure, surfaces morphology and roughness, respectively. A solution of NaCl at 3.5% was used to study the corrosion and tribocorrosion performance of the coated and uncoated surfaces. The tribocorrosion tests were carried out in a sliding-contact system with reciprocal movement, using a ball of Al_2O_3 of 10 mm such as counterbody. The corrosion test showed that the boride surfaces presented a higher tendency to the corrosion with higher E_{corr} and I_{corr} than the uncoated surfaces, nevertheless, in the tribocorrosion characterization this surface had similar kinetic friction coefficient and lower wear volume than the uncoated surfaces.

EP-ThP20 Microstructure and Tribology Behaviors of Composite Coatings on TC4 Titanium Alloy by Laser Cladded Combined with Plasma Cladding Technology*, **Wennan Su (suwennan@hrbeu.edu.cn)**, X.F. Cui, Y. Guan, Y. Zhao, G. Jin,* Harbin Engineering University, China

The composite coatings were prepared on TC4 offshore titanium alloy by laser cladded combined with plasma cladding technology. The microstructure, element distribution, phase composition, microhardness and tribology behaviors such as dry friction, corrosive wear of the composited layers were investigated. The results show that NiTi cladding coating was composed of NiTi,Ni_4Ti_3 $NiTi_2$. The TiC hard phase was in-situ generated in the interface of the compound coatings. The composite coating was well bonded with the substrate layer and showed good mechanical properties. Microhardness of NiTi cladding coating reaches to 650$HV_{0.5}$, whereas microhardness of the composite layer significantly improves near the surface (about 1100$HV_{0.5}$). Moreover, there is a slight scratch on the worn surface of plasma cladding-laser claded composite layer, while abrasive wear in micro-cutting form occurs on the surface of NiTi cladding coating.

EP-ThP22 About the Impossibility of a Mathematical Relationship between Hardness Values Measured by Vickers and Instrumented Nanoindentation Techniques*, **Esteban Broitman (esteban.daniel.broitman@skf.com)**,* SKF Research & Technology Development Center, Netherlands

The hardness of a solid material can be defined as a measure of its resistance to a permanent shape change when a constant compressive force is applied. At macro- and microscale, the Vickers hardness test is assessed from the size of an impression left under a load by a four-sided pyramid-shaped diamond indenter. The Vickers hardness number, HV, is then calculated as the indenter load L divided by the actual surface area of the impression A_c measured after the indentation. On the other hand, the instrumented nanoindentation hardness H_{IT}, using a three-sided pyramid-shaped diamond indenter, is calculated as the maximum indenter applied load L_{max} divided by the projected area of contact at maximum load A_{pml}, i.e., during the indentation [1].

There are many publications where authors try to compare their coating hardness values measured by nanoindentation with bulk hardness values that have been measured by Vickers tests. The comparison is usually made through a formula that is supposed to give an exact mathematical equivalence of hardness values between both methods: HV = 0.09 H_{IT}, with HV having units of kgf/mm^2 and H_{IT} having units of MPa. In this work, I demonstrate that this exact equivalence can be established only for hardness values of materials with 0% indentation elastic recovery. In other cases, I will show that it is impossible to establish such mathematical relationship.

[1] E. Broitman, "Indentation Hardness Measurements at Macro-, Micro-, and Nanoscale: A Critical Overview," *Tribology Letters,* vol. 65, p. 23, 2017. (Open Access Article)

EP-ThP23 Novel Micromechanical Approaches to Understand the Influence of Hydrogen on Materials Behavior*, **Jazmin Duarte Correa (j.duarte@mpie.de)**, J. Rao,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; X. Fang,* Technische Universität Darmstadt, Germany*; G. Dehm,* Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

The understanding of hydrogen interactions with different features (e.g. dislocations, grain boundaries, precipitates, etc.) in alloys and composites is essential either to control and benefit from the hydrogen technology, or to prevent the destructive outcome of hydrogen embrittlement. Failure mechanisms initiate at the atomic scale with hydrogen absorption and further interaction with trap binding sites or defects. Nanoindentation and related techniques are valuable tools to study independently such mechanisms due to the small volume probed. Even more, in situ testing while charging the sample with hydrogen can prevent the formation of concentration gradients due to hydrogen desorption.

Two custom electrochemical cells were built for in situ hydrogen charging during nanoindentation of the sample (Figure 1): “front-side” charging with the sample and indenter tip immersed into the electrolyte, and “back-side” charging where the analyzed region is never in contact with the solution and therefore the observed effects are only due to hydrogen. We discuss the advantages and disadvantages of both approaches during the study of the hydrogen effect on the mechanical behavior and incipient plasticity in bcc FeCr alloys. The newly developed back-side charging technique allows overcoming surface degradation that might occur during front-side charging. The presence of hydrogen on the top analyzed surface (Figure 1b) was assessed by Kelvin probe measurements, showing a fast hydrogen diffusion rate towards the upper surface as well as a pronounced release flow for the analyzed Fe-Cr alloys. This approach is being extended to the study of coatings, with especial interest at interfaces, often becoming hard trapping sites for hydrogen. These studies are therefore complemented with powerful characterization techniques (microscopy and analytics) to understand the role of hydrogen on the materials failure.

EP-ThP24 Tribological Properties of Sputter-deposited Mo Films on Polyimide*, E. Kobierska, S. Hirn,* Montanuniversität Leoben, Austria*; M.J. Cordill,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria*; **Robert Franz (robert.franz@unileoben.ac.at)**, M. Rebelo de Figueiredo,* Montanuniversität Leoben, Austria

In the last decade, the shift from rigid to flexible electronics has gained momentum and is mainly driven by display and touch panel technologies that are developed for flexible substrates like polymers or textiles. Unlike rigid electronics, thin film materials used in flexible electronics must withstand various static and dynamical loading conditions in order to ensure that the flexible display remains operational for a sufficiently long period of time. Tribological loading conditions are among them, in particular in the case of wearable electronics, but have only been scarcely studied in literature. Therefore, the tribological propertied of Mo films which were deposited on polyimide substrates with a thickness of 125 µm were analyzed. The Mo films were synthesized by high power impulse magnetron sputtering to a thickness of about 1 µm. To induce different residual stress states in the Mo films, two deposition distances (8 and 14 cm) and two Ar pressures (0.5 and 1 Pa) were used. The tribological tests were performed in ball-on-disk configuration with 1000 laps applying a load of 0.244 N. As counterparts, different materials were chosen including Al_2O_3, 100Cr6, PEEK (polyether ether ketone), POM (Polyoxymethylene) and NBR50 (nitrile butadiene rubber) to test the Mo films in different tribological contact situations. The recorded coefficient of friction (COF) was highest in the tests against NBR50 with values up to 3 in the beginning of the test and a subsequent steady decrease. The COF in the tests against the other counterpart materials was generally between 0.5 and 1.5. In terms of wear, higher wear was observed for in the tribological tests against counterparts of high hardness, i.e. Al_2O_3 and 100Cr6. As expected, abrasive wear mechanisms are active in these cases as observed from images of the wear tracks recorded with a 3D laser confocal scanning microscope and a scanning electron microscope. Predominant adhesive wear was noticed in the tests against the polymers and the rubber counterpart. The obtained results generally serve as a basis to explore the tribological behavior of thin films on flexible substrates like polymers.

EP-ThP25 Simulation of Adhesion between MoS_2 coated Si Scanning Probes*, **Sathwik Reddy Toom (sathwikreddy93@gmail.com)**,* North Carolina Agricultural and Technical State University, USA

Low dimensional materials and heterostructures that combine them are leading a revolution in electronic behavior which holds promise for use in flexible, wearable, and durable devices due to their unique electrical, thermal, optical, mechanical, and tribological properties. Key to the implementation of such devices is an understanding of adhesion between these materials. Recently researchers at the United States Air Force Research Laboratory have developed methods to coat scanning probe tips with 2D materials such as MoS_2 which enables researchers to directly measure adhesion in these materials. However, a fundamental understanding of the mechanisms at work is still lacking. In this work we present molecular dynamics (MD) simulations of adhesion between $MoS\text{-}_2$ coated scanning probe tips to help develop this understanding. The coated tips are constructed using a Voronoi tessellation method. Single layers of MoS_2 with randomized in-plane orientations are wrapped over a hemispherical surface centered at teach Voronoi point. Atoms from overlapping Voronoi cells are removed to create a polycrystalline shell of MoS_2. Sequential shells are created and merged to create a three layer coating over a 5nm radius Si (111) tip. Grain size is controlled by selecting a minimum allowable distance between neighboring Voronoi centers. For our adhesion studies, we constructed four different tips with MoS_2 grain diameters of 1.1nm, 1.5nm, 2.0nm and 3.1nm. To simulate adhesion, two tips are placed in position 0.5 nm above one another other. The tips are brought into contact with a velocity of 0.02 nm/ps until the desired target load is reached. After a holding period of 50 ps the tips are separated again at a velocity of 0.02 nm/ps. Force-displacement curves are generated during the indent cycle from which pull-in and pull-off forces are extracted. To investigate the stochastic nature of indentation, each simulation was repeated six different times with a peak target load of 10nN with slightly different initial starting conditions. Somewhat random pull-in and pull-off forces between 1 to 2 nN were observed for the 1.5 nm, 2.0nm, and 3.1nm MoS_2 samples. Pull-in forces were generally lower than pull-off forces. Additional factors such as load and orientation played little role in the pull-in or pull-off force.The tips with the smallest MoS_2 grain size showed much larger pull-off forces (up to 10x greater) as well as a larger variation in pull-in and pull-off forces. Observations of MD trajectories indicate bonding occurred between the two tips. In addition MoS_2 flakes were pulled from the tip surface and material transfer from one tip to the other was observed.

EP-ThP26 High-temperature Tribological Characteristics of Self-lubricated Solid Lubricants*, R.K. Gunda,* Mahatma Gandhi Institute of Technology, India*; **Suresh Kumar Reddy Narala (nskreddy@hyderabad.bits-pilani.ac.in)**,* BITS Pilani Hyderabad Campus, India

Metal working fluids are used to reduce high cutting temperature during sliding or machining process. But, application of cutting fluid creates several techno-environmental problems such as environmental pollution, biological problems, and soil contamination during disposal. Dry machining includes non-pollution of the atmosphere, no danger to health, no cleaning cost, and non-injurious to skin and allergy free. The advanced manufacturing process develops the formation of a self-lubricating film between sliding interfaces. As self-lubricating film, solid lubricants were found to be emerging lubricating properties. In the present work an attempt has been made to get the knowledge about the friction and wear characteristic at high-temperature on self-lubricated solid lubricants. Sliding tests were performed under pin-on-disc tribometer at various temperature (room temperature to 400 ^{0}C). MoS_2 solid lubricant coated WC as pin material was used to study friction and wear behaviour at elevated temperature of up to 400 ^{0}C. The results observed that MoS_2 coated surface undergoes some interesting morphological changes when exposed to high-temperature self-lubricating and these changes may affect the friction and wear characteristics.

EP-ThP27 Tribological Behavior of ZrC-Zr Coatings Deposited on Ti6Al4V and CoCrMo Alloys by HiPIMS*, **Luis Flores-Cova (luis.fcova@alumnos.udg.mx)**, O. Jiménez, M. Flores, M. Flores-Jiménez,* Universidad de Guadalajara, Mexico

Ti6Al4V and CoCrMo alloys are used in several applications. Ti6AL4V is widely used in orthopedic and dental implants due to their excellent corrosion resistance and biocompatibility. Nevertheless, the main disadvantage of titanium alloys is their poor wear resistance, whereas CoCrMo alloys are used due to their high wear resistance. In order to improve their wear resistance many coating systems have been deposited on these alloys. In this study ZrC-Zr coatings were deposited by High Power Impulse Magnetron Sputtering (HiPIMS) (Ionautics) under a selection of parameters. The growth morphology and the thickness of the films were studied from cross-sectional SEM images (Tescan). The structure of the coatings was analyzed by XRD technique (Panalytical). The mechanical properties (hardness and Elastic Modulus) were studied through nanoindentation techniques (Hysitron). The adhesion of coatings to the substrates was measured by means of scratch tests (CETR). Wear tests were performed using a tribometer (CETR) with a reciprocating sliding motion, using a 10 mm diameter Al_2O_3 ball, frequency of 1 Hz, a stroke length of 10 mm, sliding time of 30 minutes and at different normal loads (0.5, 1 and 2 N). The wear tracks were analyzed by optical profilometry (Filmetrics) and SEM (Tescan). In general, the thickness of the coatings resulted about 3 µm. Hardness on the other hand, was found to be above 10 GPa for all conditions. Wear results showed a better resistance of coatings in comparison to substrates and the multilayers showed a low coefficient of friction due to carbon content.

EP-ThP28 High Temperature Tribological Properties of WC-Co-(Cr_3C<>SUB>2-NiCr) HVOF Coatings*, N. Settar (nounousettar@gmail.com),* *N. Bacha,* Saad Dahleb University, Blida, Algeria

The authors investigated the high temperature tribological properties of WC-Co-(Cr_3C_2-NiCr) HVOF coatings. These coatings were designed to take advantage of the synergistic properties of a metallic matrix that is embedded with a wear- and corrosion-resistant chromium carbide phases in tandem with the abrasive wear-resistant tungsten carbide phase. The tribological properties (friction and wear) of this system were investigated from room temperature up to 750 oC. The morphology, chemical, and structural properties of the coatings post-tribotesting at 25°C, 300°C, 450°C, 600°C, 750°C were studied using scanning electron microscopy, energy-electron dispersive spectroscopy, and x-ray diffraction. A correlation between the frictional properties and the phases present in the wear track was deduced. In addition, in situ Raman spectroscopy was used to understand the changes in the tribochemistry in real time at different temperatures.

Keywords: WC-CrC, HVOF Coating, Wear, high temperature.

New Horizons in Coatings and Thin Films
Room Grand Hall & Foyer - Session FP-ThP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-ThP1 High Efficient Water Splitting Cell having High-entropy Oxide Catalysts*, Zi-Ting Huang (a0988248845@gmail.com),* *J.-M. Ting,* National Cheng Kung University, Taiwan

Exploring earth-abundant-electrocatalysts for oxygen evolution reaction is one of the promising ways to achieve efficient water-splitting for hydrogen production (a clean chemical fuel). At the anode, water is split into oxygen gas with accompanying protons and electrons. However, high cost and scarcity of Ir/Ru-based compounds limit their widespread use. In recent years, the concept of entropy stabilized in oxide systems has increased research activity in the field of “High entropy oxide (HEO)”, this new class of solids that have contain at least five elements, due to their special structure and application compared to ceramic with one or two elements have attracted increasing interest up to now. We have thus synthesized HEO powders under various conditions. The resulting powders were used as electrocatalysts for oxygen evolution reaction in alkaline solutions. Excellent overpotentials, high capacity, and long-term stability have been obtained. The catalysts performance will be discussed in terms of the materials characterization.

Keywords: High-entropy oxide, Anode, OER electrocatalyst

FP-ThP2 Characterization of Fe-Cr-Ni Alloy Thin Film Sputter Deposited from SUS316 Target*, Pak Man Yiu (pmyiu@mail.ntust.edu.tw),* *S.T. Wang, J.D. You, J.P. Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan

In this study we sputter deposited a Fe-Cr-Ni alloy film using SUS316 stainless steel as the target material. We deposited the film across a range of argon working pressure from 3 mTorr to 12 mTorr, and thickness ranged from ~200 nm to 1200 nm. Water contact angle of each specimen was measured. We found that the film surface showed a gradual transition from hydrophobic to hydrophilic behavior as the working pressure increased. At 12 mTorr / 1200 nm thickness the water contact angle measured was as low as ~20 degrees. We investigated the surface morphology with AFM and SEM, the images revealed that the specimens with high hydrophilicity possess a nano-pyramid structure, consisted of fibrous grains with a pyramid-like tip.

FP-ThP3 High-Entropy Perovskite Oxides as Advanced Catalysis*, Yi-Cheng Liao (luke19941221@gmail.com),* *J.-M. Ting,* National Cheng Kung University, Taiwan

When it comes to electrode catalysis, Ruthenium oxide (RuO2) and Iridium oxide (IrO2) show apparent performance. However, the high cost of these two catalysts is always a concern. In this context, perovskite oxide is receiving increasing attention as a potential replacement. Perovskite exhibits extraordinary tunability of their physical and chemical properties through composition control and structural variation. For use as a catalyst, the redox behavior, oxygen mobility, and ionic conductivity can all be tailored to enhance the catalysis performance. In this study, we have synthesized a new class of high entropy LaMO3 where M consist of 5 different metals using a chemical route. We demonstrate enhanced electrocatalyst performance as compared to common perovskite based on Lanthanum. The catalysts performance will be discussed in terms of the materials characteristics.

FP-ThP5 Hybrid Structures of p-n junction for Improving Efficiency of Photovoltaic Devices*, Paweł Jarka (pawel.jarka@polsl.pl),* Silesian University of Technology, Poland*; T. Tański, W. Matysiak,* Silesian University of Technology, Poland, Polska*; B. Hajduk,* Polish Academy of Sciences, Poland

In this paper Authors focused on production of the hybrid structures containing organic-inorganic layered structures with donor–acceptor interfaces enriched with inorganic nanoparticles. As a acceptor were chosen a narrow band gaps inorganic nanoparticle of cadmium sulfide (CdS), as a donor materials have been selected Poly [2,6- (4,4-bis- (2-ethylhexyl) -4H-cyclopenta [2,1-b; 3,4-b '] dithiophene) -alt-4,7 (2,1,3-benzothiadiazole)] (PCPDTBT) were chosen. In addition, nano-additives have been added to the active layer to facilitate charge transport .

The aim of this work has been the obtaining high efficiencies of solar energy conversion. Manufactured in this way organic - inorganic hybrid structure lead to intensify the formation and transport of the exctions. The final product was a hybrid cell containing the anode in the form of indium tin oxide layer (ITO) thinning), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT PSS) hole transporting layer (HTL), PCPDTBT/CdS heterojunction with nanoparticles and silver (Ag) cathode. The final structure hybrid cell was made of an anode in the form of indium tin oxide layer (ITO), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT PSS) hole transporting layer (HTL), bulk p-n heterojunction constituting a combination organic – inorganic materials, and alumina (Al) cathode.

The main goal of the presented work is to find optimal materials process parameters for obtaining the best efficiency of the final cells.

The studies have included structure and surface morphology of produced layers as well as optical and electrical properties. Next the obtaining hybrid cells have been subjected the tests of electrical properties and current-voltage characteristics

In this work the proposed innovation is the creating the hybrid structure by the application organic-inorganic connections in donor-acceptor junctions with inorganic nano-additives that facilitate electron transport.

FP-ThP6 The Electrospun 2D Nanomaterials And Their Application Possibilities*, Wiktor Matysiak (wiktor.matysiak@polsl.pl),* Silesian University of Technology, Poland, Polska

Over the last fifteen years, one-dimensional structures have been particularly popular in the field of both scientific research and expected wide application possibilities. Unlike other zero-dimensional, two-dimensional, or three-dimensional nanostructures, nanowires have two limited quantum directions resulting from their nanometer diameter due to which electrons can easily move in a precisely defined direction, which is determined by the length of a single nanowire. This allows for the use of this structure in elements in which the main challenge is to conduct electricity excluding the tunneling transition. In addition, due to very high energy densities occurring in single-dimensional oxide nanomaterials resulting from the nanometric diameters of individual nanowires, these materials exhibit extremely different and better optical, magnetic, and electrical properties in abducting their counterparts in the micrometer scale.

Nanomaterials in the form of nanofibers, nanowires or nanorods are characterised by a considerable length and a small cross-section whose diameter may be approximately 100 times smaller than their length. The most effective technology of production of 2D nanomaterials is producing fibres in the electrostatic field, which does not require complicated procedures and expensive equipment. This type of process allows to produce polymer and composite nanostructures on an industrial scale relatively easily and quickly. The electrospun 2D nanostructures were studied using scanning electron microscope (SEM) and transmission electron microscope (TEM) to analyse the influence of used temperature on the morphology and structures obtained ceramic nanomaterials. In order to examine the chemical structure of obtained electrospun 2D thin films, the energy dispersive spectrometry (EDS) was used. Optical property analysis was performed on the basis of UV-Vis spectra of absorbance as a function of wavelength. Using the modified Swanepoel method which the authors proposed and the recorded absorbance spectra determined banded refractive index n, real n' and imaginary k part of refractive index as a function of wavelength, complex dielectric permeability e, real and imaginary part er and ei of the dielectric permeability as a function of the radiation energy of the produced electrospun 2D thin films.

FP-ThP7 Comparison of Optical Properties of Bi_2O_3 Solid Layer and Thin Fibrous Mats Obtained via Spin-Coating and Electrospinning Techniques*,* *W. Matysiak, **Tomasz Tański (tomasz.tanski@polsl.pl)**,* Silesian University of Technology, Polska

Bismuth(III) oxide is a semiconductor with excellent physical properties, especially optical and electrical properties, such as the wide value of the energy gap contributing to the very good photocatalytic properties of Bi_2O_3 (a-Bi_2O_3 2,91 eV, b-Bi_2O_3 2,51 eV, g- Bi_2O_3 2,8 eV), high refractive index and dielectric constant, very good photoconductivity and luminescence properties.The purpose of the research were produced of two types of two-dimension Bi_2O_3 nanostructures - solid layer and thin fibrous mats obtained via spin-coating and electrospinning technique from a solution based on polyacrylonitrile (PAN), dimethylformamide (DMF) and bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$). The obtained thin films were subjected to drying at room temperature for 24 hours and then calcination in air at two different temperatures of 600°C and 800°C. A scanning electron microscope (SEM) and a transmission electron microscope (TEM) were used to determine the influence of the temperature used during the calcination process on the morphology and structures of the obtained bismuth(III) oxide ceramic nanostructures. In addition, to analyse the chemical composition and oscillatory transitions of atoms vibrating between the oscillatory levels in the molecules of the produced 2D bismuth oxide nanostructures and to determine the functional groups existing therein, energy dispersive spectrometry (EDX) and Fourier-Transform Infrared spectroscopy (FTIR) were used. To analyse the optical and electrical properties of the obtained nanomaterials, a UV-Vis spectrophotometer was used. Based on the received spectra of absorbance as a function of the wavelength, the refractive index n, real n' and imaginary k part of the refractive index as a function of the wavelength, complex dielectric permeability ε, as well as real and imaginary part εr and εi of the dielectric permeability as a function of the radiation wavelength of the produced ceramic bismuth(III) oxide thin fims, were used to determine the impact of the temperature used during the calcination process on their physical properties. In addition, using the obtained Abs(λ) spectrum, the energy band gap of the produced Bi_2O_3 thin films was determined.

FP-ThP8 Structure and Mechanical Properties of ZrB_{2+x} and $ZrAlB_{2+x}$ Hard Coatings*,* ***Tomáš Fiantok (tomasfiantok1@gmail.com)**, T. Roch, M. Truchlý,* Comenius University in Bratislava, Slovakia*; P. Švec,* Slovak Academy of Sciences, Slovakia*; M. Zahoran, M. Mikula,* Comenius University in Bratislava, Slovakia

Transition metal diborides (TMB_2) of the IVB to VIB group are in the form of films, attractive for use in the mechanical engineering industry due to their high temperature stability, excellent mechanical properties, in particular high hardness, and wear resistance. Here, we present two approaches to influencing stoichiometry, structure and mechanical properties of the perspective ZrB_{2+x}. In the first approach, we focus our efforts on investigating the effect of the amount of Ar particles and their energy on the sputtering of a stoichiometric ZrB_2 target resulting in a change in the character of the growing films. Using High Target Utilization Sputtering (HiTUS), where it is possible to influence the energy of target bombarding Ar particles (target voltage) at their constant amount (constant target current), we have grown nanocrystalline ZrB_{2+x} films over a wide concentration range (x ~ 2.4 ÷ 3.2). The highest hardness of 44.6 ± 2.0 GPa and the lowest hardness of 35.9 ± 1.0 GPa were achieved for $ZrB_{2.39}$ and $ZrB_{3.2}$, respectively. The films have a brittle character, expressed by the high Young's modulus, with the highest value of 446.0 ± 11.6 GPa for $ZrB_{2.39}$.

In the second approach we focused on investigating thermally-induced changes in the structure and mechanical properties of ZrB_{2+x} films alloyed with aluminium. The ternary system Zr-Al-B_{2+x} was prepared by magnetron sputtering of sintered $ZrAlB_2$ target with aluminium content 10 at.%. The idea is based on the theoretical prediction of B. Alling et al. [1] who, based on the different bulk moduli and volume misfits of the binary constituents ZrB_2 and AlB_2, predict that Zr-Al-B_2 is a metastable system with a tendency to spinodal decomposition during annealing. This phase separation can be accompanied by age hardening, similar to the known Ti-Al-N system. Here, we have grown Zr-Al-B_{2+x} films containing approximately 5 at.% Al, where the B/Zr ratio is approx. 2.6. The films have a hexagonal highly orientated (0001) structure. The addition of aluminium to the films reduces the hardness to 28.8 ± 1.0 and the Young's modulus to 335.6 ± 6.4 GPa. Subsequently, the annealed Zr-Al-B_{2+x} films are investigated by wave-dispersive x-ray spectroscopy (WDS), x-ray diffraction (XRD), transmission electron microscopy (TEM) and nanoindentation measurements. The experiments are supported by density functional theory (DFT) calculations.

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FP-ThP9 Structural and Photoluminescence Properties of ZnO Nanorods Grown on Various TCO Seed Layers by Chemical Bath Deposition*,* ***Tomoaki Terasako (terasako.tomoaki.mz@ehime-u.ac.jp)**, K. Hamamoto,* Ehime University, Japan*; M. Yagi,* National Institute of Technology (KOSEN), Kagawa College, Japan*; Y. Furubayashi, T. Yamamoto,* Research Institute, Kochi University of Technology, Japan

Zinc oxide (ZnO) with a wide band gap (E_g) of ~3.37 eV and a large exciton binding energy of ~60 meV has received much attention because of its wide range of applications. The use of quasi-one-dimensional (1D) nanostructures, such as nanowires, nanorods (NRs) and nanobelts, in ZnO based gas-sensing devices and photodetectors is expected to be effective for achieving higher performance. Among various methods for preparing the 1D-ZnO nanostructures, we have paid our attention to chemical bath deposition (CBD) because this is usually performed at low temperatures (<100 °C), which allows us to use polymers as substrate materials. In this paper, the influences of the difference in seed layer on the structutral and photoluminescence properties will be discussed.

The ZnO NRs layers were grown on ion-plated ZnO:Ga (IP-GZO), SnO_2:F (FTO) and In_2O_3:Sn (ITO) seed layers, by CBD using the mixed aqueous solutions of $Zn(NH_3)_2{\cdot}6H_2O$ (ZnNit) and $C_6H_{12}N_4$ (HMT). Both the concentrations of ZnNit and of HMT were varied in the range of 0.025-0.075 M. Bath temperature was kept at ~86 °C. Growth time was varied in the range from 30 to 180 min.

SEM observations revealed that the vertically aligned NRs were successfully grown on the IP-GZO seed layers. After the growth time of 60 min, their average diameter and length tended to be saturated at 80 and 600 nm, respectively. On the other hand, on the FTO and ITO seed layers, many NRs were inclined with respect to the the seed layer surface. Both the average widths and lengths of the NRs grown on the FTO and ITO seed layers were lager than those on the IP-GZO seed layers and became lager with the growth time.

All the photoluminescence (PL) spectra were composed of a near-band-edge (NBE) emmission at ~380 nm and an orange band (OB) emission at ~600 nm. Regardless of the difference in seed layer, PL intensity ratio of the NBE emission to the OB emissin (I_{NBE}/I_{OB}) became larger with the increase in the average width of the NRs. There is a possibility that the reduction of the band bending formed at the NR surafce contributes to the increse in I_{NBE}/I_{OB} with increasing the average width of the NRs [1,2].

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FP-ThP10 Characterization and Photoluminescence of Al- and Ga-doped V_2O_5 Nanostructures Synthesized by Thermally Activated Process*,* ***Chih-Chiang Wang (twinbads@yahoo.com.tw)**,* National Chung Hsing University, Taiwan*; C.L. Lu,* Chinese Culture University, Taiwan*; F.S. Shieu,* National Chung Hsing University, Taiwan*; H.C. Shih,* Chinese Culture University, Taiwan

V_2O_5 has an orthorhombic crystal structure, and narrow direct and indirect bandgaps of 2.4 and 2.0 eV. Its optoelectronic properties can be modified by adding various dopants, such as Ga, Al, and Nd, due to the formation of the defect-levels. The applications of V_2O_5 are widely used in gas sensors, catalysts, and electrochromic devices. In this study, Al- and Ga-doped V_2O_5 nanostructures were fabricated by the thermally activated process at 850°C via the V-S mechanism. The Raman and XRD patterns have showed the typical V_2O_5 orthorhombic crystal structures of Al- and Ga-doped V_2O_5. The variations of c/a and c/b ratios estimated from the XRD patterns confirmed the substitutions of the Al^{3+} and Ga^{3+} into the V^{5+} lattice sites. HRTEM images showed that the growth direction of Al- and Ga-doped V_2O_5 nanostructures were along the [110] direction. The XPS results for the Al-doped V_2O_5, metallic Al was formed inside the nanostructure and the amorphous Al-O and Al-OH phases were generated on the nanostructure surface; for the Ga-doped V_2O_5, Ga-O phase was formed in the V_2O_5 nanostructures. PL spectra showed the increasing intensities in blue (1.94 eV) and green (1.77 eV) emissions of the V_2O_5 nanostructures while the Ga dopant was in 0.5 wt.%, which can be contributed to the formation of and -defects; the Al dopant showed a decreasing intensities in blue (1.94 eV) and green (1.77 eV) emissions of the V_2O_5 while the adding of Al, which can be attributed to the formation of the metallic Al inside the V_2O_5 nanostructures. This study showed that the photoluminescence properties of V_2O_5 nanostructures can be modified by the dopants of Al and Ga. The Al dopants revealed a significantly suppressing effect while starting the addition of Al, and the Ga showed an enhancing effect while the Ga contents were in 0.5 wt.%.

FP-ThP11 Microstructure and Physical Properties of $AlCoCrCu_{0.5}FeNi$ High Entropy Alloy Nitride Thin Films Grown by Reactive Magnetron Sputtering*,* ***Naveed Aziz Khan (nkha6211@uni.sydney.edu.au)****, B. Akhavan, M.M. Bilek, Z. Liu,* The University of Sydney, Australia

High entropy alloy (HEA) thin films are immensely studied due to their excellent structural, chemical and physical properties having high hardness, superior oxidation and corrosion resistance, and high hydrophobicity. This study reports the findings of $AlCoCrCu_{0.5}FeNi$ HEA nitride thin films grown from a single stoichiometric target on Si (100) substrate at three different nitrogen flow ratios (R_N) of 6.25 %, 12.5 %, and 25 % with a substrate heating of 250 ºC. The RF power was set at 300 W and the deposition pressure was maintained at 10 mTorr for all the films grown at three different nitrogen flow ratios (R_N). The characterization results from X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) analysis revealed that the increase in R_N from 6.25 % to 25 % changes the structure from crystalline to amorphous form. The increase in nitrogen flow ratio reduces the average grain size from 150 to 85 nm as well as the surface roughness of the nitride films from 27.5 to 3.30 nm observed from the Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) micrographs, respectively. The surface chemistry analysis from the X-ray Photoelectron Spectroscopy (XPS) confirms the presence of Al_2O_3 and Cr_2O_3 on the surface of all the HEA nitride thin films grown at different nitrogen flow ratios, forming the surface protective layers for superior oxidation and corrosion resistance. Energy Dispersive Spectroscopy (EDS) measured the changes in elemental composition and mapping confirms the homogeneous distribution of all the elements throughout the films grown at various nitrogen flow ratios. The hardness data measured from the nanoindentation test demonstrates an increase in hardness from 6.13 GPa to 9.75 GPa with the increase in R_N from 6.25 to 25 %. The highest contact angle of 112 º was obtained for the film deposited at the highest R_N of 25 % confirming the hydrophobic nature of the HEA nitride thin films. The above characterization results show that the variation in nitrogen flow ratios (R_N) is an important parameter to modify the microstructure and the chemical composition of $AlCoCrCu_{0.5}FeNi$ thin films during the reactive sputtering process which controls the physical properties of the sputtered HEA nitride thin films having possible applications as hard and surface protective coatings suitable for the energy and aerospace industry.

FP-ThP12 Effect of Process Pressure on Structure and Mechanical Properties of Amorphous (AlCoCrNi)N High Entropy Nitride Thin Films*,* ***Ki Buem Kim (kbkim@sejong.ac.kr)****, Y.S. Kim,* Sejong University, Republic of Korea*; Y.K. Park,* YG-1 Co. Ltd., Republic of Korea*; K.S. Kim,* YG-1 Co. Ltd, Republic of Korea

Novel AlCoCrNi high entropy nitride films were prepared on Si substrate by a reactive DC magnetron sputter deposition. In order to identify the effect of process parameters on the microstructure and mechanical properties of the film, nitrogen flow ratio and process pressure were controlled, respectively. The structural and the chemical analysis of the films was examined using XRD and FE-SEM, respectively. For the detailed microstructure analysis of the films, a TEM was employed. The mechanical properties were measured using a nanoindenter at room temperature.

In present conditions, all the films were observed as an amorphous phase with composition of near-equiatomic ratios. However, the limited mechanical properties were identified for the films deposited under different nitrogen flow ratios. To optimize the structure and the mechanical properties of the AlCoCrNi high entropy nitride film, process pressure was systematically controlled. From the TEM observation, the microstructure of the film deposited at the process pressure of 1.33 Pa is identified as a porous and open structure with a number of density-deficient boundary and nano-scale voids. As the process pressure was decreased to 0.13 Pa, densified and smooth morphology of the film was observed. As a result, the hardness, elastic modulus, and H/E were enhanced up to 16.8, 243 GPa, and 0.0692, respectively.

FP-ThP13 Fracture Resistance Characterized by Bonding Nature Via Ab Initio Calculations*,* ***Christoph Fuger (christoph.fuger@tuwien.ac.at)****,* TU Wien, CDL-SEC, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* TU Wien, CDL-SEC, Austria

Fracture resistive thin films are of high interest, not only in the aerospace industry to improve the erosion resistance of high-performance components, but also in diverse applications in the automotive industry. As the resistance against erosion is mainly influenced by hardness and fracture resistance, it is necessary to enhance ideally both material characteristics. Initially, potential candidates are selected based on promising values of both, fracture resistance and a pronounced hardness. Screening methods by means of elastic constants evaluation (gained by DFT calculations) have evinced the previous mentioned demands for transition metal diborides [1]. The theoretically predicted ductile behaviour of various borides was confirmed in experiment, revealing also high hardness values [2].

Therefore, group V-VII transition metal diborides have been chosen to get a deeper understanding of chemical bonding and the repercussions on ductility and fracture resistance. Density functional theory using the Vienna Ab-initio Simulation Package was conducted to calculate charge density distributions of the diborides in space group 191 (α-structured, AlB_2-prototype) and 194 (ω-structured, W_2B_{5-x}-prototype). For a more detailed characterization of the prevalent bonding character within this material systems, density of states has been evaluated showing also overlapping of particular electron orbitals. Furthermore, bonding properties have been investigated after deforming the crystal lattice, as also described in [3]. Strained and unstrained structures have been compared, leading to distinct differences in bonding nature and thus, indicating consequences on macroscopic material properties.

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FP-ThP14 Combinatorial Sputtering Exploration of Zn-Sn-O (ZTO) Composition Spreads*,* ***Siang-Yun Li (m98l0217@gmail.com)****, Y.H. Shen,* National Cheng Kung University, Taiwan*; K.-S. Chang, J.-M. Ting,* National Cheng Kung University (NCKU), Taiwan

Transparent conducting oxide (TCO) films are extensively applied as electrodes in the fields of solar cells and displays due to their high transparency and excellent electrical conductivity. Multicomponent TCO such as Zn-Sn-O (ZTO) have attracted much attention. In addition, thermal stability and mechanical strength of ZTO can be tailored by varying its stoichiometry. However, making compounds having different ratios of Zn/Sn systematically is not trivial. We have therefore used a combinatorial methodology to solve this issue. This approach allows the Zn/Sn ratio continuously to change across a single sample area and a feasible intimate mix of Zn and Sn. A single ZTO composition spread sample essentially includes a full spectrum of properties to be investigated. A Zn-Sn-O (ZTO) composition spread, consisting of thickness wedges of SnO and ZnO, was prepared using a state-of-the-art combinatorial sputtering system, equipped with a moving shutter and two RF guns for the targets of Zn and Sn, respectively. The thickness gradient was determined using SEM, α-step, and SIMS. It was found a smooth thickness variation across the sample area for both ZnO and SnO with the coefficient of determination (R2) ≅ 0.99, indicating a good control of the ZTO composition spread. Structure evolution was characterized using XRD. It was found that in-situ 500 ºC annealing results in crystallization of the samples, where ZnO, Zn2SnO4, ZnSnO3, and SnO2 phases were observed, depending upon the ZnO/SnO ratio. The resistivity was characterized using a four-point probe on different substrates, which revealed lower resistivity near ZnO-rich area. Morphology and optical characteristics were studied as well using AFM, SEM, and UV-Vis spectrometry. A clear variation trend of both properties was observed. A systematic study of physical properties of ZTO has been successfully demonstrated.

FP-ThP15 Electrical and Mechanical Properties of NbMoTaW(Re) High Entropy Alloy Thin Films, ***Chuan-Feng Shih (cfshih@mail.ncku.edu.tw)***, *C.H. Yeh, W.D. Hsu,* National Cheng Kung University, Taiwan*; C.H. Hsu,* National United University, Taiwan*; B.H. Liu, S.K. Lin, Y.W. Hsiao,* National Cheng Kung University, Taiwan

The high-entropy alloys (HEA) with at least four principle elements have shown excellent mechanical properties such as high ductability and hardness. However, because of the scattering effect caused by atomic distortion, the high-conductive HEA thin films has been rarely obtained. The resistivities of the highly-conductive HEA in the literature were higher than 200 μΩ-cm, which are about one to two orders higher than the conventional pure and alloyed metals, equivalent to metallic glass.

This work studies the equal-molar HEA thin films that have both excellent mechanical and electrical properties, i.e., low resistivity. Quaternary NbMoTaW and NbMoTaWRe HEA films were studied. All of the thin films were deposited on the silicon substrate by a DC magnetron sputtering. The microstructure, composition, crystal structure, grain size, resistivity and hardness were analyzed.

As a result, the NbMoTaW HEA films showed a pure body-centered cubic solid-solution phase, which was revealed by x-ray diffraction with 2θ at 39.4˚(110) without any second phase. The additional of Re did not change the crystal structure, but slightly shifted the 2θ peak to 39.5˚. Obvious sheet-like grains were observed, which could be enlarged by increasing the dc-power and deposition time that further increased the conductivity. Post heat treatment was ignorable on the resistivity, possibly owing to the sluggish diffusion nature of this HEA material. As an optimized condition, when the thickness is close to 600 nm, the NbMoTaW HEA films showed the lowest resistivity of 54 μΩ-cm, slightly increasing to ~77 μΩ-cm upon 12% Re incorporation. On the other hand, the hardness of the NbMoTaW film was 1807 HV, markedly increasing to 2180 HV by Re incorporation. The experimental results of the crystal structure and mechanical properties were in good agreement with our simulation results. Finally, we would suggest that such HEA films have great application potential to surface protecting of soft and conducting materials.

FP-ThP16 Fabrication of Nanocomposite Thin Films of Metallic Nano Particles in Amorphous Carbon, ***Stephen Muhl (muhl@unam.mx)***, *F. Maya,* Universidad Nacional Autónoma de México, México*; S.E. Rodil,* Universidad Nacional Autónoma de México, México, México*; R.M. Calderon,* Universidad Nacional Autónoma de México, México*; A. Perez,* Unidad de Investigación y Desarrollo Tecnológico (UIDT-CCADET), Hospital General de México, México

A new planar hollow cathode design based on a combination of a toroidal electrode and the gas flow sputtering source has been developed; the Toroidal Planar Hollow Cathode (TPHC). Here a resonant discharge occurs between the upper and lower electrode surfaces and the only way that electrons can leave the discharge is via the upper or lower aperture in these electrodes. We have used the system to deposit bismuth and aluminium based thin films and nanoparticles as a function of the experimental parameters. The cathode can be operated from 1 few militorr up to >5 torr. The deposition rate is mainly dependent on the plasma power and gas pressure, and to some extent on the gas flow. The size of the nanoparticles mainly depends on the gas pressure and plasma power. Nanocomposite coatings have been made by using the plasma plume at the exit of the TPHC to remotely decompose acetylene or methane and deposit a combination of the nanoparticles and an a-C:H film. We report that the distribution of the nanoparticles is uniform throughout the thickness of the deposit, and the density of nanoparticles in the nanocomposite can be easily controlled.

FP-ThP17 Thermal Conductance at Nanoscale Amorphous Boron Nitride/Metal Interfaces, *N.R. Glavin, A. Waite,* Air Force Research Laboratory, USA*;* ***Christopher Muratore (cmuratore1@udayton.edu)***, University of Dayton and Air Force Research Laboratory, USA*; J.E. Bultman, J. Hu,* University of Dayton Research Laboratory, USA*; A.A. Voevodin,* University of North Texas, USA*; T.S. Fisher,* UCLA, USA

To combat the ever-increasing challenge of thermal management in nanoelectronic devices and reduce the risk of overheating during operation, material interfaces near the active region of a device must be designed for efficient thermal transport. In this study, metal contacts on amorphous boron nitride (a-BN) thin films, a promising dielectric material in two-dimensional (2D) systems, are evaluated for the relative thermal transport efficiency. Metals with small atomic masses and high Debye temperatures, aluminum and titanium, reveal as much as a six times improvement in interface thermal conductance, as measured by time domain thermoreflectance (TDTR), compared to metals of larger atomic masses and low Debye temperatures such as gold and tantalum. The interface transport between a-BN and higher Debye temperature metals prove to depend on the growth conditions, and good initial film wettability is crucial for ensuring a quality metal contact. Interfacial bonding is evaluated by XPS and the impact on a-BN chemistry and oxidation potential contributes to the understanding of phonon transport across the interface. The study described herein reinforces the crucial requirement to design effective thermal contacts in high-power electronic devices where Joule heating is a concern.

Surface Engineering - Applied Research and Industrial Applications
Room Grand Hall & Foyer - Session GP-ThP
Surface Engineering - Applied Research and Industrial Applications (Symposium G) Poster Session

GP-ThP1 Ultra-Low Temperature CVD Tungsten Carbide Coating to Replace Hard Chrome Plating on Aerospace Components made of Temperature-sensitive Grades of Steel, ***Yury Zhuk (yzhuk@hardide.com)***, Hardide Plc, UK

Hard Chrome plating (HCP) is widely used by aerospace industry to protect steel parts against wear, galling and corrosion. In the last 2 years the EU REACH regulations restricted the use of toxic Cr6+ salts, and the US OSHA tightened the Cr6+ exposure limits, making HCP increasingly expensive and less available. The aerospace industry has been preparing for these regulatory changes over the last 17 years and has identified several HCP alternatives, but none of them has been able to replace HCP in all its applications.

Hardide Chemical Vapour Deposition (CVD) Tungsten Carbide coating was added to the aerospace-approved HCP alternatives when it was fully qualified by Airbus in 2017. Recently a new ultra-low temperature variant of the CVD WC/W coating was developed to expand the range of substrate materials it can coat. As a result of the Innovate UK - funded research project, the coating process temperature was reduced by 150°C and the ultra-low temperature CVD coating can now be produced at 350°C. This reduced CVD process temperature allows coating S145, S80 and other temperature-sensitive grades of stainless steel as well as AerMet 100 and Custom 465 ultra-high strength steel with the CVD coating replacing HCP. These grades of steel are increasingly used by aircraft design engineers, but their mechanical properties were negatively affected by the previously used CVD WC/W coating temperature of 500°C.

The newly-developed CVD coating fills some significant gaps among other HCP alternatives as it can be precision applied to both external and internal surfaces including complex geometries and thin walled parts, which are difficult to coat by HVOF. The coating has a metal matrix composite structure made of Tungsten Carbide nanoparticles dispersed in metal Tungsten matrix. This composition and structure improve the coating fracture toughness to enable the production of exceptionally thick hard CVD coatings matching both the HCP thickness of 50…100 microns and hardness of 800…1200 Hv . This HCP thickness matching significantly simplifies the switch from HCP to CVD coating for aircraft producers as there is no need to change the pre-coating dimensions of parts or perform stresses calculations and testing.

The paper will report the coating testing for wear, corrosion, erosion and fatigue resistance. Based on the key properties the strengths and weaknesses of the ultra-low temperature CVD coating will be compared against other HCP alternatives as guidance for engineers.

This advanced coating is newly available to aerospace engineers working on the challenging task of Chromate-free aircraft design through coating facilities in Oxfordshire, UK and Virginia, USA.

GP-ThP2 On the Oxygen Radical Production in a Remote Inductively Coupled Plasma Source, ***Youbin Seol (youbin0621@kaist.ac.kr)***, *H.Y. Chang,* Korea Advanced Institute of Science and Technology, Republic of Korea

Remote plasma generators (RPG) are widely used for surface treatments in semiconductor processes. For the applications of remote plasma sources, radicals play the key roles in surface chemical reactions. Therefore it is important to generate and control specific radical species for each process. Currently, ferrite core type designs are widely used in remote plasma sources. Meanwhile, application of inductively coupled plasmas (ICP) for remote sources are also growing with their high density and energy distribution. We have adopted a unique antenna coil design for a remote ICP source with high volume-surface ratio. This remote ICP source can be operated in much higher power and larger gas flow.

In this study, we have studied our inductively coupled remote plasma source focusing on Oxygen radical production. Using a chemical simulation, we have studied the oxygen radical production with the changing pressure in different remote plasma sources. As a result, O radical production behaviour shows a maximum with increasing pressures. The maximum point of radical production is affected by the volume-surface ratio. Additionally, O radical production increases drastically with the surface material properties. We explain this result by plasma power and particle balance equation used in the Chemical simulation. Relatively small surface has low surface loss and the volume production increases, which leads to the electron density increase. This high electron density contributes to the radical production. In conclusion, remote ICPs have a great potential in the massive radical production and surface treatment.

GP-ThP3 Synthesis of Large Area ta-C Coating by Single-bend FCVA Source using in-line PVD System, ***HoeKun Kim (ndkim2@naver.com)**, K.T. Lee,* Korea Aerospace University, Republic of Korea*; J.W. Kim,* Incheon National University, Republic of Korea*; S.M. Kim,* Hyundai Steel, Republic of Korea*; S.Y. Lee,* Korea Aerospace University, Republic of Korea

Tetrahedral amorphous carbon (ta-C) coating is a hydrogen-free carbon coating with the remarkable properties comparable with those of diamond film, such as high hardness, optical transparency and chemical inertness. Moreover, ta-C coating can be synthesized through a relatively convenient method and has a much smoother surface, making the tribological performances of ta-C coating better than those of other diamond coatings. Among the various attempts used to prepare ta-C coatings, the filtered cathodic vacuum arc (FCVA) method is a particularly suitable technique for the mass-production of industrial ta-C coatings, and the performable properties make ta-C coatings suitable for potential commercially important components in applications such as automobile accessories, optical devices, and aerospace parts. In this study, large area ta-C coating on a 300x300mm STS plate was synthesized by single-bend filtered cathodic vacuum arc (FCVA) using in-line PVD system. Source and bend filter connecting 45° bent together were used to produce carbon plasma from a graphite target with a diameter of 50mm and a purity of 99.99%. Especially, raster magnet system was designed and constructed for large area synthesis in this source. The large area ta-C coatings with 1.8μm thickness were synthesized successfully, and thickness uniformity was showed as 92.4%. Raman spectroscopy analysis showed that the ta-C coatings had high sp3/sp2 fraction over 63%, and the hardness showed high values of 48.5 GPa. In addition, the ta-C coatings with 700nm in thickness, a sp3/sp2 fraction over 74%, and about 63 GPa hardness could be synthesized with a similar uniformity. Detailed experimental results will be presented.

GP-ThP4 Development, Testing and Production of Coatings on Bipolar Plates in Polymer Electrolyte Fuel Cells, ***Peter Jaschinski (jaschinski@kcs-europe.de)**,* KCS Europe GmbH, Germany*; V. Lukassek, J. Wartmann, A. Heinzel,* ZBT Gmbh The Hydrogen and Fuel Cell Center, Germany*; R. Cremer,* KCS Europe GmbH, Germany

As a result of the steadily increasing demand for energy worldwide and the associated need for the responsible use of global energy resources, efficient and sustainable energy conversion and storage is becoming increasingly important. Promising solutions in this context are new developments in fuel cell technology . Here, the chemical energy of an energy carrier (e.g., hydrogen) is directly converted into electrical energy, resulting in high efficiency. If the hydrogen required for this purpose is generated by electrolysis from renewable energies, an environmentally friendly concept is created in which no pollutant and CO_2 emissions take place.

However, for large scale commercialization of this technology, several challenges have still to be faced. In this regard, the development of novel techniques for further improvement of the individual components of Proton Exchange Membrane fuel cell stacks (PEMFC) has to be addressed. One of those components is the bipolar plate (BPP) which has various functions within the fuel cell, such as separation of the individual cells, distribution of the fuel and oxidant gas, collecting and transmitting generated electricity as well as maintaining water and heat management. Therefore, with respect to all those functions, an ideal BPP has also to fulfil a number of material requirements such as high compressive strength, sufficient electrical and thermal conductivity and also good electrochemical stability. Although metallic based materials meet all necessary requirements, the main weak point of such materials is their susceptibility to corrosion in acid environment, which is the case during fuel cell operation. While fabricating the passive layer to prevent further corrosion, it simultaneously leads to poisoning of the electrode catalyst and contamination of the polymer electrolyte membrane. Furthermore, an increase in electrical resistance is also a typical behavior induced by a passivation process of the metallic surface.

One goal of this work is the suitable series production of corrosion protection coatings with an excellent electrical conductivity on metallic bipolar plates from a PEM fuel cell. When applying these layers, the PVD (Physical Vapor Deposition) methods arc and sputtering are used. When selecting the material for the bipolar plate, attention is paid to inexpensive steel and aluminum alloys. The coating material is completely dispensed without precious metals for cost reasons. At the same time, the task is to develop a continuous coating process that meets the demands for productivity for the large number of bipolar plates.

GP-ThP5 Enhanced Plasma Nitriding by Elastic Shot Blasting Pretreatment, ***Yoshiki Handa (173453502@ccalumni.meijo-u.ac.jp)**, P. Abraha,* Meijo University, Japan

This research presents a method to improve the diffusivity of a metallic surface and enhance the plasma nitriding process while maintaining the highly polished surface. The formation of the nitride layer is caused by the diffusion of nitrogen atoms in the plasma. The diffusion roots of atoms are known as lattice diffusion, grain boundary diffusion, and dislocation diffusion. Because grain boundary diffusion is significantly faster than lattice diffusion, grain size is an important factor for improving the diffusivity. Currently, the method to improve the diffusivity is achieved by severe shot-peening. Severe shot-peening refines the grain size of a metallic surface by repeating impact stress and plastic deformation. The plastic deformation degrades surface condition and surface roughness.

In this research, shot-blasting using elastic media generates only elastic deformation on the metal sample surface, maintaining the as-finished surface, and improves the diffusivity. Shot-blasting injects elastic media by the rotation of the impeller and the speed of the shot media is controlled by the number of revolutions. An elastic medium consists of an elastic core, about 500 µm diameter, and made by rubber, and submicron diamond powder attached around it. In this shot-blasting method, when the shot media impacts the sample surface, and the absorbed kinetic energy produces plastic deformation on the asperities of the surface. The repeated impact of the elastic shot media refines the grain size.

In this experiment, the two parameters, the velocity of shot media and exposure time, were optimized to assure shot-blasting operation without plastic deformation. Plasma nitriding treatment was performed on the sample after shot-blasting, and the relationship between the two parameters and the nitriding rate was compared. The result show shot-blasting using elastic shot media achieved a faster plasma nitriding while maintaining as-finished surface.

GP-ThP6 Characterization of Tungsten-doped InZnO Thin Films with Plasma Treatment for Conductive-bridge RAM Applications, ***Chih-Chieh Hsu**, P.-T. Liu (ptliu@mail.nctu.edu.tw), K.-J. Gan, Y.-C. Chiu, D.-B. Ruan, S.M. Sze,* National Chiao Tung University, Taiwan

In this study, the impact of plasma treatment on InWZnO CBRAM was reported. The advantage of remote plasma can improve the quality of interface quality and significantly increase R_{OFF}. The a-IWZO CBRAM shows the excellent memory performances, such as stable on/off resistance ratio, high switching endurance (up to 10^3 cycles). Without high temperature process is used in the process, which will be suitable for memory in flexible substrates.

GP-ThP7 Anodic Vacuum Arc Deposited Nanostructured NiTi Coating for Hydrogen Storage, ***Indrani Banerjee (indrani.banerjee@cug.ac.in)**,* Central University of Gujarat, India*; A. Pathak,* Birla Institute of Technology, India*; S. Rai,* Birla Institute of Technology, India*; S.K. Mahapatra,* Central University of Punjab, India

Almost equal atomic composition of NiTi film is deposited by anodic vacuum arc (AVA) plasma system at 45A anodic current. Effect of plasma parameters such as electron temperature (T_e) and electron density (n_e) on growth pattern are studied using I –V plot. The surface morphology, atomic percentage and crystal structure of the deposited NiTi film is estimated using SEM, EDXS and XRD techniques. STM gauges the atomic position on the surface of the sample and determines its electronic nature. The deposited NiTi sample is exposed to hydrogen environment at 500^0 C to incorporate hydrogen in deposited NiTi thin film. The qualitative presence of hydrogen is determined by Raman Spectroscopy, whereas quantitative presence of hydrogen is determined by elemental analyzer. It is observed that NiTi shows the direct dissociative chemisorption of βhydriding with hydrogen storage of 1.465wt% of the material weight.

GP-ThP9 Thin Films for Protection of Integrated Sensor Systems on Tribological Loaded Surfaces, ***Annett Dorner-Reisel (a.dorner-reisel@hs-sm.de)***, Schmalkalden University of Applied Sciences, Germany; *W.A. Ahmad Akhtar, J. Seeger, G. Reisel,* Oerlikon Metco WOKA GmbH Barchfeld, Germany

Monitoring systems for load, damage, temperature, fatigue assessment during operating of machines, wind turbines or transportation systems are of great interest. The main focus of the present research is the development of a strain and stress sensing reliable sensor, that signals overloading and general behaviour and its protection during operating, what would give a long durability of the smart property. In addition to the sensors sensitivity against stress and strains, it needs to be adequate protected. Therefore, thin films and coatings are selected and proven.

These thin films and coatings were deposited on piezo-sensor systems. The aims are:

(a) protection of the piezo-sensor during embedding process into the metallic parts surface

(b) protection of the sensor during tribological loading during practical application of the metallic components

Alumina and C-based films are generated by plasma deposition on sensors with a high of approximately 250 µm. Following metallographic preparation, the sensor contacts and the interfaces between sensor and coatings were investigated on cross-section by Scanning electron and Digital Microscopy. For sensing the real complex of loads acting on the component, the interface between the embedding material needs to be optimal. Spaces and contactless region may not give a correct impression of the real acting load situation. Sensor signals, like p-V-curves in dependence on loads are presented. The microstructure of the thin protective alumina and/or C-based films are characterised before and after embedding in steel material as well as after loading and operation of the sensors in ambient environment by Raman spectroscopy.

GP-ThP10 Influence of Synchronized Pulsed Substrate Bias on the Deposition of Ti and TiN Films Using High Power Impulse Magnetron Sputtering Technique, ***Ying-Xiang Lin (qw36100@gmail.com)***, *P.Y. Liu, W.Y. Wu,* Da-Yeh University, Taiwan

Titanium nitride (TiN) is a widely used coating material for various applications. Especially for using as a protective coating, an adhesive Ti layer is usually deposited prior to the deposition of TiN. In addition, it has been studied that a moderate ion bombardment obtained by applying bias to the substrate leads to an enhanced performance on tribology, mechanic, anti-corrosion, and anti-diffusion. However, it was also found that a bias voltage applied to the substrate is invalid during the pulses of high power impulse magnetron sputtering process (HiPIMS). Therefore, a detail investigation of the substrate bias in HiPIMS process is required.[1]

In this study, the Ti and TiN films were deposited using HiPIMS. During the deposition, various bias voltages ranging from 0 to -150 V was applied with DC bias or synchronized pulsed bias. Meanwhile, a synchronized pulsed bias with various delays relative to the plasma pulse were investigated. The effects of bias voltage and time delay on the microstructure, mechanical and corrosion behaviour were also investigated.

Keywords: HiPIMS, pulsed substrate bias, synchronized pulsed bias

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GP-ThP11 Microstructure and Mechanical Properties of M4/D2 Hard-Faced-Surface by Direct Energy Deposition, ***Jongbae Jeon (jbjeon@kitech.re.kr)***, *GW Park, SM Shin, WJ Lee,* Korea Institute of Industrial Technology (KITECH),Republic of Korea

Research for improving mechanical properties and durability of molds, dies and tools has been continuously carried on. Improved mechanical properties and durability of such tools bring advantages to relevant industries, in a way of reduction in cost and replacement-cycles, and improvement in product quality and productivity. Recently, application of direct energy deposition (DED), one of additive manufacturing techniques, on hard-facing for dies and tools. DED allows 3D stacking on arbitrary surface shape with desired thickness, enabling uniform and rapid hard-facing on complex dies and tools. In this study, M4 powder was deposited on D2 substrate to investigate microstructure and mechanical properties of the deposited layers. The deposited surface layers rapidly solidified showed chilled zone at the interface with substrate and predominant columnar dendrite structure toward the upper surface. Unlike the bulk counterpart of M4, no coarse carbides were formed, and tens of nanometer-sized fine carbides were located in the interdendritic region. The M4 powder subjected to standard normalizing and quenching treatment, generally shows Ms point around 200 °C. Thus, the deposited layers was expected to show abundant martensite phase as deposited, but rather showed more than 40% of retained austenite surprisingly, which undoubtedly degrades hardness of the hard-faced surface. It can be thus inferred that powder for hard-facing should not be selected based on the classical estimation of Ms point, which is not considering rapid solidification process. Thus, we here propose a new approach to power alloy design which is necessary for hard-facing of steel-based dies and molds using DED method.

GP-ThP12 Effect of Cu Content and Melting Temperature on the Oxide Film Formation and the Quality of Molten 6000-Series Aluminum Alloys, *H. Jang, P. Youn, H. Kang, G. Lee, J. Park, E. Kim, J. Jeon,* ***Sunmi Shin (smshin@kitech.re.kr)***, Korea Institute of Industrial Technology (KITECH), Republic of Korea

In recent years, the interest of high strength aluminum alloys is growing due to the demand for the light-weight vehicles to meet the strengthened environmental regulations. Heat treatable 6000-series aluminum alloys (Al-Mg-Si alloys) are the typical high-strength aluminum alloys and are widely used as a panel material because of its thermosetting property, which increases the strength when baked finish. The inclusions formed during casting can affect the precipitate formation in the post heat treatment process and impede the work hardening ability of nano-precipitates of Al-Mg-Si alloys. The inclusion formation during casting is affected by the alloying elements, the liquid state oxidation of the alloy surface, and the casting process conditions. In order to reduce the internal defects and improve the mechanical properties of high-Cu-containing Al-Mg-Si alloys, the effect of Cu content on the oxide film formation on the surface of the molten alloys need to be clarified and the quality of molten alloys should be precisely controlled. In this study, the oxide film on the surface of molten Al-Mg-Si-Cu alloys was characterized by electron microscopy and DSC-TGA and the effect of Cu content and the melting temperature on the oxide film formation energy was estimated by thermodynamic calculations. In relation to the characteristics of the oxide film, the melt quality of Al-Mg-Si-Cu alloys was discussed.

GP-ThP13 Performance Enhancement of pGe MOS device with Pre- and Post- Deposition Microwave Annealing Treatment, ***Yu-Hsuan Chien (teresa.chien888@gmail.com)***, National Tsing Hua University, Taiwan; *K.-S. Chang-Liao, D.-B. Ruan, S.-H. Yi,* National Tsing Hua University; *F.-Y. Chu,* National Tsing Hua University, Taiwan

Recently, germanium (Ge) based metal-oxide-semiconductor (MOS) device with high-k gate insulator has been widely investigated for its higher electron and hole mobility than silicon, and easier integration with traditional technology than III–V materials. Beside, microwave annealing process was proposed to improve electrical characteristics for its lower thermal budget compared with the traditional annealing process. In this work, complete microwave annealing treatments have been applied on the pGe MOS device, instead of the traditional thermal process. As a result, the device with both pre- and post- deposition microwave annealing exhibits better electrical performance than other samples.

GP-ThP14 The Radiation Effect on FinFET Device with Double Pattern Lithography Process, ***Fu-Yang Chu (xxmoon666@gapp.nthu.edu.tw)***, *K.- S. Chang-Liao, D.-B. Ruan, Z.- Q. Hong, S.- H. Hsu, Y. -H. Chien,* National Tsing Hua University, Taiwan

Nowadays, Fin field effect transistors (FinFETs) were widely applied to follow the Moore’s law at 14 nm technology node. With the continuous scaling trend, the high-energy extremely ultraviolet has become the most promising light source for next-generation lithography. Hence, the radiation exposure on FinFET devices might be regarded as one of reliability issues in terms of lifetime and stability. In this work, radiation exposure, FN stress, and channel hot carrier stress are applied on the FinFET devices defined by double pattern lithography process. It may provide an important theoretical foundation for the future device design and fabrication.

GP-ThP15 TiO_2–Silicon Nanowire Arrays for Inorganic Solar Cell Applications, ***Ai-Huei Chiou (ahchiou@nfu.edu.tw)***, National Formosa University, Taiwan

Large-area ordered single crystal SiNW arrays on p-type (100) silicon wafer without the use of a template were prepared in a silver nitrate and hydrofluoric acid ($HF/AgNO_3$) solution at 50oC. The result showed that highly dominant peak at 69° is belong to (004) silicon plane which can be explained equally by preferential etching along [100] directions. The linear relationship of SiNW arrays could be adjusted by controlling the etching time. Besides, the result showed that SiNWs gave the best anti reflective properties (3.07% in the broad visible band) and well-aligned properties with 45 minutes. A n-TiO_2/p-SiNW heterojunction has been fabricated by RF magnetron sputter. The crystal structure of TiO_2 layer reveal its anatase and rutile both structured hybrid. A n-type TiO_2 thin films were deposited sputtering on the p-SiNW arrays having hydrophilicity features. In this study, a rare inorganic-inorganic heterojunction solar cells using titanium dioxide and silicon nanowires was fabricated. The present results indicated that the power conversion efficiency (PCE) of n- TiO_2/p-SiNWs better than n- TiO_2/p-Si inorganic-inorganic heterojunction solar cells. The inorganic-inorganic heterojunction solar cells used itanium dioxide and silicon nanowires, in which the Voc is of 0.139V, Jsc is of 94.81 mA/cm2 and, the FF is of 21.3% and efficiency is of 2.81 × $10^{-3\%}$. Key words: silicon nanowires (SiNWs), Electroless Metal Deposition (EMD), inorganic solar cell

GP-ThP16 Design of Surface Layers with Phase Change with Novel Properties, ***Rahul Basu (ra4499@gmail.com)***, VTU Kundana, Bangalore, India

A model for a phase change layer with thermal and mass transport is formulated/ Variable diffusivity and surface conditions are embedded in the model. Subsequently boundary lengths for mass and thermal penetration are evaluated by special techniques. Diffusivities which ares normally assumed constant, are allowed to vary as transformations progress. Solutions for specific variable diffusivities are computed where penetration lengths are evaluated. An integral method is applied along with perturbation expansions,to evaluate the boundary layer thickness. Applications are postulated for self healing paints, roofing material, radar absorbing/deflecting coatings and other possible consumer and military spinoffs.

GP-ThP17 Ni-Al_2O_3 Composite Coating for Reduction of Wear and Particle Emission of a Brake System, ***Ran Cai***, *C. Zhao, J. Sun, X.Y. Nie,* University of Windsor, Canada*; J. Tjong,* Ford Motor of Canada, Canada*; J. Zhang,* University of Windsor, Canada

Brake wear of both electric and combustion vehicles has been recognized as significant traffic-related sources and considerable contributors to particle emissions, which has a strong effect on air quality and human health in urban areas or in subway system. This research was to prepare Ni-Al_2O_3 composite coatings on cast iron brake rotors using plasma electrolytic aluminating (PEA) and electro-less plating process. The added nickel was to fit in the intrinsic pores of Al_2O_3 coating. Two commercial brake pads with different materials composition were used as the counterparts of the tribological couplings. The wear debris produced in tribotests was collected for observation of size distribution. The results show that the coefficient of friction was quite different for the composition-different pads while the wear behavior of both pads was similar. The coating can provide the brake system with almost no rotor wear and a noticeably reduced pad wear, leading to a low production of wear debris and particles. In contrast with the coated rotor, an uncoated rotor and its coupling pad presented obvious wear after tested at the same conditions. Therefore, brake rotor with the Ni-Al_2O_3 coating is a promising approach to a better brake system in terms of reduction of wear and particle emission.

GP-ThP18 Fabrication of Infrared Cut Off Filter with Wire Grid Polarizers, ***Wonyoung Kim (kim10@optrontec.com)***, *J. Kim, M. Kim, H. Lee,* Optrontec, Republic of Korea*; SJ. Lee,* Pavonine Korea, INC., Republic of Korea*; J. Kim,* Optrontec, Republic of Korea

A wire grid polarizer (WGP) comprised of 1D metal grating structure is drawing attention to industrial applications such as image and optics industry. To obtain high quality images, polarized optical systems are being actively researched. In polarizing optical systems, a polarizer is necessary. However, it is well-known that the realization of WGP with a large area requires high-cost facility such as E-beam lithography, serial etching, and deposition.

In this study, we present a fabricated the polarized infrared cut off filter (IRCF) and polarized biometric optical filter (BOF) with deposition and nanoimprint lithography (NIL) and selective metal deposition.

Polymer nanostructures were firstly patterned by NIL, which resulted in mostly 1D patterns with a pitch of 120 nm, width of 50 nm, and height of 150 nm. And then, a desired shape of Al was selectively deposited only on the ridge of polymer patterns by oblique angle deposition (OAD) method. In this study, we also fabricated a polarized optical filter using etching and compared it with a polarized optical filter using NIL and OAD.

The polarized filter fabricated by NIL and OAD has 127 * 127 mm size with Transverse magnetic (TM) polarization transmittance 70% and polarization extinction ratio 20dB or more at transmission band of each IRCF and BOF. This polarized optical filter will be widely used in the biometric recognition optical filter and the IRCF for decrease signal to noise ratio (S/N ratio) and high-quality images.

GP-ThP19 Corrosion Induced Diffusion Pathways in Thin Film Materials Investigated by Atom Probe Tomography, *O. Hudak,* CDL-SEC, TU Wien, Austria*; E. Aschauer,* TU Wien, CDL-SEC, Austria*; V. Dalbauer,* FAU Erlangen, Germany*; H. Bolvardi, M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Felfer,* FAU Erlangen, Germany*;* ***Helmut Riedl (helmut.riedl@tuwien.ac.at)***, TU Wien, CDL-SEC, Austria

Corrosion processes are common phenomena in fields of engineering and there is nearly never an instance, where a material is totally inert to its environment and its corrosive nature. Therefore, corrosion and corrosion-resistance are essential variables that play a pivotal role in the development of protective coatings. Ingenuity of next generation PVD coatings has given rise to a wide range of material concepts set out to withstand all kinds of corrosive attacks (e.g. NaCl, HCl, SO_3 and O_2). While their performance is mostly assessed on descriptors such as mass change, impairment of mechanical properties, or variance in electrochemical surface potential, little work has been dedicated to understand corrosion driven diffusion pathways, specifically on an atomic scale.

This study showcases a systematic approach on highlighting preferred diffusion pathways of corrosive media in arc-PVD thin films. For investigating the effect of grain size, droplet formation and crystallinity on the overall diffusion mechanism, a novel marker architecture was developed. Eliciting chemical and structural changes upon arrival of the diffused media, this marker system facilitates improved application of high-resolution analytical methods, such as APT and TEM, to help identify preferential diffusion paths.

GP-ThP20 Flexible Hard TiAlN Thin Films on Si (100) Substrate Deposited by Deep Oscillation Magnetron Sputtering, *Z.T. Jiang, Y.G. Li, H. Chen,* ***M.K. Lei (mklei@dlut.edu.cn)***, Dalian University of Technology, China

TiAlN thin films were deposited on Si (100) substrate by deep oscillation magnetron sputtering (DOMS) with a peak power from 58.7 kW to 129.9 kW. The microstructure of TiAlN thin films 1.1-1.5 µm thick changed from a columnar structure (Zone I in Ander's Model) at the lower peak powers than 66.2 kW to a glassylike (Zone T) at the higher peak powers than 90.2 kW. A cubic TiAlN structure was observed in all the TiAlN thin films with the average columnar width from 30.5 nm to 10.8 nm. When the peak power increased, the H/E^* ratio of the TiAlN thin films initially increased from 0.072 to the maxima of 0.081, and then decreased to 0.072, the hardness changed from 23.5 GPa up to the maxima of 28.3 GPa, and down to 24.7 GPa, the elastic recovery (W_e) was from 35.4% up to 38.1%, and down to 31.9%, and the compressive macrostress (s) was from −0.5 GPa up to −1.62 GPa, and finally to −1.48 GPa. The fracture toughness (K_{IC}) of the TiAlN thin films was measured by the indentation test with a Vickers diamond indenter. The fracture toughness of the TiAlN thin films significantly increased from 1.703 $MPa{\cdot}m^{1/2}$ to 4.206 $MPa{\cdot}m^{1/2}$ with the peak power. The flexible and hard TiAlN thin films were deposited by DOMS at the higher peak power of 129.9 kW. Note that the dense microstructure with the nanometer uniformity led to the high hard and tough TiAlN thin films on Si (100) substrate with the lower compressive macrostress.

GP-ThP21 Investigating the Water Oxidation Tendency on Metallic Oxide Doped Anodized Film Produced on SLM Ti6Al4V, ***Hafiz Muhammad Hamza (hamza1hm@cmich.edu)***, Central Michigan University, USA*; K. Mairaj Deen,* University of British Columbia, Canada*; W. Haider,* Central Michigan University, USA

Selective laser melting (SLM) process is an additive manufacturing process capable of producing components with complex geometries and varied surface morphologies. Ti6Al4V is used as dimensionally stable electrode in copper electro winning applications. In this study, metallic oxide doped film was produced on Ti6Al4V manufactured by SLM process. The water oxidation tendency on this film was investigated via cyclic voltammetry scans. The efficiency of copper electro winning process was also determined in a simulated two electrode cell assembly containing copper leached solution. The surface morphology of metallic oxide doped film was examined by scanning electron microscopy. It was found that the metallic oxide doped film increased the water oxidation tendency of selective laser melted Ti6Al4V.

GP-ThP22 Improving AlTiN Coatings by Multi-layering with ZrN/ZrON, *J. Kohlscheen,* Kennametal GmbH, Germany*; B. Macshane, D. Banerjee,* ***Zhenyu Liu (Zhenyu.Liu@kennametal.com)***, Kennametal Inc., USA

We deposited AlTiN/AlZr(O)N mono and multi-layers with different layer sequences by arc ion plating. Zirconium was chosen because of favorable mechanical properties of its oxide. Starting with an AlTiN monolayer the effect of zirconium addition either by evaporating an elemental or alloyed target was investigated. Bi- and multilayers including oxidic layers were studied as well. Cemented carbide samples were used for analysis and wear testing. Hardness and modulus were determined by nanoindentation. Resulting phases were evaluated by x-ray diffraction (XRD). Wear testing was performed by turning of ductile cast iron at different speeds. It was found that adding zirconium reduces the hardness and modulus of AlTiN resulting in inferior flank wear resistance. Single oxidic top layers could improve crater wear resistance at higher cutting speeds. The best overall performance was obtained by a combination of a proven AlTiN base layer (2-3 micron thick) and a multilayer stack of (Al)ZrO_X/AlTiN with individual layer thicknesses of some tenth of a micron.

GP-ThP23 PALMS - Plasma Additive Layer Manufacture Smoothing, ***Thomas Brzezinka (jonathan.housden@wallworkht.com)***, Wallwork Cambridge Limited, UK*; A. Fox,* Wallwork Cambridge Ltd., UK*; J. Housden,* Wallwork Cambridge Ltd, UK*; N. Laugel, A. Yerokhin, A. Matthews,* The University of Manchester, UK

Additive manufacturing (AM) offers unprecedented design freedom and the possibility to produce lightweight optimised components that are impossible to make with traditional techniques. Despite the significant progress made in AM, the surface roughness of parts produced by this method continues to be an issue. As a result, the application of AM parts in industry is being constricted, particularly in the aerospace and medical industries, where the surface finish of components is highly critical. We have developed PALMS, an innovative cost-effective macro-polishing solution based on novel electrochemical plasma technology. AM parts are rapidly treated in a highly controlled manner in less than 20 minutes, leaving a uniform, smooth micro-finish (<0.1µm), resulting in considerably improved aesthetics and mechanical performance.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Grand Hall & Foyer - Session HP-ThP

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes (Symposium H) Poster Session

HP-ThP1 ZnO Thin Films Growth at Low Temperature by PE-ALD using O_2 and H_2O Plasma, *J.R. Castillo, B. Valdez,* Universidad Autónoma de Baja California, Mexico*; E. Martinez,* CIMAV Centro de Materiales Avanzados Unidad Monterrey, Mexico*;* ***David Mateos (david.mateos@uabc.edu.mx)***, *M. Curiel,* Universidad Autónoma de Baja California, Mexico*; M. Martinez, I. Mendivil,* CIMAV Centro de Materiales Avanzados Unidad Monterrey, Mexico*; N. Nedev,* Universidad Autónoma de Baja California, Mexico

ZnO layers with thicknesses of 20, 40 and 60 nm were deposited by Plasma Enhanced Atomic Layer Deposition (PE-ALD) at 70 °C. Diethylzinc (DEZ) was used as organometallic precursor, O_2 and H_2O as oxidant agents and Ar as a purge gas. The deposition cycle consisted of 100 ms DEZ pulse, 10 s purge time and 6 s of plasma oxidation at 200 W. The optical constants and thicknesses of the grown layers were determined by spectroscopic ellipsometry, while the roughness was measured by atomic force microscopy, giving average roughness (R_a) values in the 0.20 – 0.22 nm range for films deposited under different conditions and having different thicknesses. The optical band gap of the films are 3.22 and 3.23 eV for H_2O and O_2 plasma, respectively, with a high optical transmission of 90 %, was measured by UV-Vis. X-ray diffraction (XRD) exhibit the formation of polycrystalline patterns with the predominant planes of (1 0 0) and (0 0 2). X-ray photoelectron spectroscopy (XPS) revealed a high purity of the obtained ZnO films, no C was detected. The obtained excellent optical, morphological and compositional properties of the deposited films, make them a promising candidate for electronic and optoelectronic applications, which require low temperature processes.

Keywords: ZnO, PE-ALD; thin films; low temperature

HP-ThP2 Optimization of Grain Growth for High performance Planar p-i-n Perovskite Solar Cell, ***Won Chang Lee (lwc9297@skku.edu)***, *B. Hong,* Sungkyunkwan University, Republic of Korea

Perovskite solar cell (PSC) is now one of the most promising technologies in the quest for next-generation due to their high performance, low temperature and potentially low coated solution process.

The perovskite structure is generally in organic-inorganic hybrid based ABX_3, where A is a monovalent ion such as methylammonium ion ($CH_3NH_3^+$, MA^+) and formamidinium ion ($CH_5N_2^+$, FA^+), B is a divalent ion such as lead ion and tin ion and X is a halide such as iodide ion, bromide ion and chloride ion. Among the various components, the most common organic-inorganic hybrid halide is $MAPbI_3$. In case of $MAPbI_3$, the reaction for phase formation is usually given in simple chemical equation ($MAI + PbI_2 \rightarrow MAPbI_3$).

Currently, PSC shows a power conversion efficiency of as high as 23.7 %. Theoretically, PSC may produce a high efficiency of more than 30 % with an improvement in fill factor and open circuit voltage. Many researchers are actively studying for efficiency improvement by solvent annealing, thermal treatment and use of additives to optimize the morphology of the PSC.

However, $MAPbI_3$ is relatively simple but during the process of mixing compositions, it causes the complication such as band-gap change and unexpected characteristics. In solving these problems, one of the main issues is to improve the morphology in grain growth. In general, the light energy transformation depends on the defect density at perovskite layer so that shunting can be avoided in such planar structure. Then, the grain boundaries (GBs) have a major impact on defects and reducing GBs will increase the cell performance.

In this work, we fabricate the p-i-n structure PSC based on indium tin oxide glass/p-type materials (NiO)/perovskite/n-type material (PCBM)/metal electrode and GBs are optimized under various conditions. Uniform film with large scale grain size in perovskite layer can be helpful for open circuit voltage and lead to high power efficiency of PSC.

HP-ThP3 e-Poster Presentation: Nanoindentation Analysis as a Two-Dimensional Tool for Mapping the Mechanical Properties of Complex Microstructures, ***Nicholas Randall (nicholas.randall@alemnis.ch)***, *JM Breguet,* Alemnis, Switzerland

Instrumented indentation (referred to as nanoindentation at low loads and low depths) has now become established for the single point characterization of hardness and elastic modulus of both bulk and coated materials. This makes it a very good technique for measuring mechanical properties of homogeneous materials. However, many composite materials comprise material phases that cannot be examined in bulk form ex-situ (e.g., carbides in a ferrous matrix, calcium silicate hydrates in cements, etc.). The requirement for in-situ analysis and characterization of chemically complex phases obviates conventional mechanical testing of large specimens representative of these material components. This paper will focus on new developments in the way that nanoindentation can be used as a two-dimensional mapping tool for examining the properties of constituent phases independently of each other. This approach relies on large arrays of nanoindentations (known as grid indentation) and statistical analysis of the resulting data.

HP-ThP4 Characterization of Flexible Transparent Electrodes Fabricated via Etching-free Patterning of Silver Nanowire-conductive Polymer Composites, ***Taegon Park (ppxorhs@naver.com)***, Hanyang University, Republic of Korea

With the development of electronic devices, researches on deformable devices that bend or stretch are being actively studied. Indium tin oxide (ITO), the most widely used transparent electrode material, has low sheet resistance and high transmittance. However, ITO is fragile due to structural problems and it requires a high process temperature in order to maintain crystallinity, which makes it difficult for ITO to be used in deformable devices. For this reason, many studies are being conducted on the development of new transparent electrode materials, such as metal nanowire, metal mesh, graphene, carbon nanotube (CNT), and conductive polymers, to replace ITO. Among these materials, metal nanowires are expected to be commercialized first because they are evaluated to have advantages in terms of optical and electrical properties as well as flexible characteristics. In particular, research is focused on silver nanowires (AgNWs) having excellent electrical properties as the most representative electrode material of metal nanowires. In addition, a study has been reported on coating PEDOT: PSS, a kind of conductive polymer, on AgNWs to reduce contact resistance between nanowires and further improve flexibility. However, in this case, since PEDOT: PSS is coated on the entire AgNWs, there is a problem in that the transmittance of the electrode is significantly reduced.

In this study, we propose an effective method to improve the electrical properties and flexibility of AgNWs transparent electrodes as well as to improve the visible light transmittance of these electrodes. To achieve this, a transparent electrode was fabricated using AgNWs solution mixed with PEDOT:PSS and formed to have a mesh-like pattern via etching free method. Dispersed solution with AgNWs, PEDOT:PSS, and diacetylene glycol(2,4-Hexadiyne-1,6-diol) was spin-coated on PET substrate. Diacetylene glycol is photo-sensitive material which is used for developing AgNWs and PEDOT:PSS pattern by polymerizing. The coated sample was irradiated with UV (254 nm) under a photo mask, then washed with DI water to develop the pattern in place of etchant. For the manufactured AgNWs electrodes, the surface morphology, sheet resistance and visible-light transmittance were measured via FESEM (Field Emission Scanning Electron Microscope), non-contact sheet resistance measuring system and spectrophotometer, respectively. In addition, the flexibility characteristics of these AgNWs electrodes were analyzed through bending and twist tests.

HP-ThP5 Electric Field Strength-Dependent Accuracy of TiAlN Thin Film Composition Measurements by Laser-Assisted Atom Probe Tomography*,*
Marcus Hans (hans@mch.rwth-aachen.de)*, J.M. Schneider,* RWTH Aachen University, Germany

Accurate quantification of absolute concentrations represents a major challenge for atom probe tomography (APT) since the field evaporation process is affected significantly by the measurement parameters. In the present work we investigate systematically the effect of laser pulse parameters on the accuracy of laser-assisted APT for a TiAlN thin film previously quantified by ion beam analysis, combining Rutherford backscattering spectrometry and time-of-flight elastic recoil detection analysis. The electric field strength is estimated from the Al^{2+}/Al^{+} charge state ratio for all systematically varied measurement parameters. Subsequently, the absolute concentrations from laser-assisted APT are compared to ion beam analysis data. An increase of the electric field strength from approximately 25 to 28 V nm^{-1} improves the accuracy of absolute concentrations measured by laser-assisted APT from 11.4 to 4.1 at.% for N, from 8.8 to 3.0 at.% for Al and from 2.8 to 0.9 at.% for Ti. Our data emphasize that the measurement accuracy of laser-assisted APT for TiAlN is governed by the electric field strength. It is shown that the smallest compositional discrepancies between ion beam analysis and APT are obtained for the maximum electric field strength of approximately 28 V nm^{-1} at 10 pJ laser pulse energy. This can be rationalized by considering the enhanced ionization of neutral fragments caused by the increased electric field strength.

HP-ThP6 Integrated Atom Probe/tEBSD for Grain and Phase Boundary Analysis of Coatings and Thin Films*,*
Robert Ulfig (robert.ulfig@ametek.com)*, Y. Chen, K. Rice, T. Prosa,* CAMECA Instruments Inc., USA

Transmission EBSD mapping offers the ability to target site-specific grain or phase boundaries for Atom Probe Tomography (APT) analysis, and correlate boundary chemistries with grain misorientations. In this study we demonstrate that high-resolution transmission electron back scattering diffraction (tEBSD) maps can be acquired on needle-shaped APT specimens that consist of grains of size ranging from few hundred nanometers to few micrometers. The use of this correlative technique will be demonstrated with thermal barrier coatings (TBCs) used in turbine engines to operate at temperatures greater than the melting temperatures of engine components and consequently achieve better propulsive power performance and fuel efficiency. The general structure consists of three layers: a top is a coat made of yttrium-stabilized ZrO_2 (or YSZ), which has excellent thermal resistivity, a thermally grown oxide (TGO) scale, that consists of a-alumina grains, and a bond coat layer at the coating/substrate interface that improves adhesion of the ceramic layers on the superalloy substrate.

HP-ThP7 Capacitance Transient Analysis of Oxide Semiconductor Films*,*
Pyungho Choi (cph57@naver.com)*,* Sungkyunkwan University, Republic of Korea

In this study, we introduce the carrier generation lifetime (t_g) technique for evaluating electrical properties of InGaZnO (IGZO) and InSnZnO (ITZO) channels. This method can be strongly utilized for identifying the influence of amorphous-oxide-semiconductor (AOS) channel materials on the electrical performance of the devices because the value of carrier lifetime is determined by electron-hole pairs generation from the defective sites in the channel. The experimental results here provide a comprehensive understanding on the t_g measurements, and the channel material variation effects on the electrical behaviors of the thin-film transistors (TFTs) will be discussed with a correlation between t_g and AOS materials. Device performance of IGZO and ITZO TFTs were compared, and the electrical responses were investigated by evaluating capacitance transient characteristics. Experimental results exhibit that ITZO channel layer shows higher carrier generation rate than that of IGZO. It is believed that this phenomenon is caused by the defective origins such as oxygen vacancies. We propose generation lifetime measurement technique as an excellent and powerful characterization method for evaluating and understanding channel properties of the AOS TFTs.

HP-ThP8 Microstructural Influences on the Fracture Properties of CrN Coatings*,*
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Transition Metal Nitrides (TMN) are well known for their good mechanical stability, chemical inertness, as well as tribological properties. Hence, they successfully found application in the metal forming industry, and are in use as protective coatings in the automotive and aerospace industry. Besides TiN, CrN is one of the most used and best investigated hard coatings, preferably applied in conditions that require a low coefficient of friction. A decisive disadvantage of these hard coatings, however, is their low fracture tolerance. Premature failure of the coating due to crack initiation and propagation leads to economic disadvantages or completely excludes an application. In recent years, micromechanical testing methods have made it possible to measure and specifically improve precisely fracture toughness of thin film materials. There are various methods known for measuring K_{IC} obtaining all advantages and drawbacks, especially with respect to intrinsic material characteristics and accuracy.

In this contribution, we perform distinct micromechanical tests on cathodic arc evaporated CrN coatings. These coatings were deposited with different bias voltages and deposition temperatures in order to obtain a variation in both, microstructure (specifically crystallite size) and defect density. The importance of the microstructure on fracture characteristics has recently shown by Ast et al. for Ti-Al-N deposited by diverse PVD techniques [1]. However, a clear correlation between the column size and the density of column boundaries is still missing.

We found a significant influence of the residual stress state on the fracture properties of such hard coatings using the indentation fracture method. Furthermore, we used pillar splitting and cantilever bending tests to determine the intrinsic fracture toughness of our coatings with respect to the microstructure and defect density. These results were complemented by HR-TEM investigations together with x-ray diffraction studies, and nanoindentation tests.

References

[1] Ast J., et al., (2019). Fracture toughness determination of arc-PVD and HiPIMS hard coatings by micro-cantilever and pillar splitting tests.

HP-ThP9 Nanomechanical Characterization of Thin-Layered Battery Materials*,*
Jungkyu Lee (j.lee@bruker.com)*, D. Stauffer,* Bruker Nano Surfaces, USA

Rechargeable batteries are widely used in our daily life for small handheld devices such as smartphones and more recent electric vehicles. To date, a lot of research work on battery materials has been focused much more on increasing the electrical performance in terms of the efficiency, but mechanical reliability of these material has less priority and remained as an afterthought even though it is known that rechargeable battery will gradually degrade over its lifetime. Furthermore, mechanical damage, including brittle failure of the electrodes and separator penetration, can give rise to dramatic releases of stored energy, including battery fires. Thus, for both safety and performance reasons, it is necessary to understand how these devices perform mechanically, including each component at the appropriate size scale. But doing this requires precise, sensitive techniques for analyzing and characterizing these materials and technologies.

Many battery materials react energetically with oxygen or water, therefore this poster focuses on nanomechanical testing of battery materials utilizing a specially designed nanoindentation system. This system is sealed in a controlled inert atmosphere.

There has been significant effort to obtain mechanical measurements on lithium in both ideal [1] and more real world [2] conditions. However, the non-ideal case must overcome the inherent sample roughness. Here, the bootstrapping method of Efron is utilized to look at trends in modulus and hardness over a wide range in temperature, from -60 °C to 98 °C. This is extremely important, since batteries can easily be exposed to, or operated in, these conditions.

References:

[1] E. Herbert, S. Hackney, N. Dudney, P. Phani, J.Mater.Res. 33(10), 1335-1346 (2018)

[2] Y. Wang, D. Dang, M. Wang, X. Xiao, YT Cheng, Appl.Phys.Lett. 115, 043903 (2019)

HP-ThP10 Nanoscale Analysis of Changes in Grain Structure of Titanium Subjected to Failure, ***Omkar Nafday (omkar.nafday@anton-paar.com)***, Anton Paar, USA, United States of America; *G. Paroline,* Anton Paar, USA

Surface characterization of metals subjected or caused to fail, typically involves optical microscopy, some form of elemental combined with SEM analysis. Other testing methods like micro/nano-indentation, tensile testing and bending protocols can provide hardness, Young's modulus, elasticity, fracture resistance and other material properties. Surface texture, grain structure and roughness and differences therein are important identifiers of metal failure.

Here, we leverage the nanoscale surface imaging capabilities and ease of use of the Tosca atomic force microscope (AFM) to illustrate the before and after surface structures of titanium (Ti) metal subjected to failure. Images of the titanium metal surfaces collected before and after will throw light on the type of change in microstructures and grain regions that are characteristic of their failure. This is a unique way to see metal grain structure, and check for the presence of any impurities that might have possibly contributed to failure.

Topical Symposia
Room Grand Hall & Foyer - Session TSP-ThP
Topical Symposia (TS) Poster Session

TSP-ThP1 Fragmentation of Atomic Layer Deposited Oxide Thin Films and Nanolaminates under Uniaxial Tension, *M. Ruoho, J.-P. Niemelä,* ***Barbara Putz (barbara.putz@empa.ch)***, *N. Tarasiuk, G. Robertson,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *A.A. Taylor,* University of California Santa Barbara, USA; *X. Maeder,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *C. Kapusta,* AGH University of Science and Technology Krakow, Poland; *J. Michler, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Atomic layer deposition (ALD) allows the realization of thin conformal coatings free of through thickness defects (pinholes) with nanometer-scale precision. Therefore, this growth method, which is based on self-limiting surface reactions, is attractive for applications in barrier coatings, metal coatings, integrated circuit technology and flexible electronics [1,2]. Single layers and nanolaminates of different materials (insulating and conductive) can be deposited with outstanding thickness accuracy. For instance, flexible thin film transistors have been realized using ALD materials as both, the channel and the dielectric [3]. Regarding the mechanical properties of ALD oxide thin films, crucial for the application in e.g. flexible electronics, literature is scarce with respect to the wide range of possible film materials.

In this work, we present a systematic study of fracture properties for some of the most common ALD oxide materials: alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), yttria (Y_2O_3), alumina doped yttria, and zinc oxide (ZnO) films as well as yttria/alumina nanolaminates on flexible polyimide substrate. Crack onset strains, cohesive strains, and interfacial shear strains as well as corresponding film strengths, fracture toughness, and fracture energy are obtained from uniaxial tensile experiments. Results indicate a dependence of the mechanical performance on the oxide material, layer structure and growth temperature. Polycrystalline films of ZnO show largest saturated crack densities around 550 mm^{-1}. Smallest saturated crack densities around 300 mm^{-1} were observed for Al_2O_3 films. Crack onset strains, normalized to 50nm film thickness, are ranging from 0.6% to 1.3% for the different thin films. Cohesive strain values range from 1.1% to 1.6%. The addition of an amorphous interfacial Al_2O_3 layer improved nucleation of some of the oxides on polyimide, reduced the saturated crack density, and increased the crack onset strain of Y_2O_3 films. No delamination was observed for any material within the measured tensile strain range of up to 20% indicating excellent adhesion between thin film and substrate.

The reported data starts filling the literature gap in the mechanical characterization of flexible ALD oxide thin films and highlights the potential of intelligent multilayer design for improved stretchability.

References:

[1] J. Meyer et al., Adv. Mater. 21, 2009.

[2] M. D. Groner et al., Appl. Phys. Lett. 88, 2006.

[3] Y. Y. Lin et al., ACS Appl. Mater. Interfaces 7, 2015.

TSP-ThP2 Highly Efficient Hydrogen Evolution of Copper-Doped MoS_2/MOF Composite Photocatalysts via Fabricating the 2D Periodic Structure, ***Tzyy-Leng Horng (tlhorng123@gmail.com)***, *G.-J. Lee, H.-T. Huang, J.-J. Wu,* Feng Chia University, Taiwan

A novel visible-light-driven Cu-doped MoS /MOF composite photocatalyst was successfully synthesized by the microwave irradiation. MOFs, a new class of porous crystalline materials, have attracted tremendous attention by considering their broad applications due to the repeated crystalline structures, thereby improving the harvest of solar energy and transportation of charge carriers. In addition, the Cu/MoS /MOF powders was fabricated with the 2D periodic structure (Figure 1) to improve the light absorption efficiency. In this study, it has revealed that the appropriate modification of MOF and copper could significantly enhance the photocatalytic efficiency. The hydrogen evolution for 10% v/v formic acid of Cu/MoS /MOF/2D can achieve the maximum amount of 1,351.1 µmol h cm . Therefore, this research has substantially demonstrated the potential abilityto promote the photocatalytic efficiency by MOF, copper, and 2D periodic structure modifiedMoS_2.

TSP-ThP3 Stability of Mechanical Properties of Molecular Layer-deposited Alucone, *M. Ruoho, N. Tarasiuk, N. Rohbeck, J.-P. Niemelä,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *C. Kapusta,* AGH University of Science and Technology Krakow, Poland; *J. Michler,* ***Ivo Utke (Ivo.Utke@empa.ch)***, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

We report on the effect of ageing on the mechanical properties of molecular layer-deposited (MLD) thin films. The mechanical failure of the films during uniaxial tensile testing [1] was studied and we observed an approximate order of magnitude difference in the crack-onset strain and related flexibility within the first two days after the samples were exposed to ambient atmosphere. The MLD films were made using trimethyl-aluminum and ethylene glycol and are known for exhibiting structural changes after the fabrication; we show that these changes are detrimental for mechanical robustness of the films. This information aids to plan the handling or the protection of these films to achieve better performance with these materials.

The crack-onset strains, interfacial shear strains, and cohesive strains of the shortly air-exposed 300-nm-thick films were observed to be roughly 1.8%, 0.3%, and 2.1%, respectively. These values were derived using Weibull statistics of the initial crack density slope with strain as outlined in [2] to account for the natural existence of crack-initiating flaws in the film. With continuing exposure to ambient atmosphere the crack onset strain decreases, while the elastic moduli and hardnesses of the films stay approximately constant around 40 to 50 GPa and around 1 GPa, respectively.

The above crack-onset strains values are the highest reported so far for hybrid organic-inorganic MLD thin films and would extrapolate to about 14% crack-onset strain for 5-nm-thick films, indicating potential applications as interfacial adhesion layer for films on polymer substrates and as a protective coating in battery applications.

We will discuss the changes in mechanical properties with exposure to air in relation to observations by x-ray reflection measurements and Fourier transform infrared measurements which show changes in volume as well as in the number of OH bond states.

[1] M. Ruoho, N. Tarasiuk, N. Rohbeck, C. Kapusta, J. Michler, I. Utke, Materials Today Chemistry 10 (2018) 187-194.

[2] Y. Leterrier, L. Boogh, J. Andersons, J.A.E. Månson, J. Polym. Sci. Part B Polym. Phys. 35 (1997) 1449-1461.

TSP-ThP4 Mechanical Properties of High Entropy Alloys (HEA) Thin Films on Flexible Substrate: Study of CoCrCuFeNi System*, C-H Li, F Sedghgooya,*
LSPM-CNRS, Université Paris13, France*; R Dedoncker,* Ghent University, Belgium*; F Zighem,* LSPM-CNRS, Université Paris13*; D Depla,* Ghent University, Belgium*; P Djemia,* ***Damien Faurie (faurie@univ-paris13.fr)****,* LSPM-CNRS, Université Paris13, France

. The interest in the mechanical properties of high entropy alloys has grown over the last few years. To exploit these alloys for various applications such as magnetic layers, flexible electronic, or as protective coating, their mechanical strength should be combined with a sufficient deformability.

In this study, we focused on the ferromagnetic alloy based on Co, Cr, Cu, Fe and Ni, in a roughly equimolar composition deposited by magnetron sputtering as thin films on a Kapton® substrate within the thickness range between 20 to 500 nm. The presented results focus on the mechanical behavior. This behavior is studied by in-situ uniaxial tensile test which results in multi-cracking and subsequent detachments initiated at the edge of cracks studied by confocal microscopyThese properties are closely related to the fracture and adhesion energies, respectively, which we estimated using quantitative processing of these analyzes.

As the properties of these alloys are unknown, also first-principle calculations were performed. The obtain data (including elastic constants) forms the input to analytical models. Overall, the results show brittleness (cracking at strain of about 2%) regardless of the thickness despite the dense microstructure of these films. The results are discussed in the light of Pugh's ductility/brittleness criterion and the microstructure (particularly grain size).

TSP-ThP5 Transparent nc-Z_rB_2/a-BN Films for Protection of Optical Devices*,*
Philipp Kiryukhantsev-Korneev (kiruhancev-korneev@yandex.ru)*, A.P. Kozlova, K.S. Kozlova, E. Levashov,* National University of Science and Technology "MISiS", Russia

Protection of optical devices (portholes and solar cells, solar collectors, etc.) from abrasive effects can be provided by the use of wear - and erosion-resistant ion-plasma coatings, including those based on oxygen-free ceramics. The use of hard and optically transparent Zr-B-N films is promising. Ceramic nanocomposite films were deposited by DC and pulsed DC magnetron sputtering of ZrB/2/ target in the Ar+$N_{/2}$/ gas mixtures. The targets were manufactured by means of self-propagating high-temperature synthesis. The structure, chemical and phase composition of films were studied by high resolution transmission and scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Raman and infrared spectroscopy, energy-dispersive analysis, and glow discharge optical emission spectroscopy. The films were characterized using nanoindentation, sliding pin-on-disk, impact ball-on-plate, abrasive calowear, and scratch tests. The refraction index, coefficients of transmittance (Tr) and reflectance were measured by Cary 5000 Agilent + UMA attachment for wavelength range from 200 to 2500 nm. Results obtained show that films deposited at low nitrogen partial pressure predominantly consist of nanocrystallites of hexagonal ZrB2-phase, 1-20 nm in size and amorphous regions. N-rich films exhibit amorphous structure (a-BN) with nanograins of Zr-contained phases. Specific optical properties were observed for these Zr-B-N coatings including Tr=70-100%. The hardness of 15-37 GPa and Young's modulus of 150-470 GPa were determined for films deposited onto alumina substrates. Coatings demonstrated friction coefficient 0.2-0.4. The addition of nitrogen significantly increased wear resistance in sliding and impact conditions. The work was supported by the Russian Foundation for Basic Research (Agreement No. 19-08-00187)

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-3-FrM

PVD Coatings and Technologies III

Moderators: Frank Kaulfuss, Fraunhofer IWS, Germany, Qi Yang, National Research Council of Canada, Canada

8:00am **B1-3-FrM1 Plasma-assisted Deposition of TCO Fhin Films by Sublimation in an Anodic Vacuum Arc Discharge**, ***Bert Scheffel (bert.scheffel@fep.fraunhofer.de)***, *O. Zywitzki, T. Preußner, T. Modes,* Fraunhofer FEP, Germany

The interest in transparent and electrically conducting oxide coatings (TCO) remains high for photovoltaics and displays. TCO films were prepared by sublimation from an anodic vacuum arc. This method offers relatively high deposition rates of 15 nm/s as described in this paper and potentially even significantly higher rates. The vacuum arc process using a hot hollow cathode and a hot sublimating anode was operated at a relatively low discharge voltage below 80 V. Therefore, and in contrast to magnetron sputtering process, the particles impinging the substrate surface have relatively low energies and should not damage a semiconductor substrate. The method is suitable for sublimating electrically conductive materials based on indium oxide, tin oxide or zinc oxide such as ITO, IZO, AZO or GZO. Because of the high deposition rate, excellent layer properties and good process scalability, the anodic sublimation in a vacuum arc discharge is an attractive option for thin film processing. A laboratory sublimation device was equipped with a tunable magnetic system. The electrically conducting TCO material serves as the anode of the discharge and is heated by the discharge electrons. Process parameters of the electrical discharge and the substrate temperature (20-300°C) were varied. TCO layers in the thickness range of 100-600 nm were deposited onto flat borosilicate glass sheets and silicon wafers. The obtained layers were investigated using SEM, EDX, XRD and AFM. Optical and electrical properties were investigated by UV/VIS/NIR spectroscopy and Hall measurements respectively. Results about influence of the process parameters on thin film microstructure and film properties will be presented and discussed. Low specific electrical resistance of about $2 *10^{-4}$ Ohm cm, charge carrier densities in the range of 0.5 to $1*10^{21}$ cm^{-3} and charge carrier mobilities up to 36 cm^2/Vs were measured for ITO 90/10 layers. The roughness of the ITO layers determined by AFM is very low with arithmetic roughness values Ra between 0.3 and 1.2 nm. XRD examinations show a pronounced texture of the cubic bixbyite phase. Both roughness and texture properties are strong dependent on the substrate temperature.

8:20am **B1-3-FrM2 Effect of Spatial Distribution of Chemical Species on Nitride Hard Coating Structure in Cathodic Arc PVD Method**, ***Shun Sato (satos@mmc.co.jp)***, *K. Yamaguchi, M. Takahashi,* Mitsubishi Materials Corporation, Japan

The cathodic arc physical vapor deposition (PVD) method is widely used for industrial applications such as hard coating for cutting tools. The characteristics of the coating depend on the spatial distribution of the chemical species in the furnace, and the understanding of the spatial distribution of the chemical species is very significant for the control and improvement of the coating characteristics. Although the spatial distribution of chemical species in the cathode discharge has been studied by various methods, the relationship between the transport process of each chemical species generated from the surface of the cathode target having a different composition until reaching the substrate and the effect on the coating characteristics is not clear.

In this study, the spatial distribution of chemical species in furnaces was evaluated in the case of discharging using AlCr, AlTi alloys as cathodes by the cathodic arc PVD method. In particular, the spatial distribution of chemical species and changes in coating structure were investigated in the case of varying magnetic flux densities on target surfaces in (Al, Cr)N-based hard coatings, and their relationships were investigated.

In investigating the above relationship, in order to confirm the spatial distribution of the chemical species in the vicinity of the substrate in the discharge, the luminescence from the chemical species in the discharge was directly observed, and the inflow of the chemical species during discharge into the substrate was evaluated.

As a result, the spatial distribution of the chemical species in the vicinity of the substrate could be grasped. The results showed that the Al ion/Al radicals ratio was higher in the discharge of the AlCr alloy cathode than in the discharge of the AlTi alloy cathode. When the magnetic flux density on the surfaces of the cathode targets is increased in discharging the AlCr cathode, the number density of chemical species decreases, but the spatial distributions do not change greatly. At this time, however, it was found that there was a change in the structure of the (Al, Cr)N coating.

It was found that the chemical species generated in the cathode target reached the substrate by the collision reaction between the cathode and the substrate while changing the valence, and in different alloy composition systems, the transport process from the cathode to the substrate was different by the combination of chemical species. It was also suggested that the inflow of chemical species per unit time affected the structural change of the (Al, Cr)N-based hard coatings.

8:40am **B1-3-FrM3 Industrial Scale ta-C Coating Using Laser Arc Technology**, ***Wolfgang Fukarek (wolfgang.fukarek@federalmogul.com)***, *B. Gebhardt,* VTD Vakuumtechnik Dresden GmbH, Germany; *V. Weihnacht, F. Kaulfuss,* Fraunhofer IWS, Germany **INVITED**

First reports about a Laser-initiated vacuum arc date back to 1976 /1/. Laser ignition has many advantages particularly for pulsed high current vacuum arcs when spatial and temporal control at high pulse repetition rates for millions of pulses is required. This holds especially for the carbon arc which deviates markedly from metal arcs with respect to arc movement, charge state and degree of ionization and particle generation. The carbon arc is preferentially operated at pulsed arc currents in the kA range and pulse lengths of some 100 µs. The Carbon Laser-Arc has been investigated and applied to deposition of highly tetrahedral amorphous carbon films (ta-C) since the 1990th/2/.

Only in recent years the Carbon Laser-Arc was introduced in mass production for coating of automotive powertrain components as well as for other tribological applications and cutting tools.

In this paper we discuss different aspects of upscaling ta-C Laser-Arc coating systems in order to increase the throughput and the total amount of deposited carbon per batch. The importance of process stability for long coating runs is discussed. We also report on deviating film properties that have been observed on films deposited at intermittent high-rate deposition of ta-C.

/1/ J.E. Hirshfield, Laser-initiated vacuum arc for heavy ion sources. IEEE Transact. Nucl. Sci. 23, 1006-1007 (1976)

/2/ H.-J. Scheibe et al, Laser-arc: a new method for preparation of diamond-like carbon films. Surf. Coat. Technol. 47, 455-464 (1991).

9:20am **B1-3-FrM5 New Details about Surface Modification on Multi-element Arc Cathodes Revealed by Dedicated Cathode Design**, ***Mehran Golizadeh Najafabadi (mehran.golizadeh@unileoben.ac.at)***, *F. Mendez Martin,* Montanuniversität Leoben, Austria; *S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *R. Franz,* Montanuniversität Leoben, Austria

Cathodic arc deposition is an industrial physical vapor deposition technique to grow dense and well-adherent coatings due to highly ionized plasmas having ion charge states up to 5 and ion energies from 20 to some 100 eV. The origin of such multiply charged energetic ions is known to be the cathode spot where a microvoulume explosion occurs and ions are accelerated with supersonic velocities into the surrounding atmosphere. The motion of the cathode spot over the cathode surface causes consecutive melting-solidification cycles which in case of alloy and composite cathodes leads to the formation of a so-called converted layer on the surface of cathode. The properties of this layer and its formation mechanisms are known to influence the plasma properties but are only scarcely explored.

In a first step, we designed a Mo/Al multilayer cathode to reveal the heat and pressure profiles below single craters as well as erosion stages of the cathode. The multilayer cathode consisted of two parts: a substrate, which was a standard Ti arc cathode, and a Mo/Al multilayer coating consisting of 20 alternative layers with individual layer thickness of 500 nm deposited by dc magnetron sputtering. Subsequently, composite $Al_{0.5}Cr_{0.5}$ cathodes with varying grain size were prepared and their converted layer was compared to reveal further details about the formation mechanism. The results showed that liquid-state diffusion is the dominant mechanism of material intermixing and number of cathode spot ignition per area determines the homogeneity of the converted layer. Moreover, material transport via droplets, generated during the explosive state of the cathode spot, contribute to the formation of a uniform converted layer over the composite cathodes depending on the roughness of the cathode. These findings can contribute to the refinement of cohesive energy rule which relates material properties of the arc cathode to the plasma properties.

9:40am **B1-3-FrM6 Utilization of Hybrid LACS® Technology (Lateral ARC and Central Sputtering) for the Enhancing of the DC Magnetron Sputtering Deposition**, ***Andreas Lümkemann (a.luemkemann@platit.com)***, *R. Zemlicka,* PLATIT AG, Switzerland; *M. Jilek, J. Kluson,* PLATIT a.s., Czech Republic; *B. Torp,* PLATIT Inc., USA, Denmark; *D. Blösch,* PLATIT AG, Switzerland

The flexible PVD hard coating unit π^{411+} is able to operate with ARC, sputtering and PACVD. The rotating lateral arc cathodes can be used as a source of electrons for the enhancement of the glow discharge and the magnetron sputtering deposition.

While one lateral cathode emits the electrons behind the shutter, the second lateral electrode (standardly used as the arc cathode) can be utilized as an anode to attract the electrons trough the coating chamber. When the central (placed in the middle of the chamber) rotating magnetron sputtering cathode operates, the usage of the external source of electrons leads to the higher ionization of the plasma and higher ion current to the substrate.

Moreover, the adjustment of the external electron current allows to keep the same constant substrate current for different applied bias voltages or DC magnetron sputtering powers. The possibility to adjust the arbitrary value of the substrate current independently on the other process parameters allows us to deeper investigate the role of this parameters on growing process and to tune to coating properties.

On the example of LACS-AlCrN sputtered from the AlCr alloyed target in the mixture of Ar_2 N_2 atmosphere we are going to show the effect of the substrate current, bias voltage, nitrogen partial pressure and MS power on the mechanical properties, chemical properties and the crystal structure of the coating.

Furthermore we are going to present experimental results depositing carbon based thin films using the LACS technology. With the usage of the external source of electrons one can enhance the graphite sputtering process influencing the ratio of sp2 to sp3 bonds in the deposited films obtaining desired functional properties of diamond like carbon coatings.

10:00am **B1-3-FrM7 Designing A Versatile Vacuum System For Thin Film Research And Development**, ***Allen Guastavino (sales@agsplasma.com)***, AGS Plasma Systems, USA

Increasing work in novel thin films R&D required an affordable, adaptive platform to be developed.

Work on quantum devices, photo-voltaic, electro-chromic, biologic, and battery's require new complex materials to be developed.

A flexible, compact, lightweight platform is desirable and we have developed a versatile solution.

Elements Instead of the usual huge welded stainless steel chamber system, an adaptable 12 inch cubic chamber design was selected.

The vacuum chamber consists of six equal facets. The frame is machined from a single block of aluminum, which makes the

system both weld free and provides a rigid structure.

The frame can include interchangeable panels which can easily be swapped around to achieve the desired process configuration.

Depending on on the type of panel, it can be used as: a source panel, viewport, pump panel, etch source, or an instrument panel.

The panels can be mounted onto the frame in a matter of minutes, which saves considerable time and space.

Chambers can easily be attached together to build a complex vacuum system.

The modular vacuum system enables creativity in design flexibility in construction.

The researcher can easily reconfigure deposition, etch, or instrument modules by switching panels in minutes.

Instruments of any conceivable type: OES, QCM, RGA, and Elippsometry to name a few.

Capabilities Available Now Evaporative Deposition: Both thermal and e-beam sources are available in single or multi -pocket versions.

Sputter/PVD: Single film, Co-Sputter, and Confocal sources as well as IBASD.

Ion Beam: Preclean, film modification (IBASD), and IB Sputter Deposition are proving to be invaluable in rare materials.

Surface Treatment: Both plasma etch and reactive plasma sources are available

Unique Tool to Deposit Thin Films from Rare Materials One fantastic example of what can be done is isotope IBSD. Many very rare isotopes were created after WWII. They are diminishing in supply and are terribly expensive.

The IBSD system we designed minimizes usage of the isotope target material with little waste.

Mutil-layer isotope films can be created using a moving stage for multiple targets.

Possibilities A system was developed that allows for versatile film growth and conservesdevelopent budgets through a reusable platform.

Other research systems can be designed with cubes for all types of projects.

10:20am **B1-3-FrM8 Zn Interlayer Design to Improve the Adhesion Strength of PVD Zn-Mg/Zn Coating on High-strength Steel**, ***SeungHwan Lee (tmdghks553@naver.com)***, *S.Y. Lee, H.K. Kim,* Korea Aerospace University, Republic of Korea; *J.W. Kim,* Incheon National University, Republic of Korea

It was well-known that the Zn-Mg coatings with high Mg content showed an excellent corrosion resistance compared to Zn coatings due to their dense amorphous microstructure. Low adhesion strength, however was also observed due to the brittle nature of amorphous microstructure in the coatings with high Mg content. In this study, the controlled microstructure of Zn interlayer was designed based upon the Structure Zone Model principles and double layer Zn/Zn-Mg coating was synthesized to investigate the effect of the interlayer microstructure on the adhesion strength of Zn-Mg coating with high Mg content. It was possible to synthesize a dense columnar structures of Zn interlayer using a magnetron sputtering process by controlling the working pressure and the density of Zn interlayer increased as the working pressure decreased during deposition. The adhesion strength of Zn /Zn-Mg double layer coatings was evaluated using a lap shear test and the results showed that much improved adhesion strength of above 24MPa could be possible for the magnetron-sputtered Zn/Zn-Mg coating with high Mg content. Similar approach was made for the synthesis of the Zn /Zn-Mg coatings with high Mg content using an electro-magnetic heating (EMH) system that is capable of high deposition rate. And the effect of the interlayer microstructure on the adhesion strength of EMH PVD Zn /Zn-Mg coating with high Mg content was investigated. Detailed experimental results will be presented.

10:40am **B1-3-FrM9 Characterization and Erosion Resistance Evaluation of TiAlN Thick Film by Cathodic Arc Deposition**, *D.Y. Wang,* MingDao University, Taiwan; ***Li-Chi Hsu (lhsu@aurorascicorp.com)***, *J. Hung,* Aurora Scientific Corp., Canada

A serious of titanium aluminium nitride (TiAlN) thin films have been used in various applications because of their excellent mechanical and corrosion resistance properties. However, in some applications, corrosion and erosion occur at the same time. That makes typical TiAlN thin films unable to survive in that environment. Most of the hard nitride thin films can pass the corrosion test but can not pass the erosion test due to its insufficient coating thickness. Higher thickness of hard nitride film is needed when large erosive particles are hitting the films with certain speeds and angles. In this study, high thickness of TiAlN films is deposited on Ti-Al-V-Cr alloy substrates by cathodic arc deposition (CAD) with TiAl cathode. Surface morphology, coating thickness and chemical composition are performed on scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). Nanoindentation and scratch tests are used to evaluate the coating hardness and adhesion properties. Corrosion and erosion resistance properties are examined by salt spray and solid-particle erosion tests.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-4-FrM

Properties and Characterization of Hard Coatings and Surfaces IV

Moderators: Naureen Ghafoor, Thin Film Physics Division, IFM, Linköping University, Sweden, Marcus Günther, Robert Bosch GmbH, Germany, Fan-Bean Wu, National United University, Taiwan

8:00am **B4-4-FrM1 The Structure and Properties of $V_{1-x}Mo_xN$ Thin Films Deposited by HiPIMS**, ***YiQun Feng***, *J.-H. Huang (jhhuang@ess.nthu.edu.tw),* National Tsing Hua University, Taiwan

The objective of this study was to investigate the structure and properties of $V_{1-x}Mo_xN$ nanocrystalline thin films deposited by HiPIMS. Sangiovanni et al. [1] reported that $V_{1-x}Mo_xN$ films would possess much higher toughness compared with VN by ab initio density functional theory calculation. However, our recent study on the $V_{1-x}Mo_xN$ deposited by DC magnetron sputtering showed inconsistent results, where the resultant fracture toughness (G_c) of the $V_{1-x}Mo_xN$ ranged from 10 to 14.4 J/m^2, while that of VN was about 14.8 J/m^2. The discrepancies may be attributed to the low free energy of formation for the Mo-N bonding, which degraded the thin film quality and consequently decreased the fracture toughness. Compared with DC magnetron sputtering, HiPIMS produces higher plasma density with enhanced degree of ionization, which may facilitate the formation of Mo-N bonding and thereby increasing the crystallinity of the $V_{1-x}Mo_xN$ films. Accordingly, this study adopted HiPIMS to deposit $V_{1-x}Mo_xN$ thin films on Si substrate for improving the film quality and aimed to investigate the structure and properties of the $V_{1-x}Mo_xN$ films. After deposition, the compositions of $V_{1-x}Mo_xN$ films were determined by electron probe microanalyzer, the thickness of all specimens were measured from the images observed by scanning electron microscope. X-ray diffraction was used to characterize the crystal structure and the texture. In addition, the residual stress of the specimens was measured by laser curvature method, the hardness and elastic modulus were assessed by nanoindentation. The internal energy induced cracking method [2] was used to evaluate the fracture toughness, from which the theoretical values could be verified.

[1] D. G. Sangiovanni, V. Chirita, L. Hultman, Phys. Rev. B., 81 (2010) 104107.

[2] A.-N. Wang, G.-P. Yu, J.-H. Huang, Surf. Coat. Technol., 239 (2014) 20.

8:20am **B4-4-FrM2 Study of Synergic Effects of Laser Ablation and Coating on Cemented Carbides: Surface and Mechanical Integrity Assessment**, ***Shiqi Fang (shiqi.fang@uni-saarland.de)***, *D. Bähre,* Saarland University, Germany; *N. Salan, L. Llanes,* Universitat Politècnica de Catalunya, Spain

Emerging laser precision machining, in particular using pulsed laser, enlightens the innovation and functionalization of cemented carbides, backbone materials of tooling industry and considered difficult to machine or shape by conventional abrasive approaches. Coating of cemented carbide tools, deemed to improve their mechanical and thermal properties, is nearly a compulsory treatment prior to their operation. Within this context, the aim of this investigation is to study the synergic effects of laser ablation and subsequent coating on surface and mechanical integrity of cemented carbides. Two plain WC-Co grades with different metallic binder content (10%$_{wt}$Co and 15%$_{wt}$Co) were treated by means of a short-pulsed nanosecond laser using different energy levels. Then, hard AlTiN layers were (PVD) deposited on the laser-ablated surfaces. The resulting surface integrity was assessed in terms of morphological and microstructural changes. On the other hand, mechanical integrity was evaluated on the basis of hardness and sliding contact response, the latter including adhesion strength and friction behaviour. It is found that laser ablation resulted in a rising surface roughness without any additional induced damage. Meanwhile, coating deposition translated into relevant hardness increase, this being more significant on surfaces ablated using high energy levels. However, it also affects adversely sliding contact response. Regarding substrate microstructure, these observations became more pronounced with an increase in binder content. Characterization study was complemented by an extensive and detailed scanning electron microscopy examination, including inspection of FIB-milled crossed sections at locations where specific damage events were identified. It allows to discuss fracture and damage micromechanisms for the laser-treated and coated cemented carbides.

8:40am **B4-4-FrM3 Fatigue Behaviour of Thin Coating and the Influences of Plastic Deformation of Harden-case using Irreversible Cohesive Zone Model**, ***Jiling Feng (j.feng@mmu.ac.uk),*** Manchester Metropolitan University, UK; *Y. Qin,* University of Strathclyde, UK; *T.W. Liskiewicz,* Manchester Metropolitan University, UK; *B.D. Beake,* Micro Materials Ltd, UK

Cohesive-zone modelling technique has been proved to be an efficient approach to simulate the fracture behaviour of multi-layered coatings under monotonically loading (Feng, 2012). This paper aims to investigate the fatigue failure mechanism of coating system by observing the procedure of initiation and propagation of cracks within the coating under the cyclic loads.

We developed a "three-layer" finite element model, composed of the coating, hardened case and substrate, which was validated via nano-indentation technique with 300 µm radius indenter. Homogenous material properties were assumed for both the TiN/CrN coating and the substrate, with multi-linear hardening behaviour. Prior to coating deposition, the substrate was heat-treated by plasma nitriding to enhance the load-bearing capacity of the coating/substrate system.

An irreversible cohesive constitutive equation, taking into account the energy dissipation resulted from frictional interaction of asperities along the cohesive surfaces and crystallographic slip, was employed to identify the crack initiation and to simulate the crack propagation under the cyclic loads. An in-house User Material (UMAT) subroutine was used to simulate the degradation of coating material upon cyclic loading.

Numerical results demonstrated a clear quantitative relationship between the coating stiffness degradation and its damage accumulation. It was observed from a case study that first crack (0.01 µm in width and 0.05 µm in depth) was initiated at 8th loading cycle, and it propagated through the coating thickness with increasing number of loading cycles reaching 1.4 µm at the 100th cycle. It was also noticed that the plastic deformation of the hardened case developed significantly, which might be a major contribution of the initiation of the crack.

The results observed in this study are in agreement with our recent experimental observations (Beake et al, 2019), which indicated that micro crack/wear damage was occurring at the early stage of nano-indentation loading cycles. The numerical study confirmed, that once crack was initiated, it propagated rapidly through the coating, which can lead to delamination when the crack reaches the hardened substrate interface.

Key words: Fatigue failure; Cohesive Zone Model; Cyclic loading;

Reference

1. Feng, J & Qin, Y (2012), Prediction of the critical load of a metal-rolling system by considering the damage of the coated surface, Steel Research International, Metalforming, Special Edition.
2. Beake, B.D., Isernm L., Endrino, J.L., Fox-Rabinovich, G.S., (2019), Micro-impact testing of AlTiN and TiAlCrN coatings, Wear, 418–419, 102-110.

9:00am **B4-4-FrM4 Behavior of Helium and Hydrogen on the Microstructure Evolution of He/H irradiated 6H-SiC: A Aomparison**, ***Bingsheng Li (Nabil.Daghbouj@fjfi.cvut.cz),*** State Key Laboratory for Environment-friendly Energy Materials, Southwest University of Science and Technology, Mianyang, Sichuan 621010, China; *N.I. Daghbouj,* Czech Technical University in Prague, Czech Republic; *M. Callisti,* University of Cambridge, UK

The influence of the irradiation temperature (from room temperature (RT) up to 900°C) and subsequent isothermal annealing (from 400 to 1500°C) on the microstructure of hydrogen-implanted 6H-SiC was studied by Raman spectroscopy, X-ray diffraction, transmission electron microscopy, and optical microscopy. The behavior of implanted hydrogen and helium ions in the 6H-SiC lattice was rather different. Based on the results obtained by optical microscopy, in the case of hydrogen implanted with low fluence at RT, blisters were formed after annealing at 1100°C, while at high implantation fluence no blister cavities were observed due to the formation of an amorphous layer. At an implantation temperature of 450 and 900°C amorphization of 6H-SiC did not occur and hydrogen-containing microcracks grew laterally below the surface. Thus blisters appeared on the surface at 900°C implantation temperature even without annealing, as a result of the vertical stress exerted by pressurized microcracks. For helium implantation, regardless of the fluence and implantation temperature, blisters did not form due to no coalescence between bubbles or platelets formed during irradiation. The presented results are well supported by density functional simulations. The Oswald ripening process is studied through the migration energy of H and He ions which demonstrates a much higher energy barrier for He migration making this process less likely compared to H. Moreover, the simulations reveal that the coalescence between two small bubbles is an exothermic process when the H_2-bubbles contain an unpaired hydrogen and endothermic process when the H_2-bubbles contain paired H atoms but it's energetically cheap. On the other hand, this process is endothermic and energetically very expensive to active the coalescence for the He-bubbles.

9:20am **B4-4-FrM5 Microstructure and Oxidation Behaviour of Arc Evaporated TiSiN Coatings Investigated by *in-situ* Synchrotron X-ray Diffraction***, ****Yvonne Moritz (yvonne.moritz@unileoben.ac.at)****,* *C. Saringer, M. Tkadletz,* Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Helmholtz-Zentrum Geesthacht, Germany*; M. Pohler,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

TiSiN hard coatings are a suitable candidate as a protective layer for various cutting applications, due to their advantageous mechanical properties and excellent oxidation resistance. Within this work, a detailed characterization of the microstructure of TiSiN is complemented by the investigation of its oxidation mechanism using *in-situ* X-ray diffraction (XRD) at a synchrotron radiation facility. XRD, X-ray photoelectron spectroscopy and transmission electron microscopy investigations of an as-deposited TiSiN coating grown on cemented carbide substrate indicate the presence of a nanocomposite structure, consisting of Ti(Si)N nanocrystallites embedded in an amorphous Si_3N_4 matrix. To illuminate the oxidation stability, a powdered coating was annealed in air between 100 and 1200 °C and the recorded 2D X-ray diffractograms were correlated with the results of differential scanning calorimetry. Sequential Rietveld refinement of the obtained synchrotron data provided temperature-dependent information about the phase composition and thermal expansion of the individual phases. The results revealed an oxidation stability of TiSiN up to a temperature of approximately 830 °C, followed by the formation of both, rutile and anatase TiO_2. It was shown that the quantity of the metastable anatase phase reached its maximum at a temperature of 1020 °C and then continuously transformed into the stable rutile modification at higher temperatures. The present findings provide a detailed insight into the complex microstructure and oxidation mechanism of TiSiN coatings, allowing to further optimize this system for future applications.

Keywords: TiSiN hard coatings, arc evaporated, Sequential Rietveld refinement, oxidation resistance, TEM

9:40am **B4-4-FrM6 Surface Properties of Titanium Alloy Treated with Gas Blow IH Nitriding and its Effects on Fatigue Strength***, ****Shuan-Han Huang (senkan@keio.jp)****,* *M. Hayama,* Keio University, Japan*; S. Takesue,* Kyoto Institute of Technology, Japan*; J. Komotori,* Keio University, Japan

The purpose of this study was to evaluate the effects of surface properties of β rich α + β titanium alloy SP700® treated by gas blow IH nitriding which is a combination of atmospheric-controlled induction heating and nitrogen gas blow under variable treatment time. This gas blow IH nitriding was more efficient surface treatment to form a nitrogen hardened layer on the surface of the specimen than the conventional gas nitriding. The surface properties of the specimens were characterized using X-ray diffraction, an optical microscope and a micro-Vickers hardness tester. The results showed that the nitrogen compound and diffused layers were formed on the surface of the treated specimens. Furthermore, surface hardness increased comparing to the untreated one and the thickness of the hardened layer increased as increasing gas blow IH nitriding time. Grain coarsening was also observed on the cross section of the treated specimens due to exceeding the β transus temperature of titanium alloys. The axial loading fatigue tests were performed on the treated specimens. The fatigue strength of treated specimens decreased dramatically because of grain coarsening and forming the nitrogen compound layer on the surface of the specimens. This implies that low temperature nitriding combined with fine particle peening needs to be done in order to prevent the reduction of fatigue strength.

10:00am **B4-4-FrM7 Corrosion Resistance of Cobalt Boride Layer Exposed to a Diffusion Annealing Process***, ****Angel Manuel Delgado-Brito (adelgado1600@alumno.ipn.mx)****,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; I. Mejía-Caballero,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico*; G.A. Rodríguez-Flores,* Universidad Autónoma Metropolitana- Azcapotzalco, México*; A. Ruíz-Ríos, E.J. Hernández-Ramírez, A.D. Contla-Pacheco,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, México*; I.E. Campos-Silva,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, México, Mexico

New results about the corrosion resistance of ASTM F1537 alloy subjected to the powder-pack boriding process (PPBP) and exposed to the diffusion annealing process (PPBP + DAP), were estimated in this study. The PPBP was carried out at 1273 K with 6 h of exposure using a powder mixture composed of 20% B_4C, 10% of KBF_4, and 70% of SiC. A CoB-Co_2B layer was obtained with an outer layer (CoB) ~ 20 microns of thickness and an inner layer (Co_2B) ~ 13 microns of thickness. After the application of PPBP, a DAP was carried out at 1273 K with 2 h of exposure in an argon atmosphere, in which a Co_2B -based layer with around 30 microns of thickness was obtained. The cross-sections of the CoB-Co_2B layer and the Co_2B -based layer were analyzed by scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDS) techniques to obtain the chemical composition along the depth of the cobalt boride layer-diffusion zone system.

The corrosion test was conducted according to the ASTM G3 procedure in a standard three-electrode electrochemical cell, employing an Ag/AgCl as a reference electrode (RE) and a Pt wire as an auxiliary electrode (AE). The polarization resistance of the PPBP, PPBP + DAP, and ASTM F1537 alloy (reference material) was estimated during 5 days of immersion in the Hank´s solution considering a scan among ± 150 mV from the open circuit potential (OCP), with a scan rate of 1 mVs^{-1}.

The reaction products (B_2S_3 and $CrPO_4$) formed between the PPBP surface and the Hank´s solution affected the corrosion performance of the CoB-Co_2B layer decreasing the corrosion resistance around 40 times compared to the reference material. In contrast, the presence of the Co_2B -based layer obtained by PPBP + DAP increases the corrosion resistance about 30 times compared to the CoB-Co_2B layer developed by PPBP. This behavior was associated with the high contents of chromium revealed at the outer surface of the Co_2B -based layer according to the SEM/EDS results.

10:20am **B4-4-FrM8 Finite Element Modeling of Powder-Pack Boriding Thermochemical Treatment***, ****Omar Reyes-Carcaño (mc.omar03@gmail.com)****,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico*; A. Meneses-Amador,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico, México*; I.E. Campos-Silva,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico*; G.A. Rodríguez-Castro, R.C. Vega-Morón,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico, México*; D. Fernández-Valdés,* Instituto Politécnico Nacional Grupo Ingeniería de Superficies, Mexico

A finite element simulation and an experimental validation of the boriding process is presented. A Fe_2B layer was formed at the surface of pure iron by the powder-pack boriding process at temperatures of 1173, 1223 and 1273 K for 2 and 6 h exposure times. A powder mixture of 20% B_4C, 10% KBF_4 and 70% SiC was employed for the powder-pack boriding process. The presence of borides on the surface of the borided pure iron was verified by the XRD technique. The boron activation energy and diffusion coefficients were estimated according to cited literature. Furthermore, the GDOES technique was used to obtain the boron concentration profile along the boride layer for each condition. A time dependent numerical simulation was carried out considering boron diffusion coefficient and boron concentration as initial and boundary conditions, respectively. Finally, the simulation results and experimental data of the boron concentration as a function of the boride layer depth were compared and found to exhibit a great convergence.

10:40am **B4-4-FrM9 Metal Oxynitride Thin Films: A Review on Synthesis Developments, Performance, and Applications***, ****Sharafat Ali (sharafat.ali@lnu.se)****,* Linnaeus University, Sweden **INVITED**

This talk will provide an overview of the latest research development on metal containing nitrogen rich oxynitride thin films as hard, durable and strong material. I will start giving an overview of silicon oxynitride thin, preparation of these films by different techniques and variation of properties with the N content. I will also talk about the new amorphous thin films in the metal containing -Si-O-N systems containing a high amount of nitrogen and metals. Recently we have deposited novel AE-Si-O-N thin-film materials (AE= alkaline earth e.g. Mg, Ca, and Ba), onto float glass surfaces, by magnetron sputtering. Mechanical and physical properties show hardness values up to 22 GPa, reduced elastic modulus values up to 175 GPa and refractive index values up to 2, which can be compared to the uncoated float glass having hardness of 7 GPa, elastic modulus of 65 GPa and refractive index of 1.50. These thin films can be potentially used as a protective cover for displays and touch screens in tablets, smartphones, watches, etc.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E3-FrM

Tribology of Coatings for Automotive and Aerospace Applications

Moderators: Carsten Gachot, TU Wien, Institute for Engineering Design and Logistics Engineering, Austria, Christian Greiner, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany, Oliver Hunold, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

8:00am **E3-FrM1 Determination of Method for Tribological Experiment on Ultra-Hard Coatings in Low-Viscosity Fuels***, **Kelly Jacques (kellyjacques@my.unt.edu)**,* University of North Texas, USA, United States of America*; S. Berkebile, N. Murthy, J.E. Mogonye,* Army Research Laboratories, USA*; S. Dixit,* Plasma Technology Inc., USA*; D. Berman, T. Scharf,* University of North Texas, USA

In order to expand fuel operation capability of fuel systems to multiple fuels, fuel pump materials must resist scuffing and wear when lubricated with low viscosity, low lubricity hydrocarbons and alcohols under conditions of dynamic fluid pressure and flow. In this work, a high-frequency reciprocating tribometer was used to determine a set of tribological experimental parameters that emulate conditions within a fuel pump system, instigate material scuffing, and yield reliable and repeatable results. The ASTM D6079 standard for evaluating lubricity of diesel fuels by the high-frequency reciprocating rig was used as a basis for the development of new experimental parameters, of which the grinding lay orientation, temperature, counter body, substrate, contact load, and stroke length were altered. These experimental parameters were used to determine the onset of scuffing and wear of through-hardened 52100 steel substrates and various ultra-hard material coatings, including iron boride and tungsten carbides, possible candidates for steel protection. These materials were lubricated with F-24 (JP-8) and ethanol. Scanning electron microscopy, energy dispersive spectroscopy, white light interferometry, and optical microscopy were used to characterize the extent of wear and corrosion of the materials and counter bodies during the experiments. Overall, it was found that the ultra-hard coatings experience less wear and are more resistant to scuffing at low loads than the 52100 steel.

8:20am **E3-FrM2 Tribology and Corrosion Behavior of Ni-Al_2O_3 Composite Coating on Cast Iron***, **Jiayi Sun (sun131@uwindsor.ca)**, C. Zhao, R. Cai, X.Y. Nie,* University of Windsor, Canada

Nickel is a widely used anti-corrosion material, and Alumina (Al_2O_3) is also applied for wear/ corrosion resistance. Producing Ni-Al_2O_3 composite coating could combine the anti-corrosion and anti-wear characteristics. The Ni-Al_2O_3 composite coating was prepared on cast iron using plasma electrolytic deposition (PED) and electro-less plating (EP) methods. The Al_2O_3 layer prepared in an aluminate bath by PED was to serve as a base barrier layer. Electroless plated Ni grew from the interface of the alumina layer and cast iron and then seal the micro pores of alumina in a nickel acetate bath, which could protect cast iron substrate from the pitting corrosion. The microstructure and phase composition of this composite coating were investigated with scanning electron microscope (SEM) and X-ray diffraction (XRD). The tribology test data was from pin on disk (POD) tests, and the corrosion resistance was evaluated by potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) test. Comparing with the bare sample, the composite-coated cast iron sample has much lower corrosion current density and coefficient of friction (COF). Comparing with alumina-only coated sample, it has enhanced pitting corrosion resistance and similar COF, but the material transfers and wear track was hardly observed.

8:40am **E3-FrM3 Abrasion Protection by Magnetron Sputtered Coatings of Epoxy Based Composites Exposed to Harsh Environmental Conditions***, **Dorina Mihut (dorinamm@yahoo.com)**, A. Afshar, S. Hill, N. Cordista, G. Baker,* Mercer University, USA

Epoxy and epoxy based composites are important materials for applications requiring high strength and low weight with extensive use in aerospace industry. They are working under harsh environmental conditions such as high temperature, intensive UV radiation and high moisture and therefore are suffering structural degradation processes that are limiting their mechanical performances. The degradation process is mostly affecting the surface materials properties. The current research is investigating the loss of abrasion resistance and accordingly the protection offered by using metallic coatings. Epoxy based composites were coated with metallic thin films by using high vacuum magnetron sputtering deposition and were later exposed to extensive UV radiation, high temperature and high moisture using a standardized environmental chamber. The metallic coatings improved the surface resistance of the substrate materials and enhanced the abrasion behavior of samples exposed to harsh environmental conditions. The surface morphology of all samples tested for abrasion resistance was observed using optical microscopy and the adhesion of metallic layers to the substrates was examined using scanning electron microscopy. The crystalline structure of the metallic coatings was analyzed using X-ray Diffraction technique. The research also investigated the protection of other mechanical properties such as flexural and hardness over the exposure time.

9:00am **E3-FrM4 Effect of HiPIMS Deposition on the High Temperature Tribomechanical Properties of Silicon Containing Diamond-like Carbon Films***, **Bruno Rodriguez (b.rodriguez@warwick.ac.uk)**,* University of Warwick, UK*; J.A. Santiago, I. Fernández-Martínez,* Nano4Energy SL, Spain*; P. Navabpour, H. Sun,* Teer Coatings Ltd, UK*; T. Schiller,* University of Warwick, UK

Diamond-like carbon coatings (DLC) are an amorphous form of carbon used in a wide range of applications due to their impressive properties, among which hardness, low friction coefficient, wear resistance and chemical inertness are worth mentioning[1]. Such properties allow their application in demanding sectors as the automotive or biomedical amongst others. Nonetheless, these films may also present problems as result of adhesion failure, thermal stability, fracture toughness or even the gaseous environment where the sliding contact occurs. Such limitations have been widely researched and different dopants have been suggested to overcome each problem[2]. In the case of silicon, it would increase the thermal stability of these films, while reducing the residual stresses and potentially improving the tribological properties as result of the creation of silicon oxides in the interface between counterpart and film. Silicon-doped films have recently been shown to reduce the oxygen diffusion as result of increasing annealing[3]. The aim of the present work is to prove whether denser films as the deposited by means of high-power impulse magnetron sputtering could not only improve the mechanical and tribological properties, but also such oxygen diffusion.

White light interferometry will be used to estimate the residual stresses of the films as result of the deposition process and the evolution for increasing silicon content. X-Ray photoelectron spectroscopy will be used to characterise the relative sp^3/sp^2 ratio and the chemical content of each specimen. Raman spectroscopy will be employed to probe variations in the carbon sp^2 configuration and cluster size as result of increasing silicon content as well as increasing annealing temperature. The evolution in mechanical properties and tribological properties as result of increasing temperatures will be investigated as well as the specific wear rate. The mass density will be deduced from Rutherford backscattering (RBS) measurements and the creation of oxide layers on the film and oxygen diffusion towards the interlayer will be estimated by the preparation of cross-sectional samples using focused ion beam lift-out method and transmission electron microscopy at different temperatures.

9:20am **E3-FrM5 Self-lubricating Triboactive (Cr,Al)N+Mo:S Coatings for Fluid-free Applications***, **Matthias Thiex (thiex@iot.rwth-aachen.de)**, K. Bobzin, T. Brögelmann, C. Karlscheuer,* Surface Engineering Institute - RWTH Aachen University, Germany

Tailored lubrication of geared transmissions is necessary for high load carrying capacity and efficiency. Nowadays many geared transmissions are conventionally lubricated and cannot be applied under extreme environmental conditions such as vacuum, for extreme weight or thermal requirements, hygienic applications or optical devices. Herein, fluid-free lubrication with solid lubricants is suitable, which however is not available for high mechanical loads to this day and differs significantly from conventional lubrication systems. Fluid-free tribological contacts lead to increased friction resulting in high wear rates due to frictional heat and a poor heat dissipation. Under these tribological conditions typical gear damages such as wear, scuffing and overheating appear more frequently.</p> <p>Within this study, self-lubricating and triboactive (Cr,Al)N+Mo:S coatings are developed and investigated for the deposition on components in a low temperature physical vapor deposition (PVD) hybrid process. Therefore, direct current magnetron sputtering (dcMS) and high power pulse magnetron sputtering (HPPMS) PVD were combined by using the industrial coating machine CemeCon CC800/9 HPPMS. Hereby, it was possible to deposit dense and smooth triboactive self-lubricating nitride coatings with high mechanical properties on AISI 5115 samples. By varying the process parameters coatings with different chemical compositions were deposited. The morphology and coating thickness were analyzed by means of secondary electron spectroscopy (SEM). Furthermore, the chemical composition of the coating as well as of the tribochemically formed layer after tribological testing were evaluated by Raman spectroscopy and elastic recoil detection analysis (ERDA). Tribological analyses of (Cr,Al)N+Mo:S coated and uncoated samples were conducted under fluid-free boundary friction conditions at a temperature T = 25 °C, a velocity v = 0.1 m/s, by varying the Hertzian contact pressure from 400 MPa ≤ p ≤ 1,300 MPa against steel counter parts, AISI 52100, in a pin-on-disc (PoD) tribometer. Hereby, the tribological behavior regarding friction and wear and the effect of solid lubrication by the developed triboactive (Cr,Al)N+Mo:S coatings could be analyzed. Through this, it was possible to gain a deeper understanding of the supply mechanisms of Mo:S in fluid-free tribological contacts under different loads and chemical compositions of (Cr,Al)N+Mo:S coatings

9:40am **E3-FrM6 Coating Properties and Wear Resistance of ta-C Deposited by Arc Ion Plating (AIP) Technique***, **Yoshiyuki Isomura (isomura.yoshiyuki@kobelco.com)**, T. Takahashi, J. Fujita,* Kobe Steel, Ltd., Japan*; S. Kujime,* Kobe Steel Ltd., Japan

Hydrogen free DLC, also referred to as ta-C (tetrahedral amorphous carbon), attracts a large practical interest particularly in the automotive industry because of its unique characteristics of high hardness, low friction, and wear resistance. While ta-C exhibits those excellent properties, further improvement and assurance of adhesion in sliding parts under high contact pressure in severe operating condition is a challenge. Practical requirement and evaluation of adhesion performance is sometimes even beyond the level of basic adhesion investigation such as Rockwell indentation test or scratch test.

In this study, ta-C was deposited using an industrial arc ion plating coating system equipped with a round-bar type arc evaporation source, which is specially designed and optimized for ta-C coating process. ta-C samples with controlled adhesion was intentionally deposited on the sliding test piece with controlled process parameters. Adhesion performance evaluated by the basic test was found to be not always consistent to the results of sliding test. In addition, different frictional wear characteristics were detected among samples with different adhesion performance. In order to understand the relation of sliding properties to adhesion performance more in detail, the intrinsic coating properties were also analyzed more thoroughly in terms of mechanical hardness by nanoindentation, surface roughness/macro-particle density, chemical bonding characteristics of sp2/sp3 fraction and hydrogen concentration. We aim to combine this knowledge of material science with a practical aspect of sliding and adhesion towards improvement of performance in application of ta-C coating.

10:00am **E3-FrM7 Tribological Mechanisms Leading to Moving Cracks and to Co-emission from Hip Implants***, **Michael Herbig (m.herbig@mpie.de)**,* Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany **INVITED**

Intense mechanical and/or chemical contact situations are present in a broad range of crucial technological applications such as bearings, rails or hip implants. The surface and subsurface reactions of materials to these complex conditions involves structural and chemical changes down to the atomic scale. We investigate these phenomena with a combination of scanning / transmission electron microscopy and atom probe tomography. Unlike anything that has been known about the behavior of cracks so far, our observations show, that white-etching-cracks in bearings move normal to their crack plane through the material. This happens due to continuous material transfer between the rubbing fracture surfaces and leaves behind a severely plastically deformed area – the white-etching-area. In the case of Ti/CoCrMo modular hip implants we detected the CoCrMo passive film to be partially incorporated into the Ti-subsurface. This implies that micromotions are responsible for the emission of detrimental Co-ions to the human body.

10:40am **E3-FrM9 Thermal Stability of Hydrogenated DLC Coatings on Tappet Valve Substrate***, **Funsho Kolawole (fkopresido@yahoo.com)**,* University of Sao Paulo, Brazil*; L.B. Varela,* University of São Paulo, Brazil*; S. Kolawole,* National Agency for Science and Engineering Infrastructure, Abuja, Nigeria*; M. Ramirez,* University of Vale do Paraiba, Brazil*; A.P. Tschiptschin,* University of São Paulo, Brazil

DLC-H coatings possess excellent tribological properties, this make them suitable for application in the coating of automobile engine parts, however, due to high temperature during operations (120 to 250 ^{o}C) in the automobile engine they are subjected to thermal instability which affects the structure of the DLC-H. The high temperature causes a transformational change from sp3 (diamond-like) to sp2 (graphite-like) which reduces the wear resistance and increases coefficient of friction of the DLC-H coatings. This present study would investigate the thermal stability of DLC-H deposited on tappet valve using reciprocating Optimol SRV tribometer at 250^{o}C and its wear properties would be examined. DLC-H would be deposited on tappet valve and silicon wafer using PECVD and characterized using XRD, EDS and Raman spectroscopy. SEM would also be used to measure the thickness of the DLC-H coating and study the wear tracks. 3D Profilometry would be used to measure the average surface roughness (R_a) of the tappet valve coated with DLC-H to study the wear tracks. Scratch test would be used to determine the adhesion of the DLC-H coating using CETR UMT-2M-110 tribometer, while Raman spectroscopy would be used to reveal the sp^2/sp^3 fraction in the DLC-H film.

11:00am **E3-FrM10 Duplex TiN and TiAlN Coatings on Ti-6Al-4V Alloy Formed by a Combination of Plasma Nitriding and Cathodic Arc Evaporation***, V Pankov, **Qi Yang (qi.yang@nrc-cnrc.gc.ca)**,* National Research Council of Canada, Canada

A duplex coating concept has been investigated as a mean for protecting Ti-6Al-4V aerospace components against high impacts and high localized loads. The duplex coating consisted of the first layer formed by low-pressure plasma nitriding using a high-density plasma source and the second layer deposited on the nitrided surface by cathodic arc evaporation. Substrate temperature, substrate bias, and process duration were selected as the nitriding process parameters. The substrate temperature during Ti-6Al-4V nitriding was maintained below 800°C to avoid α-to-β phase transformation. TiN and TiAlN coatings were used for the second layer. The microstructure, elemental composition, phase content, and hardness of the nitrided layer were analyzed by scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, and nanoindentation, respectively. Adhesion between the duplex coating layers was measured by scratch adhesion testing. The fabricated duplex coatings were evaluated for their wear and impact resistance using pin-on-disk and drop weight impact testing. The obtained results were used to identify optimum process parameters for producing protective coatings with duplex design characterized by high impact resistance and high load-bearing capacity.

11:20am **E3-FrM11 Effect of Ceramic Hollow Spheres on Corrosion and Tribological Properties of Magnesium Syntactic Foams***, S.S. Kartheek, S.K.R. Narala,* BITS Pilani Hyderabad Campus, India*; **Vincent Kumar (vincent@dubai.bits-pilani.ac.in)**,* BITS Pilani Dubai Campus, United Arab Emirates

The syntactic foam reinforced using hollow spheres has potential applications, including structural, marine and automotive industries. The wide range of utility is due to its lightweight, high damping capacity and mechanical properties. However, in the current scenario, there is a need to evaluate the wear and corrosive resistance characteristics of these foam materials to highlight its practical applications. Therefore, the present research was carried out to analyze tribological and corrosive properties of magnesium alloy (AZ series) based syntactic foams (MSF) with varying sizes of micro ceramic hollow spheres (MCHS) (grid size ~100mm, 150mm and 500mm) as reinforcement which affects the density of the material. These materials were produced through pressure infiltration technique under vacuum condition. The corrosion behavior of MSF is determined using the electrochemical polarization technique in a 3.5% NaCl solution. The dry sliding wear behavior of MSF samples of different volume fractions was carried out under various loading conditions at ambient temperature using Pin on Disc tribometer for the different volume fraction of hollow spheres. Scanning Electron Microscopy (SEM) examinations were carried out to explore surface morphology of samples subjected to wear and corrosion tests. An overall improvement in corrosion resistance and galvanic interaction at the matrix-sphere interface were reported and results are expected to cater to the needs of practicing engineering and current-day industrial requirements.

11:40am **E3-FrM12 Insights into Interfacial Phenomena of Nickel- and Cobalt- Based Systems in Extreme Conditions***, **Pantcho Stoyanov (pantcho.stoyanov@pw.utc.com)**, K. Harrington, E.C. Miller, A. Ignatov,* Pratt & Whitney, USA

Advancement of durable gas turbine engine components depends heavily on the development of high-performance materials that can withstand extreme environmental and contact conditions. In particular, due to the large number of complex contacting and moving mechanical assemblies in the engine, the lifetime of certain structures is limited by the tribological performance of the employed materials and coatings. This talk will provide an overview of tribological solutions and lubrication strategies employed in several sections of gas turbine engines. After a general review of aircraft engine tribology, the talk will focus on tribological behavior of nickel- and cobalt-based materials used to minimize fretting type of wear in the compressor section. Emphasis will be placed on the correlation between the third body formation process (e.g. characterized using XPS, SEM and XRD) and the tribological behavior of these superalloys.

Surface Engineering - Applied Research and Industrial Applications

Room Pacific Salon 2 - Session G1-FrM

Advances in Industrial PVD, CVD and PCVD Processes and Equipment

Moderators: Ladislav Bárdos, Uppsala University, Sweden, Vikram Bedekar, The Timken Company, USA

8:00am **G1-FrM1 New Developments in Magnetron Sputtering Devices***, D. Monaghan, **Victor Bellido-Gonzalez (victor@gencoa.com)**, T. Sgrilli, R. Brown, J. Brindley, B. Daniel,* Gencoa Ltd, UK **INVITED**

Magnetron sputtering is a mature and well establish PVD deposition technique. Since the introduction of commercial planar magnetrons in the 1970s there are few vacuum coating sectors that haven't been touched by successful implementations of this deposition technique. In the 1970s the semiconductor industry was revolutinonized by the introduction of planar magnetron sputtering as an alternative to evaporation and diode sputtering. Nearly forty years later, still magnetron sputtering is at the heart of many of the manufacturing processes from small to large area, with different degrees of functionality, from decorative, to energy, transport, architectural, automotive, aerospace, display, photovoltaic, thermal solar, electronics, etc.

Different sectors have typically required adaptation of the basic concepts of magnetron sputtering for the specific functionality and purpose. There has been a need for a continuous development of sources and process solutions. Among those, the need for better controls, and better monitoring. This presentation will give an overview of magnetron sputtering with its main breakthroughs, the current status of the technology in important for some relevant PVD coating sectors and will look at the current and future challenges ahead.

8:40am **G1-FrM3 HIPIMS –Ready on Industrial Scale for Modern Production***, **Philipp Immich (pimmich@hauzer.nl)**, G. Negrea, D. Doerwald, R. Jacobs, M. Eerden, R. Ganesan, L. Tegelaers,* IHI Hauzer Techno Coating B.V., Netherlands

Since HIPIMS enter the coating scene a lot of investigations on this topic had been carried out. Discovering new properties, different material behavior compared to convention sputtered coatings and better performance in cutting, forming and tribology applications. Most of the investigations were done on small scale deposition units. But bringing this technology to industry, larger units are needed and also process upscaling is needed.

Today real production of coated parts require not only good coating properties also production related topics like reliability, easy maintenance, cost per part and flexibility of the coating unit itself plays an important role.

In this regard different HIPIMS coatings from AlCrN-based, AlTiN-based and hydrogen free DLC such as ta-C systems were deposited on industrial scale units for tribology and tool applications. The applied coatings were investigated concerning mechanical film properties like hardness, Young´s Modulus, chemical properties like composition and phase formation. To verify the performance of the coating machine and the deposited coatings, industrial tests in automotive and tool applications are carried out. The obtained results shown, that the HIPIMS technology is ready for serial production in a modern production environment.

9:20am **G1-FrM5 DLC Coatings for the Automotive Industry***, **Rajiv Ahuja (rahuja@hefusa.net)**,* HEF US, USA **INVITED**

Challenging performance standards – in terms of, fuel consumption, carbon emissions and component durability – are the primary drivers of innovation within the automotive industry. Advancements in powertrain design aimed at achieving these stringent standards have resulted in increasing mechanical complexity and stresses on components and their contacting interfaces. To counter these stresses and improve endurance, it is imperative to reduce friction between the contacting surfaces of components and improve their tribological properties. Over the past few years, a diverse range of diamond-like carbon (DLC) coatings and technologies have emerged, which can significantly improve durability and reduce friction. These coatings, customized to specific wear and contact modes and capable of withstanding heavy loads, modify the tribological characteristics of the contact interface and resist tribofilm formation - resulting in significant friction reduction. On overview will be provided of the various DLC coating features and technologies that contribute to the superior performance of automotive components.

10:00am **G1-FrM7 Deposition of Functional Nano-Coatings Using Atmospheric Pressure Plasmas***, **Daphne Pappas (daphne.pappas@plasmatreat.com)**,* Plasmatreat USA, USA*; N. Eternal, R. Gonzalesz,* Plasmatreat USA **INVITED**

Plasma surface engineering has been employed for decades for the development of advanced materials and has offered a plethora of technological solutions. As an example, any microchip used in a computer, tablet or cell phone device, at some point during its production was subjected to a plasma etch or deposition process that took place in a vacuum environment. Over the last decade, plasma processing of materials has expanded, including the development of functional nanocoatings under atmospheric pressure and room temperature conditions. The motivation for this was the need for equipment and processes that could be incorporated in industrial production lines capable of producing large area inline coatings in a cost efficient way, negating the need for vacuum systems. In this talk, an overview of atmospheric pressure plasma jet processes for: i) the activation and cleaning of surfaces and ii) the deposition of polymer functional coatings will be presented. The surface cleaning step is important for surfaces that have residual contaminants or for materials that have low surface energy. This pre-treatment can be instrumental in improving the bonding to adhesives or coatings that are applied on the activated surfaces. Also, results from the deposition of polymer coatings with unique functionality will be presented. The coatings that were developed had a thickness that ranged from 50nm to 690 nm and can serve as anti-corrosion, water repellent, adhesion promoting or biocompatible surfaces. Due to these properties, they are applicable in several industries, including aerospace, automotive, biomedical and microelectronics.

10:40am **G1-FrM9 Hysteresis Effect in the Magnetron with Magnetized Hollow Cathode Enhanced Target***, **Hana Barankova (hana.barankova@angstrom.uu.se)**, L. Bardos,* Uppsala University, Angstrom Laboratory, Sweden

The paper shows and explains the differences in the reactive processes, and especially in the hysteresis curves, between a new sputtering device, magnetized hollow cathode enhanced target magnetron, and a classical magnetron. The magnetron with magnetized hollow cathode enhanced target, combining the magnetron and hollow cathode plasmas, exhibits higher deposition rates than conventional magnetron, moreover, the deposition rate of the compound is higher than that of metal. It is concluded that a more efficient utilization of the reactive gas takes place in this device.

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