Live Session
Room Live - Session LI-MoM1

Coatings for Flexible Electronics and Bio Applications Live Session

Moderators: Dr. Jean Geringer, Ecole Nationale Superieure des Mines, France, Dr. Grzegorz (Greg) Greczynski, Linköping University, Sweden, Dr. Christopher Muratore, University of Dayton, USA, Dr. Barbara Putz, Empa, Switzerland

10:00am **LI-MoM1-1 ICMCTF Chairs' Welcome Address**, ***Gregorz (Greg) Greczynski (grzegorz.greczynski@liu.se)***, Linköping University, Sweden; *C. Muratore,* University of Dayton, USA

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10:15am **LI-MoM1-2 Plenary Lecture: 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.

11:15am **LI-MoM1-6 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.

11:45am **LI-MoM1-8 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.

[1] M. G. Lagally, MRS Bull. 32, 57 (2007).

[2] J. A. Rogers et al., Nature 477, 45 (2011).

[3] D. Makarov et al., Appl. Phys. Rev. 3, 011101 (2016).

[4] M. Melzer et al., Adv. Mater. 27, 1274 (2015).

[5] N. Münzenrieder et al., Adv. Electron. Mater. 2, 1600188 (2016).

[6] D. Karnaushenko et al., Adv. Mater. 27, 880 (2015).

[7] M. Melzer et al., Adv. Mater. 27, 1333 (2015).

[8] M. Melzer et al., Nat. Commun. 6, 6080 (2015).

[9] G. S. Canon Bermudez et al., Science Advances 4, eaao2623 (2018).

[10] G. S. Canon Bermudez et al., Nature Electronics 1, 589 (2018).

[11] P. N. Granell et al., npj Flexible Electronics 3, 3 (2019).

[12] J. Ge et al., Nature Commun. (2019). doi:10.1038/s41467-019-12303-5

12:15pm **LI-MoM1-10 Biomimetic Extracellular Matrix Coating for Titanium Implant Surfaces to Improve Osteointegration**, ***Sriram Ravindran (sravin1@uic.edu)***, *P. Gajendrareddy, J. Hassan, 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.

12:45pm **LI-MoM1-12 Closing Remarks & Thank You!**, ***Chris Muratore (cmuratore1@udayton.edu)***, University of Dayton, USA; *G. Greczynski,* Linköping University, Sweden, USA

Thank you for Attending the ICMCTF Monday Live Session #1! Now Enjoy our On Demand sessions!

Monday Morning, April 26, 2021

Live Session
Room Live - Session LI-MoM2

New Horizons in Boron-Containing Coatings Live Session

Moderators: Mr. Marcus Hans, RWTH Aachen University, Germany, Dr. Helmut Riedl, TU Wien, Institute of Materials Science and Technology, Austria

11:00am **LI-MoM2-1 Welcome & Thank You to Sponsors***, **Marcus Hans (hans@mch.rwth-aachen.de)**,* RWTH Aachen University, Germany*; H. Riedl,* TU Wien, Institute of Materials Science and Technology, Austria

Welcome to the ICMCTF 2021 Virtual Conference! We hope you will enjoy our Live and On Demand Sessions!

11:15am **LI-MoM2-2 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. Achenbach, J. 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].

[1] Gleich, S.; Soler, R.; Fager, H.; Bolvardi, H.; Achenbach, J.-O.; Hans, M.; Primetzhofer, D.; Schneider, J. M.; Dehm, G.; Scheu, C.: Materials and Design 142, 203 - 211 (2018).

[2] Gleich, S.; Breitbach, B.; Peter, N. J.; Soler, R.; Fager, H.; Bolvardi, H.; Schneider, J. M.; Dehm, G.; Scheu, C.: Surface and Coatings Technology 349, 378-383 (2018).

11:45am **LI-MoM2-4 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.

References:

1. Yang, Y., Chemistry of Materials 18, 5088 (2006)

2. Yanguas-Gil, A. JVST A 27, 1235 (2009)

3. Kumar, N., JACS 130, 17660 (2008)

4. Babar, S. JVST A 32, 060601(2014)

5. Mohimi, E., TSF 592, 182 (2015)

12:15pm **LI-MoM2-6 A Progress Report on Bulk MAB Phases***, **Michel Barsoum (barsoumw@drexel.edu)**,* Drexel University, USA*; S. Kota,* Drexel University, USA **INVITED**

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

(TMBs), with the general formula $(MB)_{2z}A_x(MB_2)_y$($\mathbf{z}$ = 1–2; $\mathbf{x}$ = 1–2; $\mathbf{y}$ = 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.

12:45pm **LI-MoM2-8 Closing Remarks and Sponsor Thank You!***, **Helmut Riedl (helmut.riedl@tuwien.ac.at)**,* TU Wien, Institute of Materials Science and Technology, Austria*; M. Hans ,* RWTH Aachen University, Germany

We hope you enjoyed the Live Session and will now enjoy our On Demand Sessions! We will see you tomorrow!

Live Session

Room Live - Session LI-TuM1

Surface Engineering - Applied Research and Industrial Applications Live Session

Moderators: Dr. Satish Dixit, Plasma Technology Inc., USA, Dr. Christoph Schiffers, CemeCon AG, Germany

10:00am **LI-TuM1-1 Award Chair's Welcome Address, Introductions, & Thank You to Sponsors***, **Ivan G. Petrov (petrov@illinois.edu)**,* University of Illinois at Urbana-Champaign, USA

We hope you will enjoy the presentations from our three student award finalists and our invited speakers!

10:15am **LI-TuM1-2 Student Award Finalist Talk: Enhanced High-temperature Oxidation Resistance of Hard TiB_2-rich $Ti_{1-x}Al_xB_y$ Thin Films***, **Babak Bakhit (babak.bakhit@liu.se)**[1],* Linköping University, Sweden*; I. Petrov, J. 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 exhibit insufficient 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 air-annealing at 800 °C for 0.5 h results in the formation of an ~1900-nm oxide scale on $TiB_{2.4}$, the thickness of the scale formed on the $Ti_{0.68}Al_{0.32}B_{1.35}$ alloys is ~470 nm. The enhanced oxidation resistance is attributed to the formation of a dense, protective Al-containing oxide scale which considerably decreases the oxygen diffusion rate by suppressing the oxide-crystallites coarsening.

10:30am **LI-TuM1-3 Student Award Finalist Talk: The Magneto-Plasmonic Properties of Ag-Co Composite Nanostructures***, **Hoang Luong (hoanglm@uga.edu)**[2], T. Nguyen, Y. Zhao,* University of Georgia, USA

Multifunctional materials and structures with both plasmonic and magnetic properties have been receiving substantial attentions. In this work, we investigated magneto-plasmonic properties of well-identified plasmonic nano-lattices based on Ag-Co composite materials. By combining shadowing nanosphere lithography and electron beam co-deposition, composite nanotriangle and nanohole arrays with different composition ratio of Ag and Co were fabricated. The composition-dependent optical transmission, polar magneto-optics Kerr effect, Faraday rotation (FR), and Faraday ellipticity of these structures in the visible to near infrared wavelength region were studied. Finite-difference time domain calculations were performed to confirm the experimental results and to give an insight on the relationship between magneto-plasmonic properties of nanostructures and their compositions. In particular, the Ag-Co composite nanohole array showed several FR peaks at the plasmonic-related wavelength positions, *i.e.*, where the Bloch wave condition and Wood – Rayleigh anomaly condition are satisfied. With the Co content of 30%, the composite nanohole array exhibited a significant enhancement of plasmonic - magneto-optics behavior compared to that of Ti-Co composite nanohole array. On the other hand, the enhanced magneto-optic effect of the Ag-Co composite nanotriangle array was observed to be coincident with the localized surface plasmon resonance (LSPR), *i.e.*, the maximum FR effect occurred at the LSPR wavelength, which is due to high local E-field. Thus, the magneto-optics response of these magneto-plasmonic systems behave differently, depending on the nature of the plasmon resonance that the system supports (*i.e.* propagating surface plasmon wave in the nanohole array or localized surface plasmon wave in the nanotriangle array), and by adjusting the Co content, their magneto-plasmonic performances can be maximized. Such a magneto-plasmonic composite provides a new way on the design and application of magneto-plasmonic materials and devices.

10:45am **LI-TuM1-4 Student Award Finalist Talk: 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@oeaw.ac.at)**[3],* Montanuniversität Leoben, Austria*; J. Todt, J. Zalesak,* Austrian Academy of Sciences, Austria*; M. Rosenthal,* ESRF, Grenoble, France*; H. Hruby,* eifeler-Vacotec GmbH, Germany*; C. Mitterer, R. Daniel, 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.

11:15am **LI-TuM1-6 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

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[1] **Student Award Nominee**

[2] **Student Award Nominee**

[3] **Student Award Nominee**

11:45am **LI-TuM1-8 Stabilization of FCVAS Based Hybrid System for Deposition of Thick Tetrahedral Amorphous Carbon Films and its Applications***, **Jongkuk Kim (kjongk@kims.re.kr)**, Y. Jang,* Korea Institute of Materials Science (KIMS), Korea, Republic of Korea*; D. 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).

12:15pm **LI-TuM1-10 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.

12:45pm **LI-TuM1-12 Closing Remarks & Sponsor Thank You's!***, **Satish Dixit (dixsat@gmail.com)**,* Plasma Technology, Inc., USA*; C. Schiffers,* CemeCon AG, Germany

Thank you for attending the session. Join us for the Post-Session Discussion from 1:00 - 2:30 pm EDT and be sure to return for tomorrow's Live Sessions at 10:00 am EDT.

Live Session
Room Live - Session LI-TuM2

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces Live Session

Moderators: Dr. Michael Chandross, Sandia National Laboratories, USA, Dr. Giovanni Ramirez, Oxford Instruments , USA

11:00am **LI-TuM2-1 Welcome, Announcements, & Thank You to Sponsors***, **Giovanni Ramirez (Giovanni.Ramirez@outlook.com)**,* Oxford Instruments , USA

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11:15am **LI-TuM2-2 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.

11:45am **LI-TuM2-4 Insights into Indentation-Induced Cracking via 3D-FIB Tomography and HR-EBSD***, **Bo-Shiuan Li (spring46515@gmail.com)**,* 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.

12:15pm **LI-TuM2-6 Photon Beam and Plasma Cloud – Programmable Surfaces***, **Anna Buling (buling@ceranod.de)**, J. Zerrer,* ELB Eloxalwerk Ludwigsburg GmbH, Germany **INVITED**

How to face the incessantly growing demands on sustainability, efficiently and endurance, which are made on components in automotive, aerospace and machinery applications? We are sure that intelligent lightweight, which enables the multi-material mix, accompanied by the right solutions for the surfaces is the answer.

Since the application of lightweight metals leads to a fuel consumption reduction and, thus, an environmental shielding, it is necessary to unveil the whole potential of e.g. Al and Mg alloys in high-loaded applications. In this talk we will focus on innovative surface technologies, which can be adopted to different application cases to fulfill ambitious demands. With adaptable process parameters the plasma electrolytical oxidation (PEO), which is known to give hard and dense coatings on lightweight metals, could be optimized to form homogeneous nanocrystalline surfaces on Al casting alloys with high Si content. This Ultraceramic® process results in a very wear-resistant protection, unfolding the whole potential of the casting component in action with novel low-viscosity oil, which is developed for innovative engine applications, leading to low friction and also low wear. Special improvement was achieved by structuring the PEO surfaces using the direct laser interference patterning (DLIP) method. Here, the advanced micro structuring technique leads to a further reduction of friction and wear, especially on the counter body side.

A further approach to meet increasing requirements is function integration, which enablesthe application of different functions on one component. Here, a data mining process was utilized to develop an additive laser-based coating process, whereas poly-ether-ether-ketone (PEEK) can be selectively applied on lightweight metals. The employment of different nano and microscale dopants in the PEEK dispersion, their interaction within the laser process and the resulting tribological and anticorrosion performance were studied. Based on tribological findings of the single-layer coatings – collected and evaluated by data mining - a multi-layer system was preprogrammed, which provided 3 orders of magnitude increased life-time, 10 times lower wear of the coating and the counter body part and a stable and reduced friction by solid lubrication.

Special knowledge of the nanoscale phenomena of plasma, dopants and laser processes in combination with extensive analysis of the resulting surface properties utilizing tribological measurements, nanoindentation and SEM characterization give us the possibility to find right position of the “screws” to tune the surface properties in such a way to improve their macroscopic sliding and wear behavior in orders of magnitude.

12:45pm **LI-TuM2-8 Closing Remarks & Thank You's***, **Michael Chandross (mechand@sandia.gov)**,* Sandia National Laboratories, USA

Thank you for attending the Session. Please join us for our Post-Session discussion and Q & A opportunities with our invited speakers.

Live Session
Room Live - Session LI-WeM1

In-Silico Design of Novel Materials by Quantum Mechanics and Classical Methods Live Session

Moderators: Dr. David Holec, Montanuniversität Leoben, Austria, Dr. Davide G. Sangiovanni, Linköping University, Sweden

10:00am **LI-WeM1-1 Program Chair's Welcome and Introduction of our Special Interest Talk*, Gregorz (Greg) Greczynski (grzegorz.greczynski@liu.se),*** Linköping University, Sweden

Welcome to the ICMCTF 2021 Virtual Conference. We hope you will enjoy our Live Session and join us for the post-session discussion and additional Q&A opportunities following the Live Session.

10:15am **LI-WeM1-2 Special Interest Talk: 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.

[1] J. W. Gibbs, *On the equilibrium of heterogeneous substances*, Am. J. Sci. **96**, 441 (1878).

[2] E. Bykova, *et al.,* Nature Commun. **9**, 4789 (2018).

[3] M. Bykov, *et al.,* Angew. Chem. Int. Ed. 57, 1 (2018); M. Bykov, *et al.,* Nature Commun. 9, 2756 (2018).

[4] M. Bykov, *et al.,* Nature Commun. **10**, 2994 (2019).

11:15am **LI-WeM1-6 Are Protective Coatings Predictable?*, 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.

11:45am **LI-WeM1-8 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.

references

[1] G. Beensh-Marchwicka, L. Kròl-Stępniewska, W. Posadowski, Thin Solid Films, 82(1981)313

[2] O. Knotek, W. Bosch, T. Leyendecker, Proceedings of 8th international conference on Vacuum Metallurgy, Linz Austria (1985)

[3] W. D. Münz, J. Vac. Sci. Technol. A 4 (1986) 2717

[4] S. Hofmann, H.A. Jehn, M.Atzor, O. Knotek, International conference on metallurgical coating and thin films, (1989)

[5] O. Knotek, F. Löffler, H. J-. Scholl, Surf. Coat. Technol. 45(1991) 53

[6] A. E. Reiter. V. H. Derflinger, B. Hanselmann, T. Bachmann, B. Sartory, Surf. Coat. Technol. 200 (2005) 2114

[7] K. Yamamoto, T. Sato, K. Takahara, K. Hanaguri, Surf. Coat. Technol., 174–175 (2003) 620.

[8] T. Ikeda, H. Sato, The 5th international symposium on the Japan Welding Society, (1990) 363

[9] A. Sugishima. H. Kajioka, Y. Makino, Surf. Coat. Technol., 97 (1997) 590.

[10] Y. Makino, Y. Setsuhara, 9th international conference on ion beam modification of materials (1995) 736

12:15pm **LI-WeM1-10 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]

[1] P. Eklund, S. Kerdsongpanya, and B. Alling, J. Mater. Chem. C, **4**, 3905 (2016)

[2] I. Stockem et al. Phys. Rev. Lett. **121**, 125902 (2018)

[3] M. A. Gharavi, et al. J Mater Sci **53**, 4294 (2018)

[4] C. Tholander et al. J. Appl. Phys., **120**, 225102 (2016)

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[1] **2020 Bill Sproul Awardee**

12:45pm **LI-WeM1-12 Closing Remarks & Thank You's**, ***Davide Sangiovanni (davide.sangiovanni@liu.se)***, Ruhr University Bochum, Germany

We hope you enjoy the Live Session. Please join us for the post-session discussion and enjoy our On Demand Sessions. We hope to see you tomorrow!

Live Session
Room Live - Session LI-WeM2
Advanced Characterization Techniques Live Session

Moderators: Prof. Dr. Diederik Depla, Ghent University, Belgium, Dr. Prabhakar Mohan, Solar Turbines, USA

11:00am **LI-WeM2-1 Welcome, Announcements & Sponsor Thank You's***, Prabhakar Mohan (Mohan_Prabhakar@solarturbines.com),* Solar Turbines, Inc. , USA

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11:15am **LI-WeM2-2 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

1. D.R. Clarke, M. Oechsner, N.P. Padture, MRS Bull. 37, 2012, pp. 891-898.

2. C.G. Levi, J.W. Hutchinson, M.-H. Vidal Sétif, C.A. Johnson, MRS Bull. 37, 2012, pp. 932-940.

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.

11:45am **LI-WeM2-4 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.

12:15pm **LI-WeM2-6 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.

12:45pm **LI-WeM2-8 Closing Remarks and Thank You's***, Diederik Depla (Diederik.Depla@ugent.be),* Ghent University, USA

We hope you enjoyed the Live Session. Please join us for our Post-Session discussion and additional Q&A opportunities. We hope to see you tomorrow!

Live Session
Room Live - Session LI-ThM1
Hard Coatings and Vapor Deposition Technologies Live Session

Moderators: Dr. Tiberiu Minea, Université Paris-Sud, France, Dr. Farwah Nahif, eifeler-Vacotec GmbH, Germany

10:00am **LI-ThM1-1 General Chair's Welcome***, Chris Muratore (cmuratore1@udayton.edu),* University of Dayton, USA*; F. Nahif,* voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany

Welcome to the ICMCTF 2021 Virtual Conference! We hope you will enjoy the Exhibition Keynote Lecture and our invited talks!

10:15am **LI-ThM1-2 Exhibition Keynote Lecture: 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.

11:15am **LI-ThM1-6 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 $(Ti_{1-x}Al_x)N_y$ ($0.58 \geq y \geq 0.40$) 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].

[1] B. Alling et al., *Phys. Rev. B***75** (2007) 45123.

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

[3] I. C. Schramm et al., *Surf. Coatings Technol.***330** (2017) 77.

[4] I. C. Schramm et al., *Acta Mater.***129** (2017) 268.

11:45am **LI-ThM1-8 Air-based Sputtering Deposition of Gradient Oxynitride Coatings***, Fu-Hsing Lu (fhlu@nchu.edu.tw),* National Chung Hsing University, Taiwan*; Y. Liou, Y. Lee, M. 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.

12:15pm **LI-ThM1-10 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%).

12:45pm **LI-ThM1-12 Closing Remarks & Thank You's***, Tiberiu Minea (tiberiu.minea@u-psud.fr),* Université Paris-Saclay, France

Thank you for attending today's session! Please just us for the Post-Session Discussion and additional Q&A opportunities! We will see you tomorrow!

Live Session
Room Live - Session LI-ThM2

Thin Films for Energy Applications Live Session

Moderators: Dr. Peter Kelly, Manchester Metropolitan University, UK, Dr. Glen West, Manchester Metropolitan University, UK

11:00am **LI-ThM2-1 Welcome and Thank You to our Sponsors!**, ***Peter Kelly (peter.kelly@mmu.ac.uk)***, Manchester Metropolitan University, UK

Welcome to the ICMCTF 2021 Virtual Conference! We hope you will enjoy the invited talks!

11:15am **LI-ThM2-2 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.

11:45am **LI-ThM2-4 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. Amorim,* Universidade Federal de Minas Gerais, Brazil; *P. 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.

12:15pm **LI-ThM2-6 High Entropy Materials 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.

12:45pm **LI-ThM2-8 Closing Remarks & Thank You's!**, ***Glen West (g.west@mmu.ac.uk)***, Manchester Metropolitan University, UK

We hope you enjoyed the Session and will join us for the Post-Live Session for additional Q&A opportunities! We will see you tomorrow!

Friday Morning, April 30, 2021

Live Session
Room Live - Session LI-FrM

Awards Session Live

Moderators: Dr. Ivan G. Petrov, University of Illinois at Urbana-Champaign, USA, Dr. Andrey Voevodin, University of North Texas, USA

10:15am **LI-FrM-2 Special Interest Talk: 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.

11:15am **LI-FrM-6 Bill Sproul Award and Honorary ICMCTF Lecture: Transition Metal Nitride Layers: New Phases and New Properties***, Daniel Gall (galld@rpi.edu)*[1]*,* Rensselaer Polytechnic Institute, USA **INVITED**

We explore new transition metal nitride compounds using a combination of epitaxial layer growth, first-principles calculations, and measurements of electronic, optical, and mechanical properties as a function of composition and structure. Rock-salt structure nitrides are both mechanically and thermodynamically stable for group 3 transition metals. However, increasing the valence electron concentration by moving towards the right in the periodic table increases the strength of metal-metal bonds leading to a brittle-to-ductile transition and enhanced toughness, but also decreases the vacancy formation energy on both cation and anion sublattices, resulting in vacancy-stabilized compounds like cubic WN with a dramatically reduced elastic modulus, and new thermodynamically stable phases like a 5-fold coordinated base-centered monoclinic stoichiometric MoN. Conversely, reducing the valence electron concentration to reach a vanishing density of states at the Fermi level results in transition metal nitride semiconductors with promising properties for high-temperature electronic, thermoelectric, opto-electric, piezo-electric, plasmonic and magnetoresistive devices. Examples include ScN, $Ti_{0.5}Mg_{0.5}N$ and CrN with 0.92, 0.7-1.7 and 0.2+/-0.4 eV bandgaps, respectively. The carrier concentrations are controlled by F and O doping, the bandgap is engineered by alloying with Al to form $Cr_{1-x}Al_xN$, $(Ti_{0.5}Mg_{0.5})_{1-x}Al_xN$, and $Sc_{1-x}Al_xN$, the piezoelectric response is enhanced by the intentional introduction of local bonding instabilities in the wurtzite phase, and a two-dimensional electron gas is formed at the oxygen-exposed CrN(001) surface.

12:00pm **LI-FrM-9 R.F. Bunshah Award and ICMCTF Honorary Lecture: From a Sparkling Brass Chain and Twitching Frog Legs: The Astonishing Path to Plasma-Based Advanced Coatings***, André Anders (andre.anders@iom-leipzig.de)*[2]*,* Leibniz Institute of Surface Engineering (IOM), Felix Bloch Institute, Leipzig University, Germany **INVITED**

As many accomplishments of modern life, plasma-based advanced coatings are ubiquitous today.It is educational to see how observation of strange effects and careful experimentation lead to discoveries that effectually enabled what we take for granted today. When taking the time for dwelling a bit deeper we find that assuming broad priority claims (like “for the first time” and “novel approach”) should be replaced by more humble statements.Among the truly astonishing early milestones is, for example, an 18th century report on pulsed atmospheric pressure plasmas, well-adherent metal and transparent coatings and nanoparticle generation from a time well before Volta and Faraday (I admit: the terminology was different).In this lecture, I will highlight a few of such milestones to advanced, plasma-based coatings showing that each accomplishment is built on observation and experimentation, and more recently on modeling, but enabled by discoveries made before.As a community of surface engineers, we can be proud having made the steps from observation to deeper understanding, knowledge-based discovery, optimization towards desirable properties, upscaling considering the economics of processes, and broad-scale applications now penetrating all aspects of society.

12:45pm **LI-FrM-12 Closing Remarks and Thank You's***, Andrey Voevodin (Andrey.Voevodin@unt.edu),* University of North Texas, USA

Thank you for attending the ICMCTF 2021 Virtual Conference! We hope you enjoyed the event! We hope you will join us for the Post-session Discussion and some additional Q&A opportunities! Mark your calendars for ICMCTF 2022, May 22-27, 2022, in San Diego, CA!

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[1] **2021 Bill Sproul Awardee**

[2] **R.F. Bunshah Awardee**

Coatings for Use at High Temperatures
Room On Demand - Session A1

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

A1-1 PVD Cr Coatings to Mitigate Corrosion of SiC-SiC$_f$ Composite for LWR Applications*, Kyle Quillin (quillin@wisc.edu)*, *H. Yeom, T. Dabney, J. Lacy, T. Kim,* University of Wisconsin - Madison, USA*; S. Chemerisov,* Argonne National Laboratory, USA*; A. Couet, K. Sridharan,* University of Wisconsin - Madison, USA

SiC-SiC$_f$ composite is being investigated as the fuel cladding material in the next generation of light water reactors (LWRs) based on its high-temperature stability and resistance to irradiation damage. In particular, this composite offers greatly improved safety margins in the event of a loss-of-coolant accident. One challenge in the implementation of this material for cladding applications is the corrosion of SiC under normal LWR operating conditions, where the aqueous environment promotes the conversion of a protective surface silica layer to the water-soluble silicon hydroxide. To mitigate this hydrothermal corrosion of SiC, we are investigating a variety of physical vapor deposition (PVD) processes to deposit Cr coatings 5-7 microns in thickness, including conventional direct current magnetron sputtering (DMCS) and high-power impulse magnetron sputtering (HiPIMS). Coated and uncoated SiC were tested in a pressurized water autoclave at 360 °C and 18.6 MPa for a period of 720 hours. The coatings' microstructure before and after corrosion tests was characterized using scanning and transmission electron microscopy (SEM and TEM). X-ray diffraction (XRD) was used to identify phases and measure stresses in the coatings. Scratch testing using a spheroconical diamond stylus was used to achieve a qualitative assessment of the mechanical performance of the coating-substrate system. The results showed that both DCMS and HiPIMS Cr coatings provided good corrosion resistance and acted as effective barriers for water transport to the underlying SiC composite substrate. The columnar-grained microstructure of the DCMS coating showed some ingress of water along the inter-columnar boundaries as manifested by oxidation in these regions, an effect that was not observed in the more equiaxed and dense HiPIMS coatings. The results of this study and irradiation effects in the coating will be discussed, with the goal of enhancing the viability of coated SiC-SiC$_f$ composites as cladding material for LWR applications.

A1-2 High Temperature Molten Salt Corrosion Behavior of Nickel and Nickel-Molybdenum Coatings for Molten Salt Reactor (MSR)*, Ketan Kumar Sandhi (ketan.sandhi@usask.ca)*, *J. Szpunar,* University of Saskatchewan, Canada

Ni and Ni-Mo coatings were deposited on AISI 304 stainless steel samples using electrochemical deposition technique. Corrosion tests were run in molten FLiNaK (46.5 mol% LiF-11.5 mol% NaF-42 mol% KF) salt environment at 700° C for 100 h under Ar cover gas for coated and uncoated samples. Corrosion was seen to be occurring by Cr depletion from base alloy in uncoated and Ni-Mo coated specimens. Uncoated specimen showed corrosion depth up to 48 µm from the surface of specimen, however Ni-Mo coated specimen had corrosion depth of 100 µm. No significant depletion of Cr was observed from the surface of Ni coated specimen. High resolution Xray photoelectron spectroscopy (XPS) showed the increase in carbide phase at the surface of the corroded samples. Ni-Mo coated specimen showed complete depletion of Mo from the Ni-Mo coating. Results indicated Ni-Mo coated specimen performed worst and Ni coated specimen performed best for corrosion resistance in FLiNaK environment.

A1-3 Laser Cladding NiTi on the Magnesium Alloy Substrate With the Intermediated Aluminum Layer, *C. Zhang,* ***Yuyun Yang (yangyuyun@hotmail.com)****, X. Cui, G. Jin, W. Zheng,* Harbin Engineering University , China

Magnesium and its alloys are the most promising green engineering structural materials in the 21st century, has the advantage of low density, high damping intensity, etc. While the major obstacle of the magnesium alloy in widespread applications is to overcome the poor corrosion resistance. 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 favourable coating system of magnesium alloy surface strengthening. The introduction of the intermediated aluminium layer makes it feasible to cladding the NiTi alloy coating on magnesium alloy.

An aluminium intermediated layer was developed on the surface of AZ91D substrate by using laser cladding the pre-set pure aluminium powder on the surface of substrates. Laser power is set as 1,000W at 30mm/s of scanning speed. Then a top layer of NiTi alloy on the intermediated layer is obtained with the laser power of 1300Wat 30mm/s. The 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 Ti2Ni, NiTi, Ni3Ti, Ni2TiAl and the distribution of the elements. The hardness-depth profile of the layer was measured by a 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 the NiTi alloy layer presents superior wear resistance properties compared with that of magnesium alloys. Corrosion resistance in a 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 the worse working environment and higher performance requirements applications, such as aerospace, military aircraft, and car industry, etc.

A1-4 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).

[1] R. Gilblas, T. Sentenac, D. Hernandez, and Y. Le Maoult, "Quantitative temperature field measurements on a non-gray multi-materials scene by thermoreflectometry," *Infrared Phys. Technol.*, 2014.

[2] W. Brandl, D. Toma, J. Krüger, H. J. Grabke, and G. Matthäus, "The oxidation behaviour of HVOF thermal-sprayed MCrAlY coatings," *Surf. Coatings Technol.*, 1997.

A1-5 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.

[1] D. Texier, C. Cadet, et. al, Metall. Tensile behavior of Air Plasma Spray MCrAlY coatings : role of high temperature agings and process defects, *Mater. Trans. A* (2019) submitted.

[2] D. Texier, D. Monceau, et al., Micromechanical testing of ultrathin layered material specimens at elevated temperature, *Mater. High Temp.* 33 (2016) 325–337. doi:10.1080/09603409.2016.1182250

A1-6 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

, A. Agüero, ***Marcos Gutiérrez (gutierrezdom@inta.es)***, 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.

A1-7 INVITED TALK: PGM based Diffusion Coatings for Ni-based Superalloys by a Paste Method

*, **Hideyuki Murakami (MURAKAMI.Hideyuki@nims.go.jp)**,* National Institute for Materials Science (NIMS), Japan*; D. Tue, A. Ishira, L. 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.

A1-9 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. 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°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 $_{\text{vs Ag/AgCl}}$ to -1060 mV $_{\text{vs Ag/AgCl}}$. 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.

Coatings for Use at High Temperatures
Room On Demand - Session A2

Thermal and Environmental Barrier Coatings

A2-1 Improvement of TBC Coating Resistance to Simultaneous Attacksby Sulfur and Vanadium Compounds*, Jianhong He (Jianhong.He@Oerlikon.com),* Oerlikon Metco , USA*; T. Sharobem, G. Dwivedi,* Oerlikon Metco, USA

Hot corrosion attacks of various TBC systems by sulfur and vanadium compounds have been tested at 1050^{o}C for 2 hours and 4 hours in the presence of 60% V_2O_5 and 40% Na_2SO_4. The results are summarized as follows.

(A) Sulfur and vanadium compounds at high temperature aggressively attacked the conventional 7YSZ TBC, the coating has been damaged at 1050^{o}C for only 2 hours in the presence of 60% V_2O_5 and 40% Na_2SO_4.

(B) High density of coarse YVO_4 crystals are quickly formed on coating surface, removal of Y_2O_3 stabilizer from zirconia leads t'-ZrO_2 to m-ZrO_2 phase transformation and thusdramatic increase in volume. There is no evidence showing fair metallurgical bonds among YVO_4 crystal and YVO_4 crystal, and matrix, therefore, integrity of the coating is totally destroyed by sulfur and vanadium compounds.At the same time, molten salt infiltrate into entire top coat and seal splat boundaries and pores similar to molten silicate deposits to reduce strain tolerance, finally causing top coat delamination.

(C) Hot corrosion resistance of TiO_2 and Y_2O_3 co-stabilized zirconia has doubled compared to a standard 7 YSZ TBC, while single stabilizer TBCs with high Y_2O_3 ratios do not increase hot corrosion resistance in the presence of 60 % V_2O_5 and 40 % Na_2SO_4.

(D) TBC sprayed using mixture of 50% Metco 143 and 50% 48YSZ and Metco143/ A204NS-1/bi-layer TBC had the highest resistance to simultaneous attacks by sulfur and vanadium compounds, although the microstructures on the surface and cross-section of these two TBCs are totally different.

A2-2 High-Temperature Corrosion of Sintered $Er_2Si_2O_7$ With CMAS for Environmental Barrier Coatings*, Seung-Hyeon Kim (kim.seung.hyeon.726@s.kyushu-u.ac.jp),* Kyushu University, Japan*; N. Nagashima, Y. Matsushita,* National Institute for Materials Science, Japan*; B. Jang,* Kyushu University, Japan

Environmental barrier coatings (EBCs) is an element that protects silicon-based ceramic matrix composites (CMCs) from high temperatures. CMCs has high temperature performance and low density, which can greatly improve fuel consumption. CMCs low density can reduce weight by up to 30% compared to Ni-based super alloys. In addition, for the purpose of EBCs, insulation properties are important as the temperature change of the hardware inside the engine occurs at high temperatures. In addition, the demand for thermal protection of CMCs is increasing in higher temperature applications. Research and development are being conducted to investigate the effect of calcium-magnesium-aluminosilicate (CMAS) during high temperature operation. A composition similar to volcanic ash is being studied for the high temperature interaction between CMAS.

EBCs must be resistant to minimize the resistance to decomposition by molten actual volcanic ash (dust and sand) deposits. With increasing high-temperature corrosion requirements, EBCs based on rare earth (RE) monosilicates ($RESi_2O_5$), disilicates ($RE_2Si_2O_7$) and their variants are being developed. Disilicate ($RE_2Si_2O_7$) shows safety because SiC and CTE are better matched than monosilicate ($RESi_2O_5$). The process of preparing a hot corrosion specimen is as follows. The synthesized Er_2O_3-$2SiO_2$ powder was prepared to fabricate a sintered $Er_2Si_2O_7$ by the spark plasma sintering (SPS) at 1400°C for 20 min. CMAS was sprinkled on the sintered $Er_2Si_2O_7$ surface and exposed for 2, 12, and 48 h at 1400°C by isothermal heat treatment.

However, reaction layer for sintered $Er_2Si_2O_7$ by CMAS has not yet been reported. The purpose of the present work is to investigate the influence of CMAS corrosion properties at high temperatures on sintered $Er_2Si_2O_7$ fabricated by SPS. As time increases, it is a phenomenon that appears as $Er_2Si_2O_7$ particles are dissolved in molten CMAS by penetrating into grain boundaries. In addition, it was observed that some crystallization occurred at the boundary of the sintered $Er_2Si_2O_7$ molten CMAS.

Keywords: $Er_2Si_2O_7$; Corrosion behavior; CMAS; Environmental barrier coatings; Spark plasma sintering

A2-3 Experimental and Modelling Analysis of the Driving Force for TBC Damage During Thermal Cycling With Consideration of Temperature Gradients*, Lara Mahfouz (lara.mahfouz@mines-paristech.fr), V. Maurel , V. Guipont, B. Marchand,* Mines ParisTech, PSL Research University, France*; F. Coudon,* Safran Tech, Safran SA, France

The addition of Thermal Barrier systems to hot section components of gas turbines requires understanding of its degradation and failure modes, and its resulting impact on the components' lifetime. The spallation (total or partial) of the top coat will result in thermal protection loss, and hence an important reduction of the component's lifetime. The studied Thermal Barrier system is composed of EB-PDV YSZ ceramic top coat and (Ni, Al)-Pt metallic bond coat deposited on a AM1 substrate, a Ni-based superalloy. A first α-alumina layer is deposited on the substrate and grows in service (TGO).

Different approaches have been developed to asses TBC lifetime [1,2]. The main objective of this study is to provide a robust modeling of the damage and lifetime to spallation of Thermal Barrier systems, for thermo-mechanical stress conditions accounting for thermal gradients. The proposed approach is based on the analysis of the evolution of an interfacial crack. It has been widely observed for such systems, that thermal cycling induces damage at the TC/TGO interface leading to interfacial cracking and finally spallation of the TC. Laser shock test has been used to initiate a crack at the interface. The evolution of the crack is monitored during thermal cycling on a burner rig, with temperature gradients as close as possible to in-service conditions. This technique has been used and analyzed in previous studies [2,3] for furnace cycling tests. A numerical modeling of the energy evolution in a blister under thermal cycling is proposed. It relies on the evaluation of the energy release rate within the system at different cycling stages as the blister propagates. A sensitivity analysis has been achieved considering the influence of components' mechanical behaviors, as well as that of loading, ageing, and geometrical parameters.

1. J.-R. Vaunois. Modélisation de la durée de vie des barrières thermiques par le développement et l'exploitation d'essais d'adhérence. PhD thesis, Université de Grenoble, 2013.
2. R. Soulignac. Prévision de la durée de vie à l'écaillage des barrières thermiques. PhD thesis, Mines ParisTech, 2014.
3. V. Maurel, V. Guipont, M. Theveneau, B. Marchand, F. Coudon. Thermal cycling damage monitoring of thermal barrier coating assisted wth LASAT (Laser Shock Adhesion Test). Surface and Coatings Technology, Vol 380, 2019.
4. V. Guipont, G. Begue, G. Fabre, V. Maurel. Buckling and interface strength Analysis of EB-PVD TBC combining Laser Shock Adhesion Test (LASAT) to thermal cycling. Surface and Coatings Technology, Vol 378, 2019.

A2-4 Effect of Varying APS Flash Bond Coating Thickness on Furnace Cycle Lifetime*, Michael Lance (lancem@ornl.gov), K. Kane, J. Haynes, B. Pint,* Oak Ridge National Laboratory, USA*; E. Gildersleeve, S. Sampath,* Stony Brook University, USA

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.

A2-5 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.

A2-6 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. Malecka, P. 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.

A2-7 Laser Processing of Freeze Casted Yttria Stabilized Zirconia / Gadolinia Thermal Barrier Coatings to Mitigate CMAS Attack*, Said Bakkar (SaidBakkar@my.unt.edu)*, *E. Cairns, M. Vu, M. Young, D. Berman,* University of North Texas, USA*; T. Hossain,* Ceriumlabs, USA*; J. Moldenhauer, E. Steinmiller, W. Flanagan,* University of Dallas, USA*; S. Aouadi,* University of North Texas, USA

Yttria-stabilizedzirconia 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 a freeze-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 tomitigateCMAS (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. The performance of the different surface treatment systems was compared by conducting CMAS infiltration studies. Deposit of Si_3N_4 as a sacrificial layer on the top of single crystal YSZ provides a perfect seal to cover the defects on the surface.The newly designed fabrication process that combines freeze casting with laser modification and using a sacrificial layer of Si_3N_4 was shown to be a viable technique to significantly reduce CMAS infiltration in porous thermalbarriercoatings.

A2-8 Corrosion Resistance and Fatigue Behavior of Bare and Coated Ni-based Superalloys*, Sebastien Dryepondt (dryepondtsn@ornl.gov)*, *R. Pillai, J. Kurley,* Oak Ridge National Laboratory, USA

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.

Coatings for Use at High Temperatures
Room On Demand - Session A3

Materials and Coatings for Solar Power Concentration Plants

A3-1 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.

A3-2 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

A3-3 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, M. 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.

Coatings for Use at High Temperatures
Room On Demand - Session AP

Coatings for Use at High Temperatures (Symposium A) Poster Session

AP-3 Microstructural Growth and Oxidation Performance of Ti_xSi_y on γ -TiAl*, **Josefina Crespo Villegas (joseffina.crespo@polymtl.ca)**, S. Brown, E. Bousser,* Polytechnique Montreal, Canada*; M. Cavarroc,* Safran Tech, France*; S. Knittel,* Safran Aircraft Engines, France*; L. Martinu, J. Klemberg-Sapieha,* 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-4 Lowering Costs by Improving Efficiencies in Biomass Fueled Boilers: New Materials and Coatings to Reduce Corrosion (BELENUS)*, A. Illana, V. Encinas-Sánchez, M. de Miguel, M. Lasanta, G. García-Martín, **Francisco Javier Pérez Trujillo (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.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B1

PVD Coatings and Technologies

B1-1 On Electron Heating and Ion Recycling in the High Power Impulse Magnetron Sputtering Discharge*, Jon Tomas Gudmundsson (tumi@hi.is)*, University of Iceland*; D. Lundin,* Linköping University, Sweden*; M. Raadu,* KTH Royal Institute of Technology, Sweden*; T. Petty, T. 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].

[1] J A Thornton, J. Vac. Sci. Technol. 15 (1978) 171

[2] N. Brenning et al., Plasma Sources Sci. Technol. 25 (2016) 065024

[3] C Huo et al., Plasma Sources Sci. Technol. 22 (2013) 045005

[4] N. Brenning et al. Plasma Sources Sci. Technol. 26 125003 (2017)

[5] C. Huo et al., J. Phys. D: Appl. Phys. 50 354003 (2017).

[6] J. T. Gudmundsson et al. Plasma Sources Sci. Technol. 25, 065004 (2016).

B1-2 Tailoring the Chemical Composition and Microstructure of Cr_xN Deposited by HiPIMS through Duty-cycle Modifications*, Martha Cedeño-Vente (m.cedeno@posgrado.cidesi.edu.mx)*, *G. Mondragón-Rodríguez, N. Camacho, A. Gómez-Ovalle, J. González-Carmona, J. Alvarado-Orozco, D. Espinosa-Arbeláez ,* Centro de Ingeniería y Desarrollo Industrial (CIDESI), Mexico

The main challenge in hard coating manufacturing is developing dense, flawless, and smooth surface morphology coatings, which improve the performance of components exposed to severe service conditions. One of the most promising coating techniques to achieve this goal is the High-Power Impulse Magnetron Sputtering (HiPIMS), which produces highly ionized plasmas, resulting in definite improvements on the film microstructure and properties. The application of pulses (50 - 500 µs) during the deposition process attains a high ionization rate in HiPIMS. The pulse modification (*e.g.,* duty-cycle, also known as τ) affects the current density, modifying the stoichiometry and chemical composition of the coating; this indicates that the pulse appropriate selection is a viable and practical alternative for obtaining graded or multilayer metal nitrides at a fixed gas flow, thus tailoring the coating internal stress distribution, microstructure, and mechanical properties.

In this work, the duty-cycle design to modify the chemistry, microstructure, and residual stresses of Cr_xN coatings is presented and discussed. The average current tends to increase from 2.9 to 12 % with the variation of τ during the HiPIMS process. These process conditions lead to a significant increment of the deposition rate and the chromium content in the Cr_xN coating. Various crystalline phases like α-Cr, α-Cr + h-Cr_2N, h-Cr_2N, and h-Cr_2N + c-CrN were obtained in the film, resulting in graded multilayer systems. Cr-rich samples presented faceted columns with intercolumnar pores and cauliflower-like surface morphology. The growth of the h-Cr_2N phase caused a decrease of the grain sizes, and their morphology changed to pyramidal or stacked pyramids at lower duty-cycles. The transformation of the h-Cr_2N to CrN leads to highly dense columnar microstructures, while the residual stresses of the coating increased with the higher duty-cycle.

Keywords: *HiPIMS, duty-cycle, Cr_xN, graded microstructure.*

B1-3 New Approaches for AlCrN-Based Coatings for High Speed Applications*, Markus Schenkel (markus.schenkel@eifeler-vacotec.com)*, voestalpine Eifeler Vacotec GmbH, Düsseldorf, Germany*; S. Spor,* voestalpine Eifeler Vacotec GmbH, Düsseldorf, Germany, Austria*; N. Gerhards, U. Zimmermann, F. Nahif,* voestalpine Eifeler Vacotec GmbH, Düsseldorf, Germany

The CO2 debate—a global challenge requires the necessity of renewed investments and innovations by manufacturers and suppliers with a strong focus on an increase of sustainability. Especially, the automotive sector (driven by the governmentally regulated CO2 emission limit), in detail the trends for the e-mobility, which has reached higher levels of importance. Consequently, high-performance materials and versatile material combinations with focus on weight reduction and energy-efficient automotive design are replacing conventional materials. The trend to a reduction of the cycle times of the production lines, leads to new challenges in the application of tools, such as higher mechanical and thermal loads exposure during operation.

Thus, the talk will focus on the technical possibilities to overcome these challenges by the appropriate choice of coating design using the example of aluminum-chromium nitride based coatings.

B1-4 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. 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.

B1-5 INVITED TALK: Industrial Scale ta-C Coating Using Laser Arc Technology*, Wolfgang Fukarek (wolfgang.fukarek@tenneco.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).

B1-7 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.

B1-8 Monitoring Tantalum Nitride Thin Films Structure by Reactive HiPIMS Magnetron Sputtering: From Microstructure to Properties*, **Angeline Poulon-Quintin (angeline.poulon@icmcb.cnrs.fr)**, A. Achille,* ICMCB-CNRS, France*; D. Michau,* Univ. Bordeaux, ICMCB, France*; M. Cavarroc,* Safran Tech, 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).

B1-9 INVITED TALK: 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.

B1-12 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.

B1-13 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.

[1] Sputter deposition of porous thin films from metal/NaCl powder targets, R. Dedoncker, H. Ryckaert, D. Depla, Appl. Phys. Lett. 115(2019) 041601doi:10.1016/10.1063/1.51128225

B1-14 Evolution of the Microstructure of Sputter Deposited TaAlON Thin Films with Increasing Oxygen Partial Pressure*, Nina Schalk (nina.schalk@unileoben.ac.at), C. Saringer,* Montanuniversitat Leoben, Austria*; A. Fian,* Joanneum Research Forschungsgesellschaft mbH, Austria*; V. Terziyska, M. Tkadletz,* Montanuniversitat Leoben, Austria

Recently, quaternary oxynitrides of transition metals and aluminum have attracted increasing interest due to their tunable properties. Within the present work, a series of TaAl(O)N films was sputter deposited using constant nitrogen and varying oxygen partial pressures. The films were grown from single element Ta and Al targets. The deposition parameters were adjusted to obtain a Ta/Al atomic ratio of ~50/50 for the oxygen-free film and were held constant for the following depositions, with the exception of the increasing oxygen partial pressure and compensatory decreasing argon partial pressure. Elastic recoil detection analysis revealed oxygen contents of up to ~26 at.%, while the nitrogen content decreased from ~47 at.% in the oxygen-free film to ~35 at.% in the film with the highest oxygen content, resulting in a significant decrease of the metal/non-metal ratio with increasing oxygen partial pressure. The micro- and bonding structures of the films were investigated by X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy and transmission electron microscopy. All films exhibited a dominating face centered cubic TaN-based structure with indications for an additional nanocrystalline phase fraction, which increases with increasing oxygen partial pressure. In addition, the mechanical properties were evaluated by nanoindentation, yielding a decreasing hardness and elastic modulus with increasing oxygen content.

B1-15 Towards Knowledge-based Design of Multi-element Target Materials*, Mehran Golizadeh (mehran.golizadeh@unileoben.ac.at),* Montanuniversität Leoben, Austria*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), and Felix Bloch Institute, Leipzig University, Germany*; C. Mitterer, R. Franz,* Montanuniversität Leoben, Austria

The increasing demand for multi-element thin films and coatings for multifunctional purposes has pushed the target and cathode material industry to produce multi-element products. Nowadays, alloyed and composite targets are commonly employed in various physical vapor deposition technologies including magnetron sputtering and cathodic arc deposition. The targets, which serve as cathodes in the respective discharges, are exposed to the discharge plasma during the deposition process, which alters their surface properties such as phase and chemical composition. The surface modifications are particularly severe for cathodic arc deposition since the cathode spots impose countless melting-solidification cycles on the target material near the surface, leading to the formation of a network of craters and a several 10 µm thick modified layer. The formation mechanisms and properties of the modified layer, semi-empirically quantified by the cohesive energy of the constituent phases, influence the charge states and kinetic energies of the ions and, hence, the film growth conditions and coating properties.

In a first step, a Mo/Al multilayer cathode was designed to reveal information about the heat-affected zone below the craters as well as the evolution of material intermixing as the sequential cathode spot events take place. The modified layer is formed by micro-sized displacements of the cathode material during crater formation. In addition, the material intermixing predominantly occurs in liquid state while the mechanisms based on solid-state diffusion play an insignificant role due to the sharp temperature gradient (shallow heat-affected zone) below craters and very high cooling rates [1]. As a next step, the microstructure and phase composition of the modified layers of Al-Cr composite cathodes with varying grain sizes were studied. The results from high-resolution analysis techniques revealed that metastable phases, including quasicrystalline phases, are formed during the solidification of arc craters and, hence, are the constituting phases of the modified layers. The average cooling rate in these rapid solidification processes was estimated to be in the order of 10^6 K/s. Accordingly, to optimize the plasma properties for film and coating depositions it is necessary to consider non-equilibrium phases of the alloy system as they might be present on the modified surface. This means that the target's or cathode's microstructure and constituent phases need to be designed to enable the formation of phases with optimized cohesive energy during the rapid solidification of arc craters.

5. Golizadeh, M., et al., J. Appl. Phys., 2020. 127(11).

B1-16 INVITED TALK: 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

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B2

CVD Coatings and Technologies

B2-1 *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.

B2-3 Ti-Si-B-C-N PECVD Nanocomposite Coatings for Tribological Applications at Elevated Temperatures*, Alexander Nienhaus (alexander.nienhaus@ist-extern.fraunhofer.de)*, TU Braunschweig, Institute for Surface Technology, 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 conditions. The machining of aluminum (Al) and copper (Cu) is especially challenging, considering its tendency to stick at the tools surface, which is increasingly impactful at elevated temperatures. Developing Ti-Si-B-C-N PECVD nanocomposite coatings is a promising approach, because, with an adequate Si-content, 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, ncTiC, and nc-TiCN. In this study, the influence of nitrogen on its thermal and mechanical properties is under investigation. The N-content ranged from 0.0..14.6 at.-%. Chemically stable TiB2 phases are formed by adding BCl_3 to the PECVD coating deposition process. These phases are not observed in XRD-diffraction patterns, which indicates a-TiB_2 rather than ncTiB2, e.g. in contrast to Ti-B-N nanocomposite coatings. With C-contents up to 32 at.-%, formation of a-C particles in the a-matrix is likely. High temperature (T = 750-900 °C) in-situ XRD-measurements in air atmosphere provided by synchrotron radiation showed different behavior in oxidation resistance, with dependence of N-content. Furthermore, tempering in air atmosphere at 850 and 900 °C for 30 and 60 min was carried out to gain additional information on the oxidation resistance. In contact with molten or close to molten Al or Cu, Bcontaining nanocomposites are expected to reduce the adhesive wear on the tools surfaces. The multiphase coatings form compositionally complex nanostructures, leading to a universal hardness of up to 39 GPa, close to the so called ‘superhardness’ (> 40 GPa). The starting point of oxidation was determined to be in the range of 850-900 °C, underlining the possible application as protective coating for hot forming tools. Further work will focus on the nanocomposite structure, the mechanical properties, and pin-on-disc tests at T = 750 °C with Al_2O_3 counterparts.

B2-4 INVITED TALK: 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.

B2-6 INVITED TALK: 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.

[1] M. Tsumaki, Y. Shimizu, T. Ito, Materials Letters **166**, 81 (2016)

[2] M. Tsumaki, K. Nitta, S. Jeon, K. Terashima, T. Ito, J. Phys. D: Appl. Phys. **51**, 30LT01 (2018)

[3] K. Nitta, M. Tsumaki, T. Kawano, K. Terashima, T. Ito, J. Phys. D: Appl. Phys. **52**, 315202 (2019)

B2-8 High Throughput Deposition of Hydrogenated Amorphous Carbon Films using High-Pressure Ar+CH_4 Plasmas*, Kazunori Koga (koga@ed.kyushu-u.ac.jp)*, *S. 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).

B2-9 Influence of Co-enriched Surface Zones in WC-Co Cemented Carbides on the Microstructure and Mechanical Properties of $TiC_{0.6}N_{0.4}/\alpha\text{-}Al_2O_3$ Coatings*, Fabian Konstantiniuk (fabian.konstantiniuk@unileoben.ac.at),* *M. Tkadletz,* Montanuniversität Leoben, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

In metal cutting applications functionally graded near surface zones in WC-Co cemented carbide substrates are applied to optimize their properties, in particular toughness and hardness. Thus, the present work focuses on the influence of Co-enriched substrate surface zones and their thickness on the microstructure and mechanical properties of state-of-the-art $TiC_{0.6}N_{0.4}/\alpha\text{-}Al_2O_3$ coatings synthesized using chemical vapor deposition. Complementary cross-sectional energy dispersive X-ray spectroscopy and electron back-scatter diffraction maps provided insight into the grain size, preferred orientation and phase composition of coatings and substrates. While the hardness and Young´s modulus of the coatings were hardly affected by the Co–enriched surface zone and its thickness, nanoindentation maps performed on the cross-sections of the substrates confirmed a lower hardness and Young´s modulus in zones with higher Co content. Since the tensile residual stress in both, the $TiC_{0.6}N_{0.4}$ and $\alpha\text{-}Al_2O_3$ decreased with increasing thickness of the Co–enriched surface zone, as determined by X-Ray diffraction, it is suggested that stress relaxation occurs through plastic deformation of the soft Co-enriched surface zone. Despite the influence on the residual stress, the Co–enriched surface zone and its thickness was found to have no effect on the thermal crack networks of the coatings. However, Rockwell-indentation tests demonstrated a reduction of the coating adhesion with increasing thickness of the Co–enriched surface zone. The results obtained within this work contribute to a better understanding of the influence of a Co-enriched surface zone and its thickness on the performance of $TiC_{0.6}N_{0.4}/\alpha\text{-}Al_2O_3$ coated cutting tools.

B2-10 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

B2-11 Compatibility of a CoCrFeNi Multi-principal Element Alloy Substrate with Halide-based Thermal CVD Processes for TiN Deposition*, Katalin Böör (katalin.boor@kemi.uu.se),* Uppsala University, Sweden*; R. Qiu,* Chalmers University of Technology, Sweden*; A. Forslund,* KTH Royal Institute of Technology, Sweden*; O. Bäcke,* Chalmers University of Technology, Sweden*; H. Larsson,* KTH Royal Institute of Technology, Sweden*; E. Lindahl,* Sandvik Coromant R&D, Sweden*; M. Halvarsson,* Chalmers University of Technology, Sweden*; M. Boman,* Uppsala University, Sweden*; L. von Fieandt,* Sandvik Coromant R&D, Sweden

Multi-principal element alloys (MPEAs) are materials consisting of at least four metallic elements in near–equimolar amounts. These alloys can exhibit new combinations of material properties, either deriving from the new phases formed or from the individual components. Their applications may require a protective coating, it is therefore crucial to investigate their compatibility with conventional coating technologies. Titanum nitride is a widely used corrosion- and wear resistant coating, which is frequently deposited by CVD. This presentation assesses the compatibility of the CoCrFeNi substrate, an important MPEA, with a conventional CVD process for TiN deposition using $TiCl_4/H_2/N_2$ as precursors [1]. Different reactions between the substrate, the coating and the precursors will be discussed. These include substrate etching by Cl-containing species and intermetallic compound or nitride building between the substrate elements and Ti or N, respectively. Substrate etching can result in voids in the substrate and the substrate elements may be redeposited and incorporated in the coating. Intermetallic compounds and nitrides can be formed by diffusion of the substrate elements into the coatings or Ti/N diffusion into the substrate. SEM, XRD and (S)TEM combined with EDS were used to determine which of the mentioned processes take place in the $CoCrFeNi\text{-}TiCl_4/H_2/N_2$ system between 850-950 °C. Thermodynamic calculations were carried out using the Thermo-Calc software to determine the stable compounds that can be formed during the process.

The substrate was stable under the process conditions. Only Cr was reactive towards the N_2 precursor and appeared in the coating grain boundaries, shown by EDS in TEM. Thermodynamic calculations predicted that Cr-containing nitride phases could form, explaining the driving force for Cr diffusion in the grain boundaries. XRD results only indicated the presence of a TiN and a CoCrFeNi phase. No intermetallic phases were formed between the substrate elements and titanium and no signs of etching were observed.

The results provide an understanding on the processes involved in the substrate-precursor interaction and the driving forces behind. They explain why CoCrFeNi outperforms elemental Ni, Fe [2] and alloys of its components, giving a basis for determining which multi-component alloys can be compatible with conventional CVD processes.

[1] Böőr, K. *et al.*, *Surf. Coatings Technol.* 393, 125778 (2020)

[2] von Fieandt, L. *et al.*, *Surf. Coat. Technol.*334, 373–383 (2017)

B2-12 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.

B2-13 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.

B2-14 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.

B2-15 Investigation of Diamond Coating Characteristics on Chrome-Plated AISI 4140 Steel by Hot-Filament Chemical Vapour Deposition Process*, R. Vignesh, **S Boominatha Sellarajan (rayarajan2005@gmail.com)**, J. Rajaguru, N. Arunachalam , M. Ramachandra Rao,* Indian Institute of Technology Madras , India

In the modern engineering world, extensive research has led to the development of certain unique grades of steel, mostly suitable for enhanced functions. AISI 4140 steel is one such grade, having major applications in power plants, automobile and aerospace industry. HFCVD process on these steel substrates have attracted significantly to improve the mechanical performances due to the superior properties of diamond films. However, CVD diamond films on steel are a great challenge due to the formation of interfacial graphite layers; intrinsic stresses and high stiffness due to considerable differences in thermal expansion coefficients between substrate and diamond. This may lead to premature failure of diamond films. To overcome these limitations, interlayers such as Cr, Ti, Mo, W, etc., were demonstrated for an improved adhesion by different techniques (sputtering and CVD). In this work, Cr interlayer made by hard-chrome plating technique was utilized. Then, diamond film was deposited over Cr interlayer by HFCVD process. High substrate temperature (~750℃) generated during the diamond deposition can significantly affect the mechanical properties of the steel substrate as the material undergoes phase transformation. This leads to material failure in real-time applications. Despite this, the necessary investigation about the influence of diamond coating deposition temperature on the microstructure and mechanical properties of the steel substrate has not been covered yet. Hence, this work aims at analyzing the substrate properties at varying temperature (450-750℃) by adjusting the hot-filament to substrate distance (d: 20-40 mm) and the filament temperature (1800-2200℃) and deposition time (soaking time: 1-8 hrs). Tensile strength, ductility, XRD and microstructure via SEM were carried out. The results indicate that the mechanical properties and microstructural features of the steel are affected significantly by deposition temperature and time. The strength and hardness of AISI 4140 steel drop as the deposition temperature and time are increased. However, the ductility increased with increasing deposition temperature and holding time. Microstructural observations reveal that the carbide precipitates have a plate-like structure at lower temperatures, but are spheroid-like at high temperatures. Carbide formations at high temperature were also confirmed by the XRD analysis. These results suggest that it is essential to select an optimal depositing temperature and time by considering the material high-temperature behaviour. Further, a case study on diamond film formation as a function of filament-substrate gap is discussed.

B2-16 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 On Demand - Session B3

Deposition Technologies and Applications for Diamond-like Coatings

B3-1 'Hydrogenated Amorphous Carbon from Magnetized Hollow Cathode Discharges*, **John Miller (miller290@llnl.gov)**, A. Ceballos-Sanchexz, S. Elhadj, S. Kucheyev, B. Bayu Aji, S. Falabella,* Lawrence Livermore National Laboratory, USA

Diamond-like carbon is a popular hard coating material whose properties widely depend on deposition process and conditions within the process. Variations between the methods and conditions yield films with varying hydrogen, sp2 carbon, and sp3 carbon content who have densities between 1 and 3 g/cc, spanning the difference between a low-density hydrocarbon polymer and polycrystalline diamond (high density carbon). This material is becoming increasingly interesting as a new ablator material for inertial confinement fusion because it is low Z and has the potential to tune its density between that of glow discharge polymer(~1 g/cc) and diamond (3.5 g/cc), two ICF ablator materials of choice. This work investigates the use of a magnetized hollow cathode discharge for depositing thick, density tunable amorphous carbon films for future inertial confinement fusion experiments.A variety of the properties of the films will be discussed including: composition, density, impurity content, thickness limitation, deposition rate and surface morphology.

IM Release: LLNL-ABS-814679

B3-2 Effect of Mechanical and Thermochemical Tool Steel Substrate Pre-treatment on DLC Coating Durability*, **Daniel Tobola (daniel.tobola@kit.lukasiewicz.gov.pl)**,* Łukasiewicz Research Network - Krakow Institute of Technology, Poland*; T. Liskiewicz,* Manchester Metropolitan University, UK*; L. Yang,* Leeds University, UK*; T. Khan,* Manchester Metropolitan University, UK*; Ł. Boron,* Łukasiewicz Research Network - Krakow Institute of Technology, Poland

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 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. Afterwards, a vacuum nitriding process in a PVD chamber as a pre-treatment for subsequent DLC coating deposition was carried out. Coated samples were subjected to a series of ball-on-disc wear tests against Al2O3 and Si3N4 counterparts. X-ray diffraction (XRD), instrumented indentation and scanning electron microscopy (SEM) 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 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 tools tribological performance.

Keywords: DLC coatings, tool steels, vacuum nitriding, slide burnishing

B3-3 Stress Free ta-C Coatings by means of Up-Scaled Pulsed Laser Deposition for Industrial Applications*, **Hagen Gruettner (hagen.gruettner@hs-mittweida.de)**, D. Haldan, J. Maus,* Hochschule Mittweida - University of Applied Sciences, Germany*; M. Nieher,* Hochschule Mittweida - University of Applied Sciences , Germany*; S. Weissmantel,* Hochschule Mittweida - University of Applied Sciences, Germany

In many industrial applications highly wear-resistant coatings are required to protect and / or functionalize tools and components. While typical representatives of DLC coatings are already in large-scale industrial use, stress free ta-C coatings produced at the Laser Institute Mittweida (LHM) by means of a patented combination of pulsed laser deposition and pulsed laser stress relaxation are currently well under way due to their outstanding properties and the possibility to up-scale the deposition process. These ta-C coatings are special representatives of the DLC coatings and unsurpassed in terms of their hardness and usability. Moreover, they can be prepared almost free of intrinsic stress. Using optimal deposition parameters, a hardness of up to 70 GPa with Young's moduli of 700 to 800 GPa can be achieved, which leads to an extremely high operational wear resistance. Due to the low average surface roughness (Ra) of a few nanometers and the low friction coefficient these layers are also excellently suitable for tribological applications. By using optimized adhesion layers or layer systems it is possible to achieve high adhesion strengths on a variety of substrate materials. The low temperature required during the deposition process (< 90 °C) makes it also possible to coat temperature-sensitive materials. Due to their chemical resistance, biocompatibility and dopability the ta-C coatings offer a wide range of further applications, such as in medical technology, food industry or sensor technology. By means of the combined pulsed laser deposition and laser pulse annealing process the LHM is able to produce homogeneous layers with a thickness ranging from a few nanometers up to a few 10 µm with an adjustable hardness between 25 and 70 GPa and an adjustable intrinsic stress between 12 GPa and nearly zero GPa by choosing the corresponding deposition parameters. That makes it also possible to prepare material and application specific layer designs like Young's modulus gradients or multilayers. It will be shown that the deposition process can be up-scaled to industrial requirements using new high power excimer lasers, which were introduced in 2019. The LHM is now looking for interested partners and potential customers.

B3-4 DLC Coatings Deposited by Novel Doping Strategies with HiPIMS*, **José Antonio Santiago Varela (joseantonio.santiago@nano4energy.eu)**, I. Fernández-Martínez, A. Wennberg,* Nano4Energy SL, Spain*; M. Monclús, J. Molina-Aldareguia,* IMDEA Materials Institute, Spain*; V. Bellido-Gonzalez,* Gencoa Ltd, UK*; M. Panizo-Laiz,* Universidad Politecnica de Madrid, Spain*; J. Sánchez-Lopez, T. Rojas,* CSIC, Spain*; S. Goel,* Cranfield University, UK*; J. 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.

B3-5 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*; 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.

B3-6 Effects of Target Poisoning Ratios on the Microstructure, Mechanical Properties and Corrosion Resistance of WC_x Coatings Fabricated by Superimposed HiPIMS and MF System*, **Igamcha Moirangthem,*** Ming Chi University of Technology, Taiwan*; S. Chen,* National Taiwan University, Taiwan*; J. Lee (jefflee@mail.mcut.edu.tw),* Ming Chi University of Technology, Taiwan

In this work, we studied the effect of target poisoning ratios of tungsten carbide films using a superimposed HiPIMS and MF system. The flow rate of the acetylene (C_2H_2) was controlled using a plasma emission monitoring (PEM) system to feedback control the target poisoning ratio during deposition. Five coatings, WC10, WC30, WC50, WC70 and WC90, were grown under target poisoning ratios of 10%, 30%, 50%, 70% and 90% respectively, on Si, AISI420 stainless steel (SS) and AISI304 SS substrates. A small hysteresis loop area for the emission intensity of W at 429.6 nm was observed with variation of C_2H_2 gas flow rates. With increasing target poisoning ratios, the phases changed from nanocrystalline β-WC_{1-x} to amorphous. The X-ray photoelectron spectroscopy was used to study the chemical bindings of coating. The highest power normalized deposition rate of 25.20 nm $min^{-1}kW^{-1}$ was observed for WC90. The highest hardness value of 32.3 GPa was measured for WC30. WC50 showed the best adhesion among the coatings with L_{C2} value of 65.1 N. The lowest COF of 0.26 was observed for WC90. In potentiodynamic polarization test using 0.1M H_2SO_4 solution, WC90 showed colourful fringes around the corrosion micro-pits with the highest polarization resistance (R_p) of 4552.51 kΩcm^2.

Keywords: Superimposed high power impulse magnetron sputtering, middle frequency, WCx coatings, tungsten doped diamond-like carbon coating, target poisoning, nanoindentation, tribometer

B3-7 The Influence of Different Power Supply Systems on the Microstructure, Mechanical and Corrosion Properties of Titanium Carbide Coatings*, H. Yu -Tung,* Ming Chi University of Technology, Taiwan, Republic of China*; C. Li-Chun,* Ming Chi University of Technology, Taiwan*; L. Bih-Show,* Chang Gung University, Taiwan*; **Lee Jyh-Wei (jefflee@mail.mcut.edu.tw),*** Ming Chi University of Technology, Taiwan

Titanium carbide (TiC) coatings have attracted wide attention from researchers and industry due to their high hardness, good wear and corrosion resistance. In this study, the TiC coatings were fabricated by four different power supply systems including superimposed HiPIMS-MF, HiPIMS, MF, and DC in a gas mixture of acetylene and argon. During the deposition process, a plasma emission monitoring (PEM) system was used to control the Ti target poisoning status to 70%. The single crystal silicon wafers and AISI304 stainless steel plates were used as substrates. The chemical compositions of TiC films were analyzed by a field emission electron probe microanalyzer. The microstructure of thin film was examined by a field emission scanning electron microscope. The crystalline structure of thin film was analyzed by an X-ray diffractometry. The hardness, adhesion and tribological properties of TiC films were evaluated by nanoindenter, scratch test and pin-on-disk wear test, respectively. The corrosion resistance of TiC films in 0.1 M H_2SO_4 aqueous solution was examined by an electrochemical workstation. The influence of four different power supplies on the deposition rate, microstructure, hardness, adhesion, wear and corrosion resistance of TiC films were studied in this work. Although the deposition rate of the TiC coating deposited by DC power supply was the highest, the film quality was inferior to other films due to its less dense microstructure. On the other hand, the TiC coating fabricated by superimposed HiPIMS-MF power supply exhibited a dense microstructure, good mechanical property and excellent corrosion resistance.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B4

Properties and Characterization of Hard Coatings and Surfaces

B4-1 Investigating the Influence of Nanocomposite Structure on the Thermal Stability of Ag in VSiCN-Ag Coatings*, **Forest Thompson (forest.thompson@sdsmt.edu),*** South Dakota School of Mines and Technology, USA*; F. Kustas,* NanoCoatings, Inc., USA*; G. Crawford,* South Dakota School of Mines and Technology, USA

Self-lubricating coatings have been studied extensively for elevated temperature tribological applications. For coating designs in which a noble metal solid lubricant phase is continuously supplied to the surface from within a ceramic-based matrix, control of noble metal out-diffusion can be challenging. To investigate the potential of manipulating nanocomposite structure to better control solid lubricant stability and transport, VSiCN and VSiCN-Ag nanocomposite coatings were deposited by plasma-enhanced reactive magnetron sputtering. A nominal Ag content of 4 at.% was maintained while amorphous phase content was varied with the intent of modifying coating density, grain size, and grain morphology. As-deposited coatings were characterized by energy dispersive X-ray spectroscopy, scanning electron microscopy, X-ray diffraction, and transmission electron microscopy. Hardness and apparent elastic modulus were measured by nanoindentation. The thermal stability of Ag within the coatings was evaluated by inspection of the coating surfaces after vacuum annealing at 550°C. Relationships among coating microstructure and Ag thermal stability are identified and potential influences on coating performance in tribological applications are discussed.

B4-2 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. Holzapfel,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; J. 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.

B4-3 Effect of Functionally Graded Layers on Tribological Behavior of TiZrN Coatings on AISI D2 Steel*, **Jia-Hong Huang (jhhuang@ess.nthu.edu.tw)**, B. 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

[1] An-Ni Wang et al., Surf. Coat. Technol. 239(2014)20.

[2] Yu-Wei Lin et al., Surf. Coat. Technol. 350(2018)745.

B4-4 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.

B4-5 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. Liskiewicz,* Manchester Metropolitan University, UK*; B. 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

6. 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.
7. 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.

B4-6 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

B4-7 High Temperature Tribology of Hf Doped c-$Al_{0.67}Ti_{0.33}N$ Cathodic Arc PVD Coatings Deposited on M2 Tool Steel*, G. Mondragón Rodríguez, **Alvaro Enrique Gómez Ovalle (a.gomez@posgrado.cidesi.edu.mx)**, J. Alvarado Orozco, J. González Carmona, C. Ortega Portilla, J. 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 $c\text{-}Al_{0.67}Ti_{0.33}Hf_xN$ 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.

B4-8 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.

B4-9 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.

B4-10 In-plane Texturing of Silver Thin Films*, Francesca Corbella (corbella.francesca@gmail.com),* Saint-Gobain Recherche/CNRS, France

Pollution and energy waste are main concerns for today's society. In buildings, part of the waste is due to thermal radiation losses through windows1. To address the problem, low-emissive coatings were introduced in the market. By being reflective in the far IR range and transmissive in the visible light, the low-emissive coatings are designed to reduce the heat losses from inside the building to the outside, while maximizing the solar gain. Such properties are achieved through silver based multilayers, deposited on the glass through a PVD process. The efficiency of the coatings is then related to the maximization of the IR reflectance, which depends on the electrical conduction of the nanometric silver layer.2 The minimization of the Ag resistivity becomes, therefore, a key point for enhancing the optical properties of the coatings. In thin films, the conductivity of a material depends on its structural properties, which are influenced by its seed layer. Till today, ZnO was recognized as the best underlayer for Ag and the most used oxide in the industrial glazing. In particular, it was observed that the deposition of the oxide in its textured hexagonal lattice led to the growth of a Ag (111) out-of-plane textured film, with enhanced electrical properties. Film texturization can play an important role on silver conductivity.4-5 Starting from a model ZnO single crystal based stack, our study showed the impact of in-plane and out-plane texturization on silver resistivity . The system was then optimized with the introduction of a buffer polycrystalline ZnO layer, showing promising results. The ultimate goal is to reproduce the structural and electrical properties, observed on the single crystal stacks, in polycrystalline sputtered coatings through Ion Beam Assisted Deposition, a sputtering technique becoming more and more suitable for an industrial implementation.

[1] « Couches conductrices transparentes. Applications aux vitrages isolants et aux vitrages actifs. » Cours (2011)

[2] E. Hagen and F. Rubens, Annalen der Physik 11, 873 (1903)

[3] M. Philipp, PhD thesis, Universitât Dresden and UPMC (2011)

[4] D Köhl, PhD thesis, RWTH Aachen University (2011)

[5] R. Sittner, Ag workshop Paris, “Impact of diverse growth templates on the growth of Ag thin films” (2015)

B4-12 INVITED TALK: 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.

B4-14 INVITED TALK: 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.

B4-16 Influence of the Period of the Substrate Oscillation on Thin CrN Films Obtained by RF Physical Vapor Dynamic Glancing Angle Deposition Technique*, M. Jimenez, F. Cemin, A. Riul, L. Zagonel,* UNICAMP, Brazil*; C. 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 the physical properties of hard metallic nitride coatings is mandatory to obtain good performance in applications such as cutting tools. In this work, nanostructured chromium nitride (CrN) films are obtained by combining radio frequency magnetron sputtering (RFMS) and dynamic glancing angle deposition (DGLAD) using Programmable Logic Controller (PLC). By appropriate choosing the substrate oscillation frequency, the physical properties such as micro and nanostructure, morphology, hardness, texture, and crystallite size are feasible to be tailored. Samples are deposited by moving the substrates forward and backward $(-\phi 0 < \phi(t) < +\phi 0)$ by controlling the angular velocity $\omega = d\phi/dt$, inducing the formation of wavy-like periodic columnar nanostructures. Herein, we explore the effects prompted by the substrate oscillations at relatively short periods ($1 < T < 10$ min) on the CrN structure, as well as its influence on some physical and mechanical properties of the columnar films. It is observed the formation of wavy-like nanostructures, that generate the apparent formation of multilayer films. The dependence of the incident flux of particles with the angular position $\phi(t)$ of the substrate and the scattering of the sputtered particles on the gas phase prompt a complex distribution of precursors on the substrate surface. To take in account these effects, the process was simulated by the SiMTra software. Specific details of the results are reported in the Supplementary Information.

Keywords: Hard coatings, Chromium nitride, Dynamic glancing angle deposition, Numerical simulation

B4-17 Fabrication and Microstructure Evolution of Sputtering Single Element Transition Metal Nitride Multilayers*, K. Liu, Y. Yang, J. Xiang, Z. 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.

B4-18 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)**, F. Ramírez-Reyna, A. Meneses-Amador, G. Rodríguez-Castro, D. Fernández-Valdés, O. Reyes-Carcaño,* National Polytechnic Institute, 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.

B4-19 Low Temperature Deposition of TiB-based Hard Coating Films by Pulsed DC Plasma CVD*, **Takeyasu Saito (tsaito@chemeng.osakafu-u.ac.jp)**, H. Matsushima, K. Fuji, D. Kiyokawa, N. 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.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B5

Hard and Multifunctional Nanostructured Coatings

B5-1 INVITED TALK: 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 **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.

1. E.A. Levashov et al. Int Mater Rev 62 (2017) 203

2. Ph. Kiryukhantsev-Korneev et al. Corros Sci 123 (2017) 319

3. Ph. Kiryukhantsev-Korneev et al. Ceram Int (2019) doi.org/10.1016/j.ceramint.2019.09.152

4. Ph. Kiryukhantsev-Korneev et al. J. Phys.: Conf. Ser. 1238 (2019) 012003

5. K. Kuptsov et al. Acta Mater 83 (2015) 408

6. E. Sheftel et al. Phys Status Solidi 13 (2016) 965

7. Ph. Kiryukhantsev-Korneev et al. Prot Met Phys Chem 53 (2017) 873

B5-3 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.

[1] H. Bolvardi, J. Emmerlich, M. to Baben, D. Music, J. von Appen, R. Dronskowski, J.M. Schneider, J. Phys.: Condens. Matter 25 (2013) 045501

[2] H. Bolvardi, J. Emmerlich, S. Mráz, M. Arndt, H. Rudigier, J.M. Schneider, Thin Solid Films 542 (2013) 5-7

[3] L. Zábranský, V. Buršíková, P. Souček, P. Vašina, J. Dugáček, P. Sťahel, J. Buršík, M. Svoboda, V. Peřina, Vacuum 138 (2017) 199-204

B5-4 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@g-mail.nsysu.edu.tw)**,* National Sun Yat-Sen University, Taiwan*; P. 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 .

B5-5 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.

B5-6 Characteristics of Hf(*M*)SiBCN (*M* = Y, Ho, Ta, Mo) Coatings: Role of the *M* Choice, ***Martin Matas (matasma@kfy.zcu.cz)***, *M. Prochazka, J. Vlcek, J. Houska,* University of West Bohemia, Czech Republic

Thin films based on light main group elements are attractive due to a unique combination of properties ranging from high hardness through optical transparency to high–temperature stability and oxidation resistance. The properties, in the first place electrical conductivity, can be further modulated by addition of early transition metals. Properties of amorphous Hf(*M*)SiBCN films are investigated by combining their preparation using pulsed magnetron sputtering of boron–rich composite targets B_4C–Hf–*M*–Si (45–65% B_4C, 15–20% Hf, 5% Y/Hf/Ho/Ta/Mo, 15–30% Si) in 85% Ar + 15% N_2 discharge gas mixture with *ab-initio* calculations. First, we study the effect of the *M* choice and fraction on calculated mechanical properties and formation energy (E_{form}) of binary *M*N and ternary $Hf_xM_{1-x}N$ crystals. We discuss the dependence of E_{form} on the crystal structure and on the distribution of Hf and *M* in the metal sublattice. The calculated mechanical properties of *M*N (rather than $Hf_xM_{1-x}N$) very well correlate with measured mechanical properties of a–Hf*M*SiBCN. The driving force towards N incorporation, monotonically decreasing with increasing periodic-table group number of *M* according to the calculated E_{form} of *M*N, very well correlates with measured electrical conductivity and extinction coefficient of a–Hf*M*SiBCN. Second, we use *ab–initio* molecular dynamics to model the a–Hf*M*SiBCN materials of experimental compositions and densities themselves. The calculated band gap, localisation of states around the Fermi level and bonding preferences of the *M* element (in particular the tendency of the *M* element to bind with N) also correlate with the measured increasing metallicity with respect to the periodic-table group number of *M*, and confirm the possibility of predicting the trends of characteristics of a–Hf*M*SiBCN using those of *M*N. Third, we study the a–Hf*M*SiBCN properties as a function of each other, and we identify an optimum target composition (B_4C covered by 15% Hf, 5% Ta and 15–20% Si) leading to hard (>20 GPa) films with relatively high conductivity at a given extinction coefficient and vice versa. The results are important for the design of hard, conductive and/or transparent high–temperature coatings.

B5-7 Thermal Stability of Nanostructured TiAl(Si,B)N Coatings Deposited by HiPIMS with Positive Pulses, ***Álvaro Méndez Fernández (alvaro.mendez@nano4energy.eu)***, *J. Santiago, I. Fernández-Martínez, A. Wennberg,* Nano4Energy SL, Spain; *M. Panizo-Laiz,* Universidad Politecnica de Madrid, Spain; *M. Monclús, J. 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

B5-8 Tuning Fracture Characteristics of Superhard Tm Carbide Coatings by Nitrogen Alloying, ***Thomas Glechner (thomas.glechner@tuwien.ac.at)***, *R. Hahn,* TU Wien, CDL-SEC, Austria; *D. Primetzhofer,* Uppsala University, Sweden; *H. Zaid, S. Kodambaka,* University of California Los Angeles, USA; *D. Holec,* Montanuniversität Leoben, Austria; *P. Mayrhofer,* TU Wien, Austria; *S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *H. Riedl,* TU Wien, CDL-SEC, Austria

Cubic transition metal (TM) nitrides and carbides are well-established protective coating materials due to their specific combination of remarkable thermo-mechanical properties but also chemical inertness. Nevertheless, their unique bonding nature – in particular combination of strong covalent and metallic bonds – is also the origin for their lack in fracture tolerance compared to metals and metallic alloys.

To overcome these limitations the formation of carbonitrides by substitutional alloying of the non-metallic sublattice exchanging C with N atoms is an interesting approach. The so obtained adjustment of the valence electron concentration has strong consequences on intrinsic material properties, e.g. Young's modulus, melting temperature, phase decomposition as well as fracture toughness. Therefore, within this study the impact of non-metallic alloying – exchanging C with N atoms – has been explored systematically for two model systems, TaC and HfC, respectively. TM-C thin films were deposited via non-reactive magnetron sputtering, while ternary TM-C-N coatings have been deposited in mixed Ar/N2 atmospheres. We combined ab initio calculations (DFT by VASP) with experimental studies to correlate predicted properties such as fracture tolerance enhancement with increasing VEC (due to nitrogen alloying). The mechanical characteristics have been assessed by micro cantilever bending, pillar compression or splitting tests in correlation to well-established nanoindentation to gain a comprehensive view on the mechanical characteristics – also at elevated temperatures. Furthermore, detailed insights on the phase formation during coating synthesis (also considering influence of structural defects such as vacancies), and hence morphology as well as chemical composition has been studied via ERDA and SEM/HR-TEM, respectively.

B5-9 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. 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.

B5-10 Dislocation Confinement in Core-Shell Nanostructures: A Molecular Dynamics Study, ***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 roles of the core material and core-shell interface structure, along with supporting stress calculations.

B5-11 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. 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. 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.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B6

Interplay Between Computational and Experimental Design of Coatings and Processes I

B6-1 Data-driven Assessment of Chemical Vapor Deposition of MoS2: a Meta-Study Based on Published Growth Experiments*, A. Costine,* University of Virginia, USA*; P. Delsa,* Lousiana School for Math, Science, and the Arts, USA*; T. Li,* ***Petra Reinke (pr6e@virginia.edu)****, P. Balachandran,* University of Virginia, USA

Transition metal dichalcogenides (TMD) are highly coveted materials with unique properties. The growth of high quality two-dimensional TMD monolayers is critical for enabling key technological solutions. Proof-of-concept devices can be assembled using micromechanical exfoliation from multilayer material, but this is a prohibitively slow process. Another challenge remains the control and minimize defects including point defects and grain boundaries, which have an outsized impact on electronic properties. It is therefore necessary to understand the complex parameter space of TMD monolayer growth, and then adapt, and extrapolate to conditions suitable for materials integration. For this purpose we asked a deceptively simple question: how much can we learn from the published data on MoS_2 growth with chemical vapor deposition from solid precursors (MoO_3 and S)? Can machine learning predict the processing conditions resulting in single layer MoS_2? [1] This work consists of two parts, which are equally important, and combine experimental and computational expertise: firstly, the data mining of the literature, assessment of the experimental descriptions, and isolation of suitable and reliable parameters which can be entered into ML algorithms, and secondly, testing and identification of suitable ML approaches. This is a non-trivial problem because the processing space is vast and lack of *a priori* guidelines impedes rapid progress. Starting from the literature data on MoS_2 thin films a database is manually constructed from 82 publications. Unsupervised and supervised machine learning methods are used to learn from the compiled data by extracting trends that underlie the formation of MoS_2 monolayers. Design rules are uncovered that establish the phase boundaries classifying monolayers from other possible outcomes such as incomplete layers, and multilayer, which offers future guidance of CVD experiments. Ideally the design rules can be connected to fundamental processes of growth, but the data sparsity and missing critical information did not allow us to take this path. The presentation will focus on the challenges of constructing a suitable database, the statistical challenges incurred due to its relatively limited size, and offers a view into the wealth of information which can be accessible from a combination of experiment and ML in advancing complex growth processes. An important conclusions remains a call to experimentalists to report failed experiments, which are an important aspect in building an informative map of the multidimensional growth parameter space. [1] A. Costine, P. Delsa, T. Li, P. Reinke, P.V. Balachandran, J. Appl. Phys. **128** 235303 (2020)

B6-2 Kinetic Monte Carlo Simulations of Residual Stress Evolution*, Eric Chason (eric_chason@brown.edu), A. Bower,* Brown University, USA

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.

B6-3 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 »34%, and that they contain many unbonded N_2 molecules at N contents above »42%. 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 Si-C-N [2]. Increasing Si/C ratio from 0 to 100% leads to increasing maximum achievable content of bonded N: from 34% to 57% in the case of no N_2 formation and from 42% to 57% when the amorphous network forms in parallel to N_2 formation. The evolution of experimentally achieved N contens in Si-C-N films prepared by reactive magnetron sputtering is in an excellent agreement with the prediction. Further analysis shows that while the N_2 formation at a given total N content and in a wide range of Si/C ratios is given only by the packing factor, the lowest-energy packing factor increases with Si/C. 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.

[1] J. Houska, Acta Mater. 174, 189-194 (2019)

[2] J. Houska, ACS Appl. Mater. Inter. 12, 41666-41673 (2020)

B6-4 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. 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.

References

[1] K. Balasubramanian, et al., Valence electron concentration as an indicator for mechanical properties in rocksalt structure nitrides, carbides and carbonitrides, Acta Mater. 152 (2018) 175–185.

[2] T. Glechner, et al., Assessment of ductile character in superhard Ta-C-N thin films, Acta Mater. 179 (2019) 17–25.

B6-5 INVITED TALK: 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. 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.

B6-7 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. Sangiovanni,* Linköping University, Sweden*; M. Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; P. 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.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B7

Plasma Surface Interactions, Diagnostics and Growth Processes

B7-1 INVITED TALK: Energy and Momentum Fluxes at Plasma Processing of Materials*, Holger Kersten (kersten@physik.uni-kiel.de),* *T. Trottenberg, M. Klette, L. 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,

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[1] **2020 Student Award Finalist**

measurements are compared with TRIM simulations for different experimental discharge conditions.

B7-3 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.

References

[1] A. Goehlich et al., *Nucl. Instrum. Methods,***179**, 351 (2001)

[2] C. Bundesmann et al., *Contrib. Plasma Phys.*, **55**, 737 (2015)

[3] T. Trottenberg und H. Kersten, *Plasma Sources Sci. Technol.*,**26**, 055011 (2017)

[4] A. Spethmann et al., *Phys. Plasmas*, **24**, 093501 (2017)

[5] J. Biersack und L. Haggmark, *Nucl. Instrum. Methods*, **174**, 257 (1980)

B7-4 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.

B7-5 Oxygen Diffusion Barrier On Interfacial Layer Formed With Remote Nh3 Plasma Treatment*, **Fu-Yang Chu (xxmoon666@gmail.com)**, K. Chang-Liao, D. Ruan, H. Yeh, S. Yi, Y. 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.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B8

HiPIMS, Pulsed Plasmas and Energetic Deposition

B8-1 INVITED TALK: 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.

B8-3 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.

B8-4 The Single-Shot Spatial-Resolved OES of the Spoke in Non-Reactive HiPIMS*, Marta Šlapanská (slapanska@physics.muni.cz), M. Kroker, J. Hnilica, P. Klein, P. Vašina,* Masaryk University, Czechia

The rotating plasma patterns, also known as ionisation zones or spokes, firstly observed in non-reactive high power impulse magnetron sputtering discharges (HiPIMS) are at certain conditions present in direct current magnetron sputtering (dcMS) and radio frequency magnetron sputtering discharges (rfMS) as well. The spokes are investigated due to their high impact on the deposition process and sputtered species' transport. To better understand the spoke phenomena, it is necessary to acquire comprehensive data of the plasma parameters inside the spoke; however, in HiPIMS, preferably by non-invasive diagnostics.

This contribution presents the non-invasive spatial-resolved optical emission spectroscopy (OES) of the plasma inside the spoke conducted in non-reactive HiPIMS discharge. The pulses have a duration of 100 µs with a repetition rate of 5 Hz. The 3-inch titanium target was utilised. The experiment was run at argon pressures of 0.4 Pa, 1.0 Pa, and 1.6 Pa to investigate both triangular and round spokes.

The fast photodiode and the cylindrical probe were used to capture and determine the passing spoke position. The photodiode's signal and the probe signal were synchronised with the optical emission spectrum acquisition by the intensified charge-coupled device (ICCD) detector with a gate time of 100 ns. By processing these three signals and creating the normalised time scale for each spoke, the unified spoke (UNI-spoke) has been created. Consequently, the evolutions of the selected emission lines can be shown within the UNI-spoke.

The spatially resolved emissions of Ar atom and ions and Ti atoms and ions spectral lines were investigated within the UNI-spoke. The spatial resolved OES measurements have shown that the Ar and Ti atoms and ions spectral lines have the characteristic evolution of a specific species' intensity and is the same for all observed spectral lines of this species within the spoke independently of applied pressure. The Boltzmann plot method was utilised to determine the excitation temperatures within the UNI-spoke. The excitation temperatures obtained using the Ar ions and Ti atoms and ions are 13000 K, 8000 K, and 19000 K. The ionisation fraction has been calculated from the selected spectral lines of titanium atom and ion. The ionisation fraction reaches approximately 40%, and its evolution and excitation temperature evolutions remain constant in the margin of standard error within the UNI-spoke for all investigated working pressures.

This research was supported by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA19-00579S funded by the Czech Science Foundation.

B8-5 Understanding and Influencing the Energy Delivered to the Film in Bipolar HiPIMS*, Tomas Kozak (kozakt@ntis.zcu.cz), A. Pajdarova, J. Capek,* University of West Bohemia, Czech Republic*; M. Cada, Z. Hubicka,* Institute of Physics, Academy of Sciences of the 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.

References

[1] Sarakinos K, Alami J and Konstantinidis S, *Surf. Coat. Technol.***204** (2010) 1661

[2] Bradley J W and Welzel T *J. Phys. D: Appl. Phys.***42** (2009) 093001

[3] Santiago J A, Fernández-Martínez I, Kozák T, Capek J, Wennberg A, Molina-Aldareguia J M, Bellido-González V, González-Arrabal R and Monclús M A *Surf. Coat. Technol.* (2019) **358** 43

B8-6 The Use of HiPIMS with Positive Pulses to Tailor Film Ion Assistance and the Resulting Microstructural Properties*, Ivan Fernandez (ivan.fernandez@nano4energy.eu), J. 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.

L. Velicu et al., Surface & Coatings Technology 359 (2019) 97.

J. Keraudy et al., Surface & Coatings Technology 359 (2019) 433.

N. Britun et al., Appl. Phys. Lett. 112 (2018) 234103.

F. Avino et al., Plasma Sources Sci. Technol. 28 (2019) 01LT03.

J.A.Santiago, I Fernandez-Martinez et al., Surface & Coatings Technology 358 (2019) 43.

B.Wu et al., Vacuum 150 (2018) 216.

G. Eichenhofer, I Fernandez-Martinez et al., UJPA 11(3), (2017) 73

B8-7 Measurements and Modeling of Residual Stress in Sputtered Nitride Films: Dependence on Growth Rate and Gas Pressure*, Zhaoxia Rao (zhaoxia_rao@brown.edu), 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.

B8-9 Wafer-scale Metallic Nanotube Arrays (MeNTAs): Fabrication and Application*, Alfreda Krisna Altama (d10904819@mail.ntust.edu.tw)*, *J. Chu,* National Taiwan University of Science and Technology, Taiwan*; A. Purniawan, S. Wicaksono,* Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia

Sputter deposition has been widely used in the manufacturing of high-performance on-chip interconnect. The metal connecting lines at each layer can be formed by filling trenches and vias in the interlayer dielectrics (ILD). High-power impulse magnetron sputtering (HiPIMS) techniques as a novel ionized physical vapor deposition (IPVD) technology has been developed in view years for metallization in integrated circuits and nanostructures manufacturing with high aspect ratio (AR). HiPIMS is an IPVD technique based on pulsed power technology where the peak power exceeds the time-averaged power by roughly two orders of magnitude so. HiPIMS deposition offers a route for depositing uniform coatings onto complex-shaped substrates and structures. In this research, we formed high AR trenches using photoresist lithography on silica wafers. The deposition process was performed using a 6 inch diameter metallic alloy target using HiPIMS and DCMS. The plasma properties were measured using a Langmuir probe at a distance of 70 mm from the target face and below the racetrack. The measurement results show that the plasma produced by HiPIMS has a higher ion and electron density value compared to DC plasma. We consider the experimental condition of high density plasma as the favorable process condition for the trench deposition. In this condition, the film was deposited at different power and working pressure. The cross-sectional pictures performed by scanning electron microscopy (SEM) shows that the film had good trench step coverage and amorphous structure. Furthermore, the results of this study can be used as a reference for trench filling and the manufacture of nanostructures with high aspect ratio using HiPIMS.

B8-10 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. Sugumaran, P. 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.

B8-12 On the Influence of the Micropulse on Nb Thin Films Deposited by MPPMS and DOMS: A Comparative Study*, Y.G. Li (ygli@dlut.edu.cn)*, *Z. Jiang, H. Yuan, N. Pan, M. Lei,* Dalian University of Technology, China

Nb thin films deposited by modulated pulsed power magnetron sputtering (MPPMS) and deep oscillation magnetron sputtering (DOMS) were comparatively studied under similar average power by controlling the micropulse duty cycle. It was found that DOMS discharge showed both higher discharge peak current and peak voltage, time delay between the current and voltage was much shorter with respect to a MPPMS discharge. All Nb thin films were observed with Nb(110) preferred orientation and compact columnar structure with DOMS Nb thin films hardness with higher hardness and elastic modulus. The increase of micropulse duty led to the gradually movement of Nb(110) to the high scattering angle direction, meanwhile the DOMS Nb(100) diffraction peaks were all on the left of MPPMS Nb(110). An anomalous increase could be observed for compressive residual stress s of Nb thin films for both techniques. The anomalous increase in s also led to the deterioration of scratch adhesion. Despite, the grain sizes of DOMS Nb thin films were all smaller than MPPMS Nb thin films, s in DOMS Nb thin films generated by the adatom diffusion and ion irradiation still overwhelmed the tensile stress generated by the volume shrinkage of the growing grains. The special afterglow of DOMS in microsecond time scale gave a new dimension controlling the grown thin films.

B8-13 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. Aksakalli,* Atatürk University, Turkey*; B. Gumus, E. Tan,* Aselsan Inc., Turkey

Ternary and quaternary hard coatings based on carbonitrides of transition metals with amorphous matrix have many advantages; these have 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 and tribological properties were investigated by adding Nb and Zr transition elements to TiBCN based coatings. The coatings were deposited on 4140 tool steel and the silicon wafer. TiBCN-based coatings with high adhesion and dense microstructure were synthesized with CFUBMS (Pulsed-dc+HiPIMS) using Cr, Ti, TiB$_2$, Nb, Zr targets and Ar, N$_2$, C$_2$H$_2$ gases. Microstructural properties of the coatings were obtained from the coatings on the silicon wafer and 4140 steel using SEM, XRD, and XPS. The mechanical properties of coatings synthesized on 4140 steel base materials have been characterized by Microhardness and Scratch tests. The hardness and adhesions of TiBCN-based coatings, which were grown by adding Nb and Zr, respectively on Cr:CrN graded structure (~200nm) as the transition layer, were optimized depending on the process parameters. Scratch test results showed that the adhesion strength varied as a function of the Nb and Zr target negative bias voltages. The highest adhesion strength was obtained as Lc:80N at -800V with adding Zr. In the case of the Nb adding, the highest adhesion strength was obtained as Lc:57N. Adhesion and microhardness test results showed that the utilization of bias-voltage with HiPIMS to the targets and pulsed-dc to the base material was the most effective coating parameter in the critical load and the hardness properties. Friction coefficients were observed as the lowest value, μ≈0.163 in TiBCN-Nb coatings, while it was observed as μ≈0.337 in TiBCN-Zr coatings.

Keywords: TiBCN:Zr/Nb, Adhesion, Microhardness, CFUBMS-HiPIMS,

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session BP

Hard Coatings and Vapor Deposition Technologies (Symposium B) Poster Session

BP-1 Investigation of Ionized Density Fraction in Reactive Hipims*, Katarína Bernátová (kbernatova@mail.muni.cz),* Masaryk University, Czechia

In High Power Impulse Magnetron Sputtering (HiPIMS), high plasma density is achieved by focusing the applied power into the short pulses with a duty cycle of around 2%. Discharge properties, such as a density of sputtered species, are strongly nonlinearly dependent on the reactive gas supply influencing properties as well as the stoichiometry of the deposited layers.

In our study, the effect of nitrogen gas admixture on the temporal evolution of discharge current, voltage, pressure, and ionized density fraction of sputtered species in the HiPIMS process is analyzed. The ionized density fraction is estimated from the sputtered titanium atom and ion absolute ground state number densities both near the target surface and near the substrate region. For the determination of sputtered species density, a well-established spectroscopic method based on effective branching fractions was utilized.

Three regimes within the hysteresis curve were investigated and compared: metal, transition, and compound regime. In both, target and substrate regions, after the pulse ignition, the nonzero value of titanium atom density is always detected, indicating the presence of residual particles originating from the preceding pulse. Near the target, in the metal regime, the Ti atom density increases through the pulse, causing enhanced argon rarefaction near the target. From the quarter of the pulse, the concentration of Ti ions is always higher than Ti atoms and the ionized density fraction is most pronounced around middle of a pulse. With the nitrogen gas addition, the ionized density fraction increases, despite the overall Ti atom and ion densities decrease. In the substrate region, the evolution of Ti atom and ion densities changes, as the distance from the target is increased, therefore the transport time of particles to the measured area is higher. Furthermore, when operating in the transition and compound regime the pressure increases, resulting in even stronger delay of particle transport. Due to argon rarefaction near the target in the metal regime, Ti atoms travel towards the substrate where they are accumulating over the second half of the pulse. In contrast, in the transition and compound regime, the sputtering is not effective, and the transport is strongly delayed, therefore the Ti atom and ion densities are decreasing through the pulse. Here, the ionized density fraction is again enhanced with nitrogen gas admixture.

BP-2 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. 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-3 Properties of Boron Carbide Thin Films Deposited by Pulsed Laser Deposition*, Falko Jahn (falko.jahn@hs-mittweida.de), S. Weissmantel,* Laserinstitut Hochschule Mittweida, Germany

Boron carbide is the third hardest known material behind diamond or ta-C and cubic boron nitride (c-BN). Intensive contact of diamond or ta-C with ferrous materials lead to carbide formation and thus a chemical wear of the layer. Because of this, films of diamondlike carbon are not suited for applications e.g. as wear protective layers in steel processing. For cubic boron nitride on the other hand there is yet no successful deposition method that meets industrial requirements.

Boron carbide could be a promising compromise for these applications. Indeed, it doesn't reach the hardness values of ta-C or c-BN, but due to its better thermal and chemical stability it is suitable for ferrous materials.

Using Pulsed Laser Deposition (PLD) super hard coatings of boron carbide have been produced with a resulting indentation hardness up to 47 GPa which almost reaches the highest values reported so far. The substrate temperature during deposition has been varied between room temperature and more than 500°C. That temperature has been found to have the most impact on the mechanical properties of the coatings. The influence of the ablation fluence on the mechanical properties is shown although it is less significant. The produced layers show good film adherence properties but a very bad surface quality at layer thicknesses sufficient for practical applications and which is characterized by too many particulates and droplets.

Following, research results of applying an alternative boron carbide target are presented. This target is produced by depositing a several ten microns thick boron carbide layer on a steel substrate using PLD. The as deposited film is subsequently used as the new target for the deposition process and results in boron carbide thin films with a significantly better surface quality. Comparing these B_4C films to the first deposited ones resulting from commonly used targets it can be shown that both number and size of the droplets decrease.

BP-4 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-5 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).

[1] J. Houska and T. Kozak, J. Appl. Phys. 121, 225303 (2017)

[2] J. Houska and T. Kozak, Surf. Coat. Technol. 392, 125685 (2020)

BP-6 Phase Formation, Thermal Stability and Mechanical Properties of Nb-B-C Thin Films Prepared by Magnetron Sputtering Using a Combinatorial Approach*, Stanislava Debnarova (408573@mail.muni.cz), P. Soucek, V. Bursikova,* Masaryk University, Czechia*; S. Mraz, M. Hans, J. Schneider, D. Holzapfel,* RWTH Aachen University, Germany*; P. Vasina,* Masaryk University, Czechia

The performance and lifetime of a tool can be significantly improved by the use of an appropriate protective coating. The most commonly used materials for these applications are ceramic-based coatings, favoured due to their high hardness. However, these coatings are inherently brittle which enables the spreading of cracks and coating failure. Therefore, new materials are being explored, which would combine the hardness of ceramics with a degree of ductility.

Ab-initio calculations have predicted that such a combination of properties could be present in a crystalline X_2BC material where X is a transition metal such as Mo, Ti, V, Zr, Nb, Hf, Ta or W [1]. Out of this group, only crystalline Mo_2BC has been successfully prepared and studied so far. There have been attempts to prepare a W2BC phase but these remain unsuccessful due to the near-zeroenthalpy of formation of this material. However, these studies have shown that the X-B-C system exhibits interesting mechanical properties even in an amorphous state [2, 3].

This study focuses on the Nb-B-C system as Nb_2BC is predicted to have a lower enthalpy of formation. The coatings have been prepared by magnetron sputtering from 3 targets using a combinatorial approach. A wide range of compositions has been studied and evaluated in regard to their structure and mechanical properties. As thermal and oxidation stability is a vital requirement for protective coatings, the studied coatings have been annealed up to 900°C in argon and up to 1000°C in an Ar/O_2 gas mixture. The study examines the effect of annealing on the structure and mechanical properties of the coatings.

References

[1] H. Bolvardi, J. Emmerlich, M. To Baben, D. Music, J. Von Appen, R. Dronskowski, J.M. Schneider, Systematic study on the electronic structure and mechanical properties of X2BC (X = Mo, Ti, V, Zr, Nb, Hf, ta and W), J. Phys. Condens. Matter 25 (4) (2013) 045501

[2] S. Debnárová, P. Souček, P. Vašina, L. Zábranský, V. Buršíková, S. Mirzaei, Y. Pei, The tribological properties of short range ordered W-B-C protective coatings prepared by pulsed magnetron sputtering, Surface and Coatings Technology (2019) 357 364-371

[3] S. Debnárová, L. Zábranský, P. Souček, V. Buršíková, P. Vašina, Study of W-B-C thin films prepared by magnetron sputtering using a combinatorial approach, International Journal of Refractory Metals and Hard Materials (2019) 85

BP-7 Mechanical and Tribological Performance of V-C-N Coatings Deposited by RF Magnetron Sputtering*, Akram Alhussein (akram.alhussein@utt.fr),* Universite de Technologie de Troyes (UTT), France*; L. Aissani,* Khenchela University, Larbi Ben M'Hidi University, Algeria*; C. Nouveau,* CER Arts et Metiers Paris Tech, 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. This work aims to evaluate 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 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 the desirable coatings (good adhesion and performance). It has been found that compared to the VN system, the VC-N films showed a smooth surface and the films deposited at 0.06 Pa presented the best mechanical and tribological 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. Multiple 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.*

References:

[1] Linda Aissani, Akram Alhussein, Corinne Nouveau, Lamia Radjehi, Issam Lakdhar, Elia Zghei, Evolution of microstructure, mechanical and tribological properties of vanadium carbonitride coatings sputtered at different nitrogen partial pressures, Surf. Coat. Tech. 374 (2019) pp. 531-540.

[2] Linda Aissani, Akram Alhussein, Corinne Nouveau, Laala Ghelani, Mourad Zaabat, Influence of film thickness and $Ar-N_2$ plasma gas on the structure and performance of sputtered vanadium nitride coatings, Surf. Coat. Tech. 378 (2019) 124948.

BP-8 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. 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.

[1]. R.W. Grimes et al. Nature Materials 7 (2008) 683.

[2]. Xinghang Zhang et al. Prog.Mat. Sc. 96 (2018) 217.

[3]. A.J. Van Vuuren, V.V. Uglov et al. Phys. Status Solidi C 13 (2016) 886.

[4]. V.V. Uglov, G. Abadias et al. Sur. Coat. Technol. 344 (2018) 170.

[5]. V.V. Uglov, G. Abadias et al. Nucl. Instr. Meth. Phys. Res. 435 (2018), p. 228.

BP-9 Physical and Mechanical Properties of Cr-Al-N and Cr-v-N Ternary Systems*, **Ahlam Belgroune (ahlam.belgroune@utt.fr)**,* University of Technology of Troyes, France*; L. Aissani,* University of Abbes Laghrour, Algeria*; A. Alhussein,* University of Technology of Troyes, France

In the present work, ternary systems (Cr-Al-N and Cr-V-N) thin films were deposited on steel substrates by magnetron sputtering process. The effect of Al and V additions on the properties of the binary Cr–N system was evaluated. The morphology and surface topography of the coatings were investigated. The hardness and elastic modulus were measured by nanoindentation and the friction coefficient was determined by pin-on-disc tribometer.

We found that Al addition improved the mechanical properties of the Cr–N system (H= 27 GPa, E= 304 GPa) presenting a dense structure. Contrary, the V addition deteriorated the mechanical properties of films presenting rough surfaces (H= 10 GPa, E= 280 GPa). The friction coefficient of the CrAlN films slightly increased with rising Al percentage and varied between 0.42 and 0.61. For the Cr-V-N coatings, the friction coefficient was lower than those obtained for Cr-Al-N and Cr-N films. The wear resistance of Cr-Al-N and Cr-V-N coated steel substrates decreased with increasing Al and V contents.

Keyword: *Magnetron sputtering; Cr-Al-N; Cr-V-N; Cr-N; Hardness; Wear.*

BP-10 Understanding Residual Stress in Thin Films: Analyzing the Stress Evolution Using a Kinetic Model for Ag, Cu, Ni, Fe, Ti, and Cr*, **Zhaoxia Rao (Zhaoxia_Rao@brown.edu)**, S. Berman,* Brown University, USA*; D. Depla ,* Ghent University, Belgium*; E. Chason ,* Brown University, USA

An analytical model for the evolution of residual stress in polycrystalline thin films is used to analyze numerous previously-reported wafer curvature measurements obtained for a variety of processing conditions and materials (Ag, Cu, Ni, Fe, Ti Cr). The model includes the effects of film growth kinetics by considering stress-generating mechanisms at the grain boundary that forms between adjacent grains as well as subsurface grain growth.Non-linear least-squares fitting is used to obtain a set of parameters for each material.Some of the parameters are material-dependent and are made to be the same for all the data for each material independent of the processing conditions; others are allowed to change with the processing conditions.The dependence of the fitting parameters on the material and processing conditions is compared with the behavior expected from the physical mechanisms in the model.

BP-11 Effect of Target Poisoning Ratios on the Fabrication of TiO$_X$ Coatings Using Superimposed HiPIMS and MF System*, W. Chen,* Ming Chi University of Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*; **Jyh-Wei Lee (jefflee@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

Titanium oxide film is characterized by its clean surface, sterilization, good abrasion resistance and good corrosion resistance, which make it become a functional coating with a wide range of applications.The superimposed high power impulse magnetron sputtering (HiPIMS) and mid-frequency (MF) system (superimposed HiPIMS-MF) is a relatively new deposition system, which adds MF pulses to the off-time of the HiPIMS for higher deposition rate.In this study, a superimposed HiPIMS-MF system was used to fabricate the titanium oxide films. During the deposition process, a plasma emission monitoring (PEM) system was used to feedback control the target poisoning ratio of Ti target. Titanium oxide (TiOx) films grown at five different target poisoning ratios were deposited on single crystal silicon wafer, glass slide and AISI304 stainless steel plate substrates. The microstructure of thin film was examined by a field emission scanning electron microscope. The crystalline structure of thin film was analyzed by an X-ray diffractometry. The optical transmittance measurement of thin films was performed with a UV–vis spectrophotometer. The hardness, adhesion and tribological properties of TiOx films were evaluated by nanoindenter, scratch test and pin-on-disk wear test, respectively. The corrosion resistance of TiOx films in 0.1 M H_2SO_4 aqueous solution was examined by an electrochemical workstation. The influence of target poisoning ratios on the deposition rate, microstructure, transmittance, hardness, adhesion, wear and corrosion resistance of TiOx films were studied in this work.

BP-12 The Role of Oxygen Flow Rate on the Structure and Stoichiometry of Cobalt Oxide Films Deposited by DC Reactive Sputtering*, **Nilton Francelosi Azevedo Neto (nilton.azevedo@unesp.br)**, L. Affonco,* São Paulo State University, Brazil*; C. Stegemann, D. Marcel Gonçalves Leite ,* Aeronautics Institute of Technology, Brazil*; J. Humberto Dias da Silva ,* São Paulo State University, Brazil

The cobalt oxide films were grown on amorphous silica (a-SiO$_2$) in order to investigate the influence of the oxygen gas supply on the stoichiometry, structure and orientation texture of polycrystalline cobalt oxide films. The films were grown by direct current (DC) reactive magnetron sputtering using a metallic Co target and different oxygen partial pressures by controlling the inlet flow rate (0.5 to 5.0 sccm) over a dominant argon atmosphere (40 sccm) keeping constant the deposition power (80 W) and the total working pressure (0.67 Pa). X-ray diffraction results evidence a strong influence of the oxygen flow over the film's stoichiometry and structure, where low oxygen flows (< 2.0 sccm) favor the formation of the rocksalt CoO phase, while higher oxygen flows (>2.5 sccm) favor the spinel Co_3O_4 phase formation. The coexistence of monoxide and tetraoxide phases is observed only for 2.5 sccm oxygen flow condition. Strain and orientation texture effects related to the oxygen partial pressure are also observed and discussed. Computer simulations indicate that low oxygen flow (<2.0 sccm) occur in the metallic regime, while higher oxygen flow favor the poisoned regime. Consistent with the simulations, cobalt emission (Co^I = 340.5 nm) from the plasma show a significant decrease while the oxygen emission (O^I = 777.3 nm) is significantly increased when the oxygen flow is increased.

BP-13 e-Poster Presentation: Bipolar HiPIMS for Tailoring Ion Energies in Thin Film Deposition*, **Daniel Lundin (daniel.lundin@liu.se)**, R. 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-14 Nb-C Thin Films Prepared by DC-MS and HiPIMS: Synthesis, Structure and Tribo-mechanical Properties*, **Neus Sala (neus.sala@iqs.url.edu)**, M. Abad,* Institut Químic de Sarrià, Universitat Ramon Llull, Spain*; J. Sánchez-López,* Instituto de Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, Spain*; J. Caro,* Eurecat, Centre Tecnològic de Catalunya, Spain*; C. Colominas,* Institut Químic de Sarrià, Universitat Ramon Llull, Flubetech S.L. , Spain

Nanostructured Nb-C thin films were prepared by direct current magnetron sputtering (DC-MS) and via high power impulse magnetron sputtering (HiPIMS). The films have been characterized in depth by XRD, GIXRD, SEM, AFM, EPMA and Raman spectroscopy. The mechanical properties have been measured by means of nanoindentation and the tribological properties by pin-on-disk test in ambient air.The wear tracks and the ball scars were analyzed by Raman spectroscopy in order to elucidate the tribochemical reactions appearing at the contact and to determine the wear mechanism present in each specimen type. The obtained DC samples were very dense with tunable mechanical and tribological properties depending on the amorphous carbon (a-C:H) content incorporated in the coatings. The crystal and phase composition changed from pure nanocrystalline (formed by Nb_2C and NbC phases) to nanocomposite structure (NbC/a-C:H). The samples prepared by HiPIMS developed a marked columnar morphology with a NbC/a-C:H nanocomposite structure. Hardness values range from 11 to 20 GPa depending on the deposition technique and the amount of a-C:H soft phase present in the samples. The tribological properties of all the coatings were remarkably good when the carbon content was around 50 at. %. The formation of alubricant sp^2-rich C tribofilm between the ball and the coating during the pin on disk tests was observed by Raman spectroscopy, preferentially in the samples prepared by HiPIMS technique with higher C content.

BP-15 Impact of Stacking Sequence with InWZnOx/InWZnOy Bilayer Conductive Bridge Random Access Memory*, **Chih-Chieh Hsu (cchsu.06g@g2.nctu.edu.tw)**, P. Liu, K. Gan, D. Ruan, Y. Chiu,* National Chiao Tung University, Taiwan*; S. Sze,* Naitonal Chiao Tung University, Taiwan

This work investigates the hybrid oxide devices with different stacking sequence of Cu/TiW/IWZOx/IWZOy/Pt memristor. Typical bipolar resistive switching can be observed in all CBRAM devices. The hybrid oxide device shows good non-volatile memory characteristics, such as endurance cycle, low operation voltage, data retention time and stable on/off ratio. The oxide stacking sequence can improve the endurance cycles to 104, retention time to 104s and more resistance state uniformity. These results have given a prospect for simple and fast method to optimize the oxide-based memory device.

Fundamentals and Technology of Multifunctional Materials and Devices

Room On Demand - Session C1

Optical Materials: Design, Synthesis, Characterization, and Applications

C1-1 INVITED TALK: 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.

References

[1] Alain C. Diebold, Anthony Antonelli, and Nick Keller, Perspective: Optical measurement of feature dimensions and shapes by scatterometry, APL Mat. **6**, (2018), 058201. doi: 10.1063/1.5018310.

[2] Sonal Dey, Alain Diebold, Nick Keller, and Madhulika Korde, Mueller matrix spectroscopic ellipsometry based scatterometry simulations of Si and Si/SixGe1-x/Si/SixGe1-x/Si fins for sub-7nm node gate-all-around transistor metrology, Proc. SPIE 10585, Metrology, Inspection, and Process Control for Microlithography XXXII, 1058506 (6 June 2018); doi: 10.1117/12.2296988

[3] Madhulika Korde, Subhadeep Kal, Cheryl Pereira, Nick Keller, Aelan Mosden, Alain C. Diebold, Optical Characterization of multi-NST Nanowire Test Structures using Muller Matrix Spectroscopic Ellipsometry (MMSE) based scatterometry for sub 5nm nodes, Proc. SPIE Metrology, Inspection, and Process Control for Microlithography XXXIII, (2019).

C1-3 Optical Probing of Vanadium Oxide Thin Film Composition and Phase*, 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.

C1-4 INVITED TALK: 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.

C1-6 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.

References: [1] T. Terasako *et al.*, Thin Solid Films 677 (2019) 109-118. [2] S. Shi *et al.*, J. Appl. Phys. 109 (2011) art. no.103508. [3] C. Soci *et al.*, Nano Lett. 7, (2007) 1003-1009.

C1-7 IR Mirror Coating for Evacuated Thermal Collectors: Design and Optical Characterization*, Daniela De Luca (daniela.deluca@na.isasi.cnr.it),* UniNa and CNR-ISASI, Italy*; E. Di Gennaro,* UniNa Università degli studi di Napoli "Federico II", Italy*; C. D'Alessandro, A. Caldarelli, D. De Maio, E. Gaudino,* UniNa and CNR-ISASI, Italy*; M. Musto,* UniNa Università degli studi di Napoli "Federico II", Italy*; R. Russo,* CNR-ISASI, Italy

Capturing solar radiation as high-temperature heat in solar thermal devices is challenging, especially if flat panels are used instead of concentrating systems. While a high-vacuum encapsulation helps suppressing the conductive and convective losses, the radiative term rise with temperature, according to the Planck's law of blackbody radiation.

To reduce that loss and increase the panel efficiency, we propose an optimized infrared mirror coating. The underlying mechanism is based on the cold-side external photon recycling: the mirror has to be highly reflective in the mid-IR region, to reflect and thus recapture infrared emission back at the absorber. On the contrary, in the visible and near-IR region it has to be highly transparent, to transmit the incident solar power. To obtain its best configuration, optical simulations have been performed and results showed that the best configuration is reached if a rugate filter design is used. Rugate filters are made of alternating layers of dielectric materials, with a continuous and periodic variation of the refractive index as a function of optical thickness.

Previous theoretical [1] and experimental works [2] show that the continuous profile of a rugate filter can be approximated by a reduced number of layers with steps in the refractive indices. Here, we extend prior works and include a realistic set of materials for ease of fabrication.

The Physical Vapor Deposition (PVD) technique has been used for thin films deposition of Si-based materials, i.e. Silicon Oxides, Oxynitrides, and Nitrides. Their strong dependence on the environmental conditions during deposition (pressure, gases flux,...) allow us to obtain different refractive indices from the same cathode of Si, meeting the limitation of most deposition tools on the number of target available.

We present here the optical characterization of the produced samples, including measurements performed with the ellipsometer, integrating sphere connected to an optical spectrum analyser, profilometer, and FTIR spectroscope. This analysis is useful to deeply study all the additional parameters (thickness, roughness, refractive index coupling and matching) that can interfere with the optical and physical properties of the materials. Preliminary results on multilayer structures are also shown and compared, with the aim of choosing the most promising ones for the realization of the final structure.

[1] Baumeister, P., Appl. Opt.25,2644–2645 (1986), doi: 10.1364/AO.25.002644

[2] De Luca, D. et al., Proc. SPIE 11496, New Concepts in Solar and Thermal Radiation Conversion III, 1149605 (2020), doi:10.1117/12.2574604

Fundamentals and Technology of Multifunctional Materials and Devices

Room On Demand - Session C2

Functional Coatings and Thin Films for Electronic Devices

C2-1 Interference Signal Induced by Ultra-Thin Amorphous Carbon Films Over Flexible Copper Foils Demonstrated by Electromagnetic Boundaries Calculations*, Ângela Elisa Crespi (angela.crespi@universite-paris-saclay.fr), C. Ballage, M. Hugon, J. Robert,* Université Paris Saclay, France*; D. Lundin,* Linköping University, Sweden*; T. Minea,* Université Paris Saclay, France

Interferences of amorphous carbon thin films (a-C) deposited over flexible copper foils by direct current magnetron sputtering were theoretically and experimentally demonstrated. Destructive interference is observed at specific a-C thicknesses when reflection occurs from the copper foil and the a-C film. As waves are out of phase, they interfere. Experimental diffusive reflectance (DR) was measured using a PerkinElmer lambda35 spectrometer (λ=400-1000 nm) at normal incidence. The theoretical results were calculated using electromagnetic boundary conditions varying from 0 nm to 350 nm a-C thickness. The simple double-layer system presents destructive interferences in thicknesses lower than 100 nm from near-ultraviolet (UV) to near-infrared (IR). At UV visible spectrum around 20-60 nm, a-C films indicate the proximity of an antinode. At IR, the a-C thickness increases to around 70–80 nm due to the skin depth effect. The compromise thickness/minimum DR reflectance depends on the wavelength, although it is lower than 100 nm for the analyzed spectrum. Thicker a-C films are less efficient for reflectance reduction. Keywords: interferences; electromagnetic boundary conditions; amorphous carbon; copper foils.

C2-2 INVITED TALK: High k Dielectrics for MIM Architecture: From Capacitors to Non-volatile Memories Applications*, Christophe Vallee (CVallee@sunypoly.edu),* SUNY POLY, Albany, USA*; 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.

[1] P. Gonon and C. Vallée, *Appl. Phys. Lett.* 90 (2007) 142906

[2] A. Chaker et al, *Appl. Phys. Lett.* 110 (2017) 243501

[3] P. Gonon *et al*, *J. Appl. Phys*.107 (2010) 074507

[4] T. Wakrim *et al,Appl. Phys. Lett.* 108 (2016) 053502

[5] W. Jeon *et al*, IEEE Trans. on Elect. Dev. 66 (2018) 402-406

C2-4 Study of Polycrystalline BiMnO3 Thin Films Grown by Radio-Frequency Magnetron Sputtering*, **Glory Umoh (glory.umoh@cimav.edu.mx)**, J. Holguín-Momaca , R. Talamantes,* Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), Mexico*; G. Herrera-Pérez,* Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), USA*; S. Olive-Méndez, A. Hurtado-Macias,* Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), Mexico

Multiferroic magnetoelectric $BiMnO_3$ thin films simultaneously exhibit more than one type of ordering, including

ferromagnetism (FM), ferroelectricity (FM) in a single-phase. Consequently, they have a spontaneous magnetization that can be switched by an applied

magnetic field, a spontaneous polarization that can be switched by an applied electric field, also coupling between them. $BiMnO_3$ thin films were grown

on (111) $Pt/TiO_2/SiO_2/Si$ substrates with 100 nm thickness via radio frequency magnetron sputtering.

The growth of these thin films was extremely sensitive to substrate deposition temperatures, single-phase $BiMnO_3$ could only

be attained in a narrow temperature window of around 700 °C. Working pressure 3×10^{-3} Torr was kept constant throughout the

sputtering deposition process. Loss of Bi during thin film growth of bismuth-based compounds is a major challenge to obtaining

stoichiometric films, because of the desorption nature of Bismuth, to compensate this loss, Bi was added to a crucible were

the sample was annealed at 700 °C in a rich oxygen atmosphere in a tubular furnace for 7hrs with heating and cooling rates

of 3°/min. The $BiMnO_3$ films were found to be strongly (0,2,0) oriented. X-ray diffraction, was in Bragg Brentano configuration,

electronic transmission microscopic (TEM) in scanning image mode (STEM), SAED confirmed a monoclinic structure with space

group C_{12}/C_1. The lattice constants are a = 9.5415 Å, b = 5.61263 Å, c = 9.8632 Å, b = 110.6584°,

with a high-quality textured film. While the surface morphology observed by scanning electron microscopy (SEM) indicates

homogeneity in the grain growth, crack-free and an increased surface uniformity. The root mean square roughness was evaluated

using AFM in tapping mode, with rms = 35±0.7 nm. Moreover, ferroelectric properties were analyzed by means of hysteresis loop.

The structural, chemical composition and ferroelectric properties of these thin films demonstrate that they have the capability

to be used in cantilever-type energy harvesters.

C2-5 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.

C2-6 Effect of Substrate Bias on Properties and Microstructure of Nanotwinned Copper Thin Films Deposited by Magnetron Sputtering System*, **Tsung Lin (a0917320902@gmail.com)**,* NTHU, Taiwan*; S. Chang,* +886-3-5715131 ext 34321, Taiwan*; F. Ouyang,* NTHU, 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 researches 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 results show that the columnar nanotwin structure grows straighter as bias increases. The Cu films deposited under higher bias have columnar nanotwinned structures. On the other hand, Cu films deposited at lower bias voltages have no columnar microstructure and few twins. XRD results indicate that all the deposited Cu films exhibit structure with (111) preferred orientation and the (111)-oriented grains become more dominant in the films with increasing bias. The percentage of (111) orientation can reach 98.4% when bias is -100 V. The optimum substrate bias to form high density nanotwinned structure is -120 V and the films has hardness of 3.12 GPa, which is about 3 times higher than that of its bulk counterpart. The resistivity of the samples is relatively low in bias voltage lower than -80 V, and once the bias voltage increases over -80 V, the resistivity becomes comparably higher. The maximum of resistivity is 2.17 μΩ – cm at the bias voltage of -140 V, but it is still very low and acceptable for being a good conductor. All samples have quite small surface roughness without any CMP process. Small surface roughness is beneficial to Cu-Cu direct bonding process. The residual stress of all samples is tensile. The maximum of residual stress appears at the bias voltage of -140 V, and decreases from 224 GPa to 124 GPa with the bias decreasing to -100 V. Then the residual stresses of samples deposited at relatively low bias voltage region are comparably small. With the further decrease of bias voltage, the residual stress increases a to 127 and 162 GPa at the bias of -20 V and 0 V. The mechanism of the effect of the bias on properties and microstructure will be discussed in details in this study.

C2-7 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 $CuWO_4$).

C2-8 Study of Thermal Stability of Highly (111)-Oriented Nanotwinned Ag Films by Using Unbalanced Magnetron Sputtering*, Po-hsien Wu (sky268455@gmail.com)*, *Y. Hao, L. Chang, F. Ouyang,* National Tsing Hua University, Taiwan

The metal strengthening methods generally company a significant reduction in electrical conductivity due to the scattering of electrons. Recently, metals with nanotwins have attractive properties, which can solve the issue on the contradiction of mechanical strength and electrical conductivity. Nanotwinned (NT) metal film, especially copper, possesses high mechanical strength, good ductility, acceptable conductivity and low cost, is still a popular material in academic research and industrial applications until now. Silver seems to be a potential candidate, which possesses prominent electrical and thermal conductivity, most importantly, excellent oxidation resistance. In addition, Ag also contains a lower stacking fault energy value (16 mJ m^{-2}) than copper (45 mJ m^{-2}), causing the glide of a {111}<112> partial easily begets a fault in the FCC stacking sequence. Therefore, the formation of dense twins will prominently increase the obstacle density of dislocation. The transmission in the form of twin boundaries, thereby enhancing the strength and thermal stability of the film, while maintaining a low resistivity.

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 XRD analysis results showed that Ag(111) and Ag(222) were the main diffraction peaks and the ratio of integrated intensities of these two oriented grains was up to 99.9%. 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.

C2-9 Enhanced Reliability and Uniformity for Ge pMOSFET with Low Temperature Supercritical Fluid Treatment*, Bo-Lien Kuo (eji1i6xu06@gmail.com)*, *K. Chang-Liao,* National Tsing Hua University, Taiwan*; D. Ruan,* National Tsing Hua University, China*; J. Li,* National Tsing Hua University, Taiwan

Significant improvement on uniformity and reliability characteristics in Ge pMOSFET are achieved with a novel low temperature supercritical phase CO_2 fluid treatment with H_2O cosolvent. Devices with the proposed treatment also exhibit a lower subthreshold swing, a higher on/off current ratio, and a lower interface trap density. The improvement can be attributed to the reduction of oxygen vacancy and low oxidation states in the interfacial layer (IL), and the quality enhancement on both IL and high-k gate stack.

C2-11 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. Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA*; E. 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.

C2-12 High-performance Thermochromic VO_2-based Coatings Prepared on Glass by a Low-temperature Scalable Deposition*, Tomáš Bárta (tomasnep@seznam.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.

References

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[1] **2020 Student Award Finalist**

[1] J. Vlček, D. Kolenatý, T. Kozák, J. Houška, J. Čapek, Š. Kos, Ion-flux characteristics during low-temperature (300 °C) deposition of thermochromic VO_2 films using controlled reactive HiPIMS, J. Phys. D: Appl. Phys. 52 (2019) 025205.

[2] J. Houska, D. Kolenaty, J. Vlcek, T. Barta, J. Rezek, R. Cerstvy, Significant improvement of the performance of $ZrO_2/V_{1-x}W_xO_2/ZrO_2$ thermochromic coatings by utilizing a second-order interference, Sol. Energy Mater. Sol. Cells 191 (2019) 365-371.

C2-13 Investigation of Resistive Switching in TAOs-Based Memristor With Ultraviolet Irradiation*, **You-Xuan Li (youxuan.eo08g@nctu.edu.tw)**, P. Liu, C. Hsu, K. Gan, D. Ruan, Y. Chiu,* National Chiao Tung University, Taiwan

The effect of ultraviolet (UV) irradiation on TAOs (W doped InZnO, IZO-W) based ECM type memristor has been studied. The typical bipolar I-V curve of TAOs memristors with and without UV irradiation method were revealed in the voltage sweep mode. For the characteristics of IZO-W memristor, high DC endurance cycles (> 8 ´ 10^3), low compliance current (10 mA), large on/off ratio (> 10^4) and long retention time at 85 °C were performed in this study. X-ray photoelectron spectroscopy (XPS) of all devices were analyzed the interaction of metal ion in IZO-W film after UV irradiation. UV irradiation is the low thermal budget method for IZO-W memristors, which is the compatible method for BEOL in future IC industry.

Fundamentals and Technology of Multifunctional Materials and Devices
Room On Demand - Session C3

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

C3-1 Au and Ag Nanoparticle Effects on the Electrical Properties of Pulsed Laser Deposited Cdte/Cds Photovoltaic Thin Films*, **Mehmet Alper Sahiner (mehmet.sahiner@shu.edu)**, J. Emerson, F. Akinlade, M. Herington, V. Castillon,* Seton Hall University, USA

We have used pulsed laser deposition to deposit nanoparticles (Ag, Au) to investigate

the effects of these impurities on the photovoltaic properties of the CdS/CdTe based thin films. The main

objective was to investigate how the inclusion of nanoparticles will affect light scattering in the at the interfaces

and whether the different size and shape of nanoparticles will have a positive effect on the overall electrical

performance of these thin film solar cells. In our previous studies, we have investigated the effects of the

embedded Ag nanoparticles on the photoelectric conversion efficiency on CdS/CdTe based thin film solar cells

as synthesized by Pulsed Laser Deposition (PLD). Silver was shown to enhance the photovoltaic performance

by almost doubling the photovoltaic conversion efficiency of the conventional CdS/CdTe films [1]. A careful

comparison of photovoltaic performance of Au/Si versus Ag embedded thin films of CdS/CdTe on indium tin

oxide coated glass substrates have been performed. Our results on the Ag case revealed electrical

performance of these cells have correlates with the particles density and the particle size on the CdS/CdTe

interface. This study concentrates on the Au and Ag nanoparticle deposition on the CdS/CdTe interface with

varying particle size and distributions. Structural and compositional characterization were performed using

XRD, AFM, and SEM/EDX. Photovoltaic properties were measured using a LabView assisted Keithley

Sourcemeter set-up. The comparison of Ag vs Au nanoparticles on the structure and photovoltaic

conversion efficiency will be presented. Ag and Au nanoparticles have contrasting effects on the

photovoltaic conversion efficiency in terms of their relative coverage at the interface, This will be discussed in

the light of plasmonic resonances and effective light scattering for Ag and Au particles.

[1] Olivia Rodgers, Anthony Viscovich, Yunis Yilmaz, Mehmet Sahiner, “The Effect of Embedded Ag

Nanoparticle on the Photovoltaic Conversion Efficiency in CdTe/CdS Thin Films”, American Physical Society

Bulletin, X17.13 (2018).

This work is supported by NSF Award #:DMI-0420952

C3-2 Transparent Thermoelectric TiO_2:Nb Thin Films*, J. Ribeiro, F. 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 $W\cdot m^{-1}\cdot K^{-1}$), and a high absolute Seebeck coefficient (>200 $\mu V\cdot K^{-1}$) 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.

C3-3 Multilayers for Efficient Thermal Energy Conversion in High Vacuum Flat Solar Thermal Panels*, D. De Maio,* Unina and CNR-ISASI, Italy*; C. D'Alessandro, A. Caldarelli, E. Gaudino,* UniNa and CNR-ISASI, Italy*; M. Musto,* UniNa - Università degli studi di Napoli "Federico II", Italy*; D. De Luca,* UniNa and CNR-ISASI, Italy*; E. Di Gennaro,* UniNa - Università degli studi di Napoli "Federico II", Italy*; **Roberto Russo (Roberto_russo@cnr.it)**,* CNR - ISASI, Italy

The solar thermal flat panel insulated with high vacuum can have excellent efficiency performances in the mid temperature range (150-300°C) if equipped with an optimized selective solar absorber. We present 3 multilayer coatings optimized to work at 100, 200 and 300°C. Optimization has been obtained by maximizing the efficiency at the designed operating temperature by a genetic algorithm. The coatings (based on Cr and Cr2O3) have been deposited by DC reactive magnetron sputtering starting from a Cr target on glass and on 3 industrial copper substrates (OFE, OF, ETP). The single layers have been measured by standard characterization techniques (ellissometry, integrating sphere, AFM, X-Rays Diffraction…), whereas the produced multilayers have been also investigated by using a proprietary system [1] able to measure the absorber efficiency as function of temperature up to the stagnation temperature and above[2]. Influence of several deposition parameters on the multilayer performance will be presented. To enhance the absorptivity the multilayers have been covered with antireflective coatings based on SiO2 and/or SiNx.

[1] R.Russo et al. Optic Express 26 (2018) A480

[2] C. D'alessandro et al. submitted to this conference

C3-4 Development of Efficient Perovskite Solar Cells Under Ambient Conditions via Fine Tuning of Compact TiO_2 Layer, ***Navjyoti Bhagat (navjyotibhagat@gmail.com)**,* Guru Nanak Dev University, India*; V. Saxena,* Bhabha Atomic Research Centre, India*; A. Mahajan,* Guru Nanak Dev University, India

Organic inorganic perovskites have attracted a great attention as next generation solar cells due to their excellent properties such as high molar extinction coefficient, low temperature processability, ambipolar nature, large diffusion length and small exciton energies. The compact or blocking layers have been studied extensively in dye sensitized solar cells, however, there are only a few reports on the effect of these layers on perovskite solar cells (PSCs). Herein, we employed a thin compact layer of spin coated TiO_2 (c-TiO_2) (<50 nm) in order to reduce series resistance and improve transmittance. Thethickness of c-TiO_2 (7-35 nm) was optimized by changing the precursor concentration as well as spinning speed. The prepared c-TiO_2 as well as mesoporous layer of TiO_2 (m-TiO_2) were thoroughly characterized using UV-Vis spectroscopy, Raman, Atomic Force Microscopy, Cyclic voltammetry and electrochemical techniques.Further, PSCs were fabricated under ambient conditions with high humidity (~RH 80%) using CuSCN as hole transporting layer (HTL). The power conversion efficiency of the optimized device found to be improved by 50 % on increasing the thickness of ETL from 7 nm to 15 nm.

Fundamentals and Technology of Multifunctional Materials and Devices

Room On Demand - Session CP

Fundamentals and Technology of Multifunctional Materials and Devices (Symposium C) Poster Session

CP-1 Freestanding ZnO Nanowire For Multifunctional Application in RRAM Memory and Gas Sensing, ***Pragya Singh (pragyasingh@mail.ntust.edu.tw)**,* National Taiwan University of Science and Technology, Taiwan*; T. Tseng ,* National Chiao Tung university , Taiwan*; J. Chu,* National Taiwan University of Science and Technology, Taiwan

In current research, the focus of nanoscale community is to produce various nanostructures in such a way that can be easily modified as desired applications ranging from nanoptoronics to biomedical engineering. Nanoscale structure from various metal oxide materials has got great attention due to its various fabrication strategies, characterizations, surface morphology, structure-property correlations, and various remarkable milestones indeed have been entrenched. Zinc oxide (ZnO) is a well-known n-type semiconductor with a wide bandgap (3.37eV) and large excitation binding energy (60eV) material, that has been extensively investigated in multifunctional devices due to the low production cost, chemical stability, doping, and the non-toxic property. In this study, we fabricated the ZnO nanowires by hydrothermal method, applicable in resistive random access memory (RRAM) as well as in gas sensing devices. The hydrothermal growth technique is a solution-based process used to synthesize ZnO nanowires on ITO coated glass substrate. Electrical characteristics were carried out by a semiconductor device analyzer (Agilent Tech. Inc. B1500) and gas sensing electrical measurement system (model 2400, Keithley Source Meter) at room temperature. After introducing ZnO nanowire thin film between conductive electrodes, both devices show significant enhancement in their resistive switching and sensing properties. To check the surface morphology and orientation of nanowire thin film, ZnO nanowires were examined by using scanning electron microscopy (SEM). The crystal structures of the ZnO nanowire thin film were investigated through X-ray diffractometry (XRD). The defect concentrations in the nanowire thin film were evaluated using an X-ray photoelectron spectroscopy (XPS). To understand the filament formation during resistive switching analysis and gas sensing behavior, a schematic representation is used. Our study proposes that ZnO-based devices have been shown effective results and this technique can be easily adopted by other oxide and may encourage the fabrication of various hybrid devices in near future for multifunctional applications.

CP-2 Introducing Thin HfO_2 Layer to Inhibit the Power Consumption of InWZnO CBRAM, ***You-Xuan Li (youxuan.eo08g@nctu.edu.tw)**, P. Liu, C. Hsu, K. Gan, D. Ruan, Y. Chiu,* National Chiao Tung University, Taiwan

In this study, the memory performance of IWZO-based CBRAM device can be greatly improved by inserting a thin HfO2 layer with different process methods. The bilayer structure (IWZO/ALD-HfO_2) device also exhibit excellent memory characteristics, such as high endurance cycle (more than 2 ´ 10^3), long retention time (more than 2 ´ 10^4 s), lower set and reset voltage. The IWZO-based memory device with bilayer structure can be operated at 10 mA for low-power device application. This improvement in resistive switching characteristics are attributed to Gibbs free energy of HfO_2 lower than IWZO layer, which is easily occur oxidation reaction in HfO_2 layer. These results proposed a method that inserting a thin ALD-HfO_2 layer in IWZO-based CBRAM device can not only reduce the off-state leakage current, but also enhance the reliability of the memory, which has great potential for future memory-in-pixel applications in low-power Internet of Things (IoT) generations.

CP-3 Improved Electrical Performance for Indium Tungsten Oxide Thin-Film Transistor with Asymmetric Source and Drain ElectrodeMaterial, ***Chia-Yu Lin (mandylin21107@gmail.com)**, P. Liu,* National Chiao Tung University, Taiwan*; D. Ruan,* National Chiao Tung University, China*; K. Gan, Y. Chiu, C. Hsu,* National Chiao Tung University, Taiwan*; S. Sze,* National Chiao Tung University, USA

In this work, high mobility indium tungsten oxide thin-film transistor (TFT) with asymmetric schottky contact has been fabricated, while the improvement on electrical characteristics was also discussed. In general, metal material with low work function is often selected as the source and drain (S/D) electrode. It can be attributed to a low schottky barrier which was formed with channel material naturally. However, a high conductivity channel material with low schottky barrier may induce an undesirable negative threshold voltage and poor on/off current ratio. Utilizing asymmetric S/D schottky barrier, a lower off-state current and subthreshold swing can be achieved, while the on-state current and field effect mobility have been kept. The research may provide a new approach to enhance the electrical performance and adjust threshold voltage for TFT with high conductivity channel material.

Coatings for Biomedical and Healthcare Applications

Room On Demand - Session D1

Surface Coating and Surface Modification in Biological Environments

D1-1 Physical Vapor Deposition for Growth of Large Area Molecular Sensor Arrays, *N. Glavin, D. Austin, D. Moore, M. 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.

D1-2 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. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico*; 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.

D1-3 Behavior of a-C:H with Different fs-laser Micro-Patterns against Diamond Tip 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 obtain micrpatterns, like leaves of the lotus plant or cactus family.

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 fluence H (H: 1.71J/cm^2 or 3.70 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 earlier, while nanotribology was performed for investigating the sliding properties of the micro-patterned a-C:H surfaces. In addition to dry movement for testing the emergency operation, hyaluronic acid is used as an intermediate substance for testing the friction behaviour against a diamond tip in the present study. First impressions about potential interaction of carbon allotropes with hyaluronic acid are discussed.

D1-4 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.

D1-5 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.

D1-6 INVITED TALK: Embroidery of Conductive E-Threads: Opportunities and Challenges in Healthcare*, Z. Dalisky, S. Alharbi, V. Mishra, **Asimina Kiourti (kiourti.1@osu.edu)**, K. Guido,* 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.

Coatings for Biomedical and Healthcare Applications
Room On Demand - Session D2

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

D2-1 INVITED TALK: Behavior Of Additively Manufactured 316L Stainless Steel Fabricated By Selective Laser Melting In Comparison To Wrought 316L And 317 L Stainless Steels*, **Mobin Salasi (mobin.salasi@curtin.edu.au)**, K. Wang, E. Hornus,* Curtin University, Australia*; M. Pabbruwe,* Curtin University, Royal Perth Hospital, Australia , Australia*; T. Pojtanabuntoeng,* Curtin University, Australia , Australia*; M. Iannuzzi, Z. Quadir, W. Rickard,* Curtin University, Australia*; M. Salem, P. Lours,* Ecole de Mines Albi, France*; J. Bougoure,* Curtin University, Australia , Australia*; P. Guagliardo,* Curtin University, Australia **INVITED**

Selective laser melting (SLM) is a type of additive manufacturing (AM) with applications in, e.g., the biomedical and aerospace industries. Studies have been carried out on the localised corrosion behavior of SLM fabricated 316L (UNS S31603) stainless steel. Little is known, however, on the effects of tribocorrosive conditions on the response of stainless steels fabricated by SLM. In orthopedics applications, for example, it is known that the alloys often encounter different modes of tribocorrosion. In this research, the effects of abrasive particles on the tribo-electrochemical behavior of AM 316L (UNS S31603) stainless steel produced by SLM was investigated.

Two series of as-printed and solution annealed samples were first characterized using scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Then, the corrosion-only behavior of these samples was investigated by cyclic potentiodynamic polarization in a 0.6 M NaCl electrolyte. The corrosion resistance of SLM fabricated 316L (UNS S31603) was compared to that of wrought UNS S31603 and S31703 stainless steels in the same environment. Three-body tribocorrosion tests were performed with silica sand abrasive particles, delivered to the interface of the sample and a rotating rubber counterface. Additionally, cyclic and potentiostatic polarization methods were used to gain a better understanding of the interaction between corrosion and abrasion. Lastly, the microstructure and the morphology of the tribocorroded regions were characterized using focused ion beam (FIB-SEM).

It was found that presence of Mo had a much more effective role in the tribocorrosion behavior than the manufacturing method. To understand the role of Mo nano-scale secondary ion mass spectroscopy (nanoSIMS) were used to understand the effects of Mo on the passivity. The implication of passivity and tribocorrosion behavior is discussed.

Key words: additive manufacturing, tribocorrosion, polarization

D2-3 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 lifetime 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.

D2-4 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. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico

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 surface 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.

D2-5 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. 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.

Coatings for Biomedical and Healthcare Applications
Room On Demand - Session D3

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

D3-1 Very Thin Gold Films Deposited Collagen to Improve Skin Wound Healing in Animal Study

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Collagen has been widely used in different forms for biomedical purposes. In combination with gold element, it may bring synergistic effect for more precise therapy. In this study, very thin gold film deposition on collagen fabric was conducted by high-power impulse magnetron sputtering (HIPIMS). Specimens with different deposition time (0, 6, 12, 24, 48 and 96 seconds) were prepared. Animals of 175-200 gm Sprague Dawley (SD) male rats were chosen for skin wound healing test and grouped according to the created full thickness wounds of back skin. In the experimental group, wounds were covered with coated collagen specimen and sterilized gauze, while wounds were covered with sterilized gauze only in control group. Visual observation for wound recovery was done during renewing dressing on a daily base. Histology study of wounded skin was performed on post-operative day 3, 7 and day 14. In addition to morphological observation, scoring of wound healing, consisting of neovascularization, collagen deposition and inflammatory cell infiltration was also calculated and compared. The results showed that an improved wound healing and less soft tissue fibrosis can be observed in the presence of very thin gold film. This animal study reveals that the use of such gold coated collagen material on skin wound is beneficial and promising.

D3-2 New Cytocompatible and Antibacterial Porous Ta_2O_5 Surface: Dental Implant Prototype

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An innovative surface able to overcome the failures of the dental implants used nowadays, regarding their bioactivity and consequent capacity for osseointegration, was developed. The first functional treatment (plasma electrolytic oxidation (PEO)) develop a tantalum oxide (Ta_2O_5) surface in order to mimic the bone morphology and chemistry and consequently enhancing the surface bioactivity. Thereby, the anodizing parameters were optimized in order to achieve a porous structure enriched with calcium (Ca) and phosphorous (P), such as Ca/P ratio near to 1.67 (theoretical value of hydroxyapatite). The second treatment endows this surface with antibacterial activity. With this purpose, zinc nanoparticles (Zn NPs) were deposited onto the bioactive surfaces by DC magnetron sputtering with (or without) an additional thin carbon (C) layer, for NPs release control.

The morphological analysis by SEM and STEM revealed the formation of a micro/nano-porous oxide layer with incorporation of Ca and P. The deposition of Zn NPs did not affect the surface morphology and the NPs were around and inside the pores. The additional presence of the C layer slightly covered the nano-pores. The BF-STEM results showed that the Zn NPs had irregular shapes and a core-shell structure with two crystalline phases: HCP Zn and ZnO. The initial osteoblasts adhesion was ensured with a significant proliferation on the surface with Zn NPs. The surfaces with Zn NPs substantially reduced the planktonic bacterial with a greater sessile bacteria inhibition on the surfaces.

Furthermore, a preliminary prototype was created. A PEO-optimized Ta dental implant was developed to reproduce the bone surface morphology and chemical composition. Then, the Ta implants were inserted onto a pork jawbone and, by SEM and X-rays analysis, the surface fracture was analysed. The results showed a good adhesion and mechanical resistance of the anodic layer.

In sum up, these findings are promising for biomedical applications.

Keywords: tantalum oxide; zinc oxide nanoparticles; plasma electrolytic oxidation; magnetron sputtering; antibacterial activity; cytocompatibility.

Coatings for Biomedical and Healthcare Applications
Room On Demand - Session DP

Coatings for Biomedical and Healthcare Applications (Symposium D) Poster Session

DP-1 Optimisation of Electrolytic Plasma Oxidation (PEO) Coatings Formed on Magnesium for Biological Applications

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Magnesium has shown great potential for the next generation of resorbable implant materials. It has well biocompatibility and biodegradability, high strength-to-weight ratio and stiffness similar to that of the human bone. However, magnesium exhibits poor corrosion behaviour, leading to the early deterioration of the implant. Therefore, appropriate surface treatments have to be applied to improve the corrosion resistance of magnesium.

Electrolytic Plasma Oxidation (PEO) is a plasma-assisted technique to form ceramic-like coatings containing oxides comprising constituents of both the parent metal and the electrolyte. PEO coatings can increase corrosion resistance and mechanical properties of the metal substrate, improving the longevity and reliability of the implant. Furthermore, the coating properties can be adjusted by tailoring parameters of the PEO process, such as electrolyte composition and pulsed electrical regime. Previous studies have been mainly focused on the influence of current density, frequency and duty cycle of rectangular pulses, whereas very few works were dedicated to the influence of the pulse shape.

The objective of this work is to investigate a possibility of increasing the corrosion resistance of PEO coatings on Mg by tailoring the current pulse shape. Triangular pulses are given particular attention in comparison with the commonly used rectangular shapes. Two types of rectangular pulses are generated – a Slow ON pulse, where the applied current increases linearly at a certain rate followed by an instant drop of the current; and a Slow OFF pulse, where the applied current increases instantly before decreasing linearly. Characteristics and properties of the coatings produced under different waveform are thoroughly studied. Corrosion tests are performed to evaluate the corrosion resistance. The results have shown a positive effect of the Slow OFF pulse. A more uniform and defect-free coating surface morphology is obtained. The coating exhibits higher corrosion resistance correlated to the better morphology.

DP-2 The Property of Adhesion and Biocompatibility of Silicon and Fluorine Doped Amorphous Carbon Films

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Application of nickel-titaniumu (NiTi) alloys to medical implant devices is increasing due to their unique characteristics. To ensure good biocompatibility in the human body, fluorine-doped amorphous carbon (a-C:H:F) coating is a promising candidate. Generally, a-C:H:F coating shows poor adhesion on metallic alloys, so that silicon-incorporated interlayer is introduced between a-C:H:F and metallic alloys. However, this membrane design has a risk of delamination at the outermost interface (a-C:H:F // interlayer), and also there is a practical problem that coating time becomes long because the deposition process in multiple stages is required. Here we develop silicon and fluorine doped amorphous carbon (a-C:H:Si:F) film which exhibits high adhesion and excellent biocompatibility.

The a-C:H:Si:F film and a-C:H:F film (control) were deposited on NiTi substrates using radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) equipment. Chemical compositions and bonding states of the surfaces were determined by X-Ray photoelectron spectroscopy (XPS). Surface free energy was estimated based on Owens-Wendt method using the results of contact angle measurement. Nanoscratch tests were conducted in order to quantify the adhesion strength. Platelet adhesion test and leukocyte adhesion test were conducted in order to evaluate biocompatibility.

First of all, a-C:H:Si:F was deposited from a mixture of TMS ($Si(CH_3)_4$) and C_3F_8 at TMS flow rate of 6.0 sccm and C_3F_8 flow rate of 50 sccm. Although this shows the possibility of new film deposition from a mixture of TMS and C_3F_8, the adhesiveness and biocompatibility of a-C:H:Si:F were not higher than a-C:H:F with Si-interlayer. Therefore, "C_2H_2-doped" a-C:H:Si:F film, which was deposited using a mixcure of TMS, C_3F_8 and C_2H_2 at a TMS flow rate of gradually changed from 6.0 sccm to 0.0 sccm, C_2H_2 flow rate of gradually changed from 0.0 sccm to 3.0 sccm and C_3F_8 flow rate of gradually changed from 0.0 sccm to 50.0 sccm, was newly deposited and this film showed similar chemical composition, bonding state, surface free energy, and higher adhesive strength than a-C:H:F with Si-interlayer, and the same number of adhesive platelets and leukocytes as a-C:H:F.

These results demonstrated that a single film with both adhesion of Si-interlayer and biocompatibility of a-C:H:F was fabricated. Furthermore, this a-C:H:Si:F coating can be anticipated as an effective film coating method in a practical point of view, because the film deposition is completed in one process.

DP-3 *In Vitro* Study of Very Thin Gold Film Deposited Collagen Fabric*, Sheng-Yang Huang (huangmochiqqegg@gmail.com)*, *. Hsieh,* Feng Chia University, Taichung Veterans General Hospital, Taiwan*; R. Chang,* Feng Chia University, Taiwan*; C. Chou,* Taichung Veterans General Hospital, National Yang-Ming University, Taiwan*; C. Chung,* Central Taiwan University of Science and Technology, Taiwan*; J. He,* Feng Chia University, Taiwan

The goal of this study is to test a novel collagen fabric biomedical material with very thin gold film successfully deposited by using high-power impulse magnetron sputtering (HIPIMS). Previous study show that the gold layer is morphologically tunable from island distribution to continuous layer by manipulating deposition time. Here, this study aims to explore the *in vitro* response of the specimens deposited for 0, 3, 6, 51, and 81 seconds, representing the gold layer coverage percentage from 3.07% to 51.22%, respectively. Cell attachment test based on Alamar Blueassay using WS1 fibroblast and antibacterial test based on Kirby-Bauer disk diffusion method were carried out. Experimental results reveal that the gold layer prohibits fibroblast attachment, regardless of the gold layer coverage percentage. Microscopic observation disclosed the fibroblasts inactivation on the gold layer surface. For pseudomonas aeruginosa pathogen, randomly selected specimens with 3 and 6 seconds gold deposition showed inhibition zone of 13 and 11 mm, respectively. The results of this work support the use of this biomedical material in early phase of wound healing for its evidence of fibroblast attenuation and antibacterial effects.

DP-4 e-Poster Presentation: Metallization of Polymers for Medical Applications using HiPIMS*, Aarati Chacko (aarati.chacko@empa.ch)*, *K. Thorwarth, R. Crockett, U. Müller, H. 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-5 TiZrSiN Coatings, Structural Characterization, and Corrosion Resistance in Ringer's Lactate*, Claudia Patricia Mejía Villagrán (clapamevi21@gmail.com)*, Universidad Nacional de Colombia*; M. Chellali,* Karlsruhe Institute of Technology (KIT), Libya*; C. Garzón Ospina,* Universidad Nacional de Colombia*; H. Hahn,* Karlsruhe Institute of Technology (KIT), Germany*; J. Olaya Flórez,* Universidad Nacional de Colombia*; L. Velasco Estrada,* Karlsruhe Institute of Technology (KIT), Germany

TiZrSiN coatings produced by Physical Vapor Deposition in dual condition are characterized. Power density in Zr target was adjusted at three different values (2.0 Wcm^{-2}, 2.9 Wcm^{-2}, and 3.5 Wcm^{-2}), while power density on the TiSi target was fixed (0.55 Wcm^{-2}). As a result, three types of coating were obtained; one with a mostly amorphous structure (2.0 Wcm^{-2}), one with crystalline structure with some amorphous structure (2.9 Wcm^{-2}), and a third one with mostly crystalline structure (3.5 Wcm^{-2}).

Corrosion tests using electrochemical impedance while dipping the coatings in ringer's lactate, showed that coatings with TiZrSiN demonstrate better corrosion resistance than their ZrN peers. From all studied conditions, the one with the best resistance to corrosion (2.9 Wcm^{-2}), also demonstrated the highest hardness and the best performance and stability at the tests of electrochemical impedance spectroscopy with time. The improved properties in 2.9 Wcm^{-2} condition/case are attributed to the lattice stabilization for solid solution and adequate portion of silicon content.

DP-6 A Novel Synthesis Method of Carbide Derived Carbon (CDC) Surface Modification for Hip Implants*, Yani Sun (ysun98@uic.edu)*, University of Illinois at Chicago, USA*; K. Cheng, M. Mathew,* UIC College of Medicine at Rockford, USA*; M. McNallan,* University of Illinois at Chicago, USA

The inferior tribocorrosion behavior of commonly used biomedical alloys has led to the early failure of total hip replacements (THRs) and serious complications. In 2011, the tribolayer comprising graphitic carbon was found from the retrieved implant, and it was reported as solid lubrication which can reduce the friction between the femoral head and cup. Inspired by this interesting discovery, we have proposed a surface modification method, carbide-derived carbon (CDC), to mimic the tribolayer to improve the tribocorrosion resistance. The results have shown that CDC produced by direct chlorination can provide excellent protection to Ti6Al4V and has high durability.

In this study, a novel method has been developed to synthesize CDC on Ti6Al4V substrates by electrolysis from a low melting point halide salt. Compared to previous preparation processes, this newly developed approach eliminates the exposure to chlorine gas and the requirement of the inert gas environment, which makes the synthesis process more controllable and the CDC layer more uniform. X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM) were utilized for characterization. Based on the results, the produced CDC has a porous structure which may contain nanocrystalline graphite (NCG) and amorphous carbon (a-C). The theoretical thickness of the sample is estimated by a calculation which is approximately 1.44 µm. In addition, the performance of the new coating was tested in a tribocorrosion hip simulator. A system has a pin on ball contact and immersed in bovine calf serum of 30g/L protein concentration, with a pH of 7.6 and a temperature of 37˚C. We applied a normal force of 16N to obtain a contact pressure of around 10MPa and ran the test for 3600 cycles with 1Hz. A Gamry made Potentiostat is connected to the test system, monitoring the electrochemical responses induced by the tribological activity. According to the recordings of normal and tangential forces, the evolution of the friction coefficient is deducted and reported in the results.

The findings have shown that the CDC samples prepared by the electrolysis method exhibit smaller friction coefficient (approximately 0.1), wear loss and potential drop (less than 100 mV compared to 600mV for substrate). Therefore, it is promising that the CDC prepared by the novel electrolysis approach can protect Ti6Al4V substrates from the tribocorrosive damages. For future work, we propose to conduct the adhesion test, the tribocorrosion experiments under potentiostatic mode and the biocompatibility test to fully evaluate CDC's value as a novel material for hip implants.

DP-7 Enhancing Osseointegration on PEEK Spinal Implant by Using Laser Surface Roughening and HIPIMS Titanium Coating*, Ping-Yen Hsieh (pyhsieh@fcu.edu.tw)*, Feng Chia University, Taiwan*; H. Tsou,* Taichung Veterans General Hospital, Taiwan*; C. Chung,* Central Taiwan University of Science and Technology, Taiwan*; J. He,* Feng Chia University, Taiwan

Current spinal interbody fusion cages are most widely adopted from polyetheretherketone (PEEK) due to its favorable biomechanical properties and X-ray radiolucency characteristics. Unfortunately, the smooth and bioinert surface of PEEK may limit the osseointegration and inhibit bone fusion. Plasma spraying, providing porous and rough titanium layer over the PEEK spinal implant, has been commercialized in clinical application though, this study aims to develop an alternative approach by firstly laser roughening PEEK surface, followed by high power impulse magnetron sputtering (HIPIMS) to deposit a strongly adhered titanium layer for improving osteointegration of PEEK spinal implant. The experimental results showed that properly controlled laser condition gives micrometer-scale topography over the PEEK surface as opposed to the smooth bare PEEK. After HIPIMS deposition, the obtained titanium film presented an adhesion of 5B grade even after immersion in simulated body fluid (SBF) environment for 28 days based on the Scotch-tape adhesion test. Such excellent film adhesion performance is ascribed to the advantage of high ion energy and high-density plasma characteristics of the HIPIMS discharge. In addition, the titanium film on roughened PEEK presented better osteoblast compatibility and osseointegration than the commercial product, so as to provide the high spine stability after implantation. Finally, the long-term assessment results revealed the high stability and no degradation concern for the modified PEEK, which can avoid the malignant reaction between implant and host to ensure the safety after implantation in the human body. In summary, the two-step surface modification on PEEK satisfy the requirements for enhancing osseointegration, suggesting clinical application consideration.

DP-8 Superamphiphobic Stainless Steel Surface Prepared by Femtosecond Laser Patterning and Pulsed Plasma-Polymerization*, C. Lin,* Central Taiwan University of Science and Technology, Taiwan*; C. Chou,* Taichung Veterans General Hospital; National Yang-Ming University, Taiwan*; **Chi-Jen Chung (cjchung@seed.net.tw),*** Central Taiwan University of Science and Technology, Taiwan*; J. 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-9 Light-activated High Efficiency Antimicrobial and Antiviral 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.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room On Demand - Session E1

Friction, Wear, Lubrication Effects, and Modeling

E1-1 Multi-sensing Nano-wear with Electrical Contact Resistance and Friction Measurement*, **Ben Beake (ben@micromaterials.co.uk)**,* Micro Materials Ltd, UK*; T. Liskiewicz,* Manchester Metropolitan University, UK*; A. Harris,* Micro Materials Ltd.*; S. 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.

E1-2 Interlayer Design to Increase Adhesion of a-C Coatings onto C17200 Copper-Beryllium Alloy Surface*, **Marcos Dantas dos Santos (mdantas@usp.br)**, N. Fukumasu,* Polytechnic School of the University of Sao Paulo, Brazil*; A. Tschiptschin,* Metallurgical and Materials Engineering Department, University of Sao Paulo, Sao Paulo, Brazil*; R. de Souza, I. Machado,* Polytechnic School of the University of Sao Paulo, Brazil

Copper-beryllium (CuBe) alloys are widely used in the aeronautic and automotive industries due to its good thermal properties and corrosion resistance. However, reduced hardness and wear resistance can limit the use in manufacturing applications. To overcome these limitations, hard ceramic coatings can be applied to the tool surface, increasing the wear resistance, and reducing the friction coefficient. Among several coating options, amorphous carbon (a-C) coatings were selected in this work since this coating can present high hardness and a very low friction coefficient. Nevertheless, the main challenge in using a-C coatings onto CuBe alloys is the low adhesion between copper and carbon. This work focused on the development of a complex interlayer to increase adhesion under high contact, pure sliding, and dry tribological conditions. Two interlayer compositions (Ti/Si and Ti/TiN/Si) were analyzed based on the improved bonding between copper and titanium, while the amorphous silicon layer was applied to reduce the diffusion of carbon into the titanium-based layer. Pulsed Direct Current Magnetron Sputtering (pDCMS) system configuration was used to deposit the coatings using polycrystalline titanium, monocrystalline silicon, and polycrystalline graphite targets. The TiN interlayer was obtained by a reactive deposition process using argon and nitrogen gases. A polycrystalline graphite target was used to produce a hydrogen-free amorphous carbon coating over the tailored interlayers. The coatings were deposited onto C17200 CuBe discs, and silicon wafers substrates. Instrumented indentation tests were carried out in a Bruker Ti950 Triboindenter to evaluate coating hardness and elastic modulus. Increasing load scratch tests, using a diamond Rockwell C tip in a Bruker UMT-2 system, were conducted to evaluate coating adhesion to CuBe alloy substrate and measure friction coefficient and critical loads. Dry reciprocating ball-on-disk tribological tests were also conducted with this system, using two constant normal loads (10N and 20N) and a stroke of 4 mm. Scanning Electron Microscope (SEM), Raman spectroscopy and coherence correlation interferometry (CCI) were used to characterize the coatings and wear tracks after the tests. Results indicate that the Ti/TiN/Si compound interlayer improved the adhesion of the a-C coating, showing higher critical failure loads compared to other combinations. Also, ball on disc tests indicate the formation of a transfer layer at the ball surface, promoting reduced wear and failure of the coating when in contact with AISI5200 steel balls.

E1-3 Tribologically Enhanced Self-healing of Niobium Oxide Surfaces*, **Samir Aouadi (samir.aouadi@unt.edu)**, A. Shirani, 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.

E1-4 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, UK*; 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.

E1-5 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.

E1-6 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.

E1-7 INVITED TALK: 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.

[1] C. Lee *et al.***Science**, 328, 76 (2010).

[2] S. Li *et al.* **Nature** 539, 541 (2016).

[3] Q. Li *et al*., **Nano Lett.** 14, 5212 (2014).

[4] K. Hasz *et al*., **Phys. Rev. Mat**. 2, 126001 (2018).

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

E1-9 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.

E1-11 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. Mogonye,* Army Research Laboratories, USA*; D. Berman, S. 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.

E1-13 Analysis of Coating Layers and Defects Using Atomic Force Microscopy*, Stefan Kaemmer (stefan@parksystems.com)*, *G. 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.

References

[1] Ciacotich, N., Din, R. U., Sloth, J. J., Møller, P., Gram, L. (2018). An electroplated copper–silver alloy as antibacterial coating on stainless steel. Surface and Coatings Technology, 345, 96-104.

[2] Aliofkhazraei [https://www.sciencedirect.com/science/article/pii/B9780080965321007123?via%3Dihub#!], M (2014). AFM Applications in Micro/Nanostructured Coatings

Comprehensive Materials Processing, Vol 7, 191-241

[3] Lee, M., Kim, J., Lee C. (2019), Park Systems Application Note #35.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room On Demand - Session E2

Mechanical Properties and Adhesion

E2-1 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.

E2-2 INVITED TALK: 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.

E2-4 Industrial Applied Measurement Method of Localized Coating Property and Stress Profiles Within a Calotte Wear Crater via Nano-Indentation*, **Troy vom Braucke (troy@gpplasma.com)**,* GP Plasma, Canada*; F. Papa,* GP Plasma, USA*; A. Harris, B. Beake,* Micro Materials Ltd, UK*; J. Gutiérrez, I. Martinez, A. Wennberg,* Nano4Energy, Spain*; C. Shin, J. Yun,* DONGWOO HST CO., Korea (Democratic People's Republic of)*; N. Bierwisch, N. Schwarzer,* Saxonian Institute of Surface Mechanics SIO, Germany

Current measurement techniques for the determination of coating stress, hardness, elastic modulus etc. rely on several assumptions when modeling or directly measuring lattice stress or stress relaxation. These measurement techniques can be time consuming, costly and lack the flexibility to be used in the rapid development cycles needed for industrial applications. We will discuss the shortcomings, potential error and uncertainty assumptions highlighting that we might be missing some fundamental properties of interest to better design functional coatings.

Results are presented which show that it is possible to determine localized (relative to a reference) intrinsic stress profiles via a series of nano-indentations within a Calotte crater while mitigating the need to make several assumptions regarding material properties. These profiles can be determined from the indentation curve data through the application of the fundamental equation of elasticity combined with a holistic top-down approach, including uncertainty quantification. We demonstrate the method on a thick DLC coating and on thick sputtered AlTiN HiPIMS coatings, comparing stress depth profiles for samples deposited on single, two and three-fold rotation axes along with other important properties.

This method allows one to characterize stress profiles quickly and simply for industrial applications with nanoscale resolution. The benefit being that one can quickly relate the effects of process changes on stress states as a function of depth to better design coatings for functional use. Future work is proposed to further validate the method for absolute stress measurement.

E2-5 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.

E2-6 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. 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.

E2-7 Thin-film Adhesion: A Comparative Study Between Colored Picosecond Acoustics and the Stressed Overlayer technique*, Arnaud Devos (arnaud.devos@univ-lille.fr),* Iemn, Umr Cnrs, France*; M. 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 quantitavely 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.

References:

[1] M. J. Cordill, D. F. Bahr, N. R. Moody and W.W. Gerberich, IEEE Transactions on Device and Materials Reliability, 4, 40 (2004).

[2] A. Devos, Ultrasonics 56, pp. 90-97 (2015) DOI 10.1016/j.ultras.2014.02.009

E2-8 Comparing the Residual Stress Gradient Measurement of ZrN using FIB-DIC and Xray Diffraction*, W. Lin, Y. Chou,* National Chung Hsing University, Taiwan*; J. 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^{2}asin^{2}j 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.

E2-9 Investigation of Deformation Behavior Under Different Loading Directions in Transition Metal Thin Films*, Markus Schoof (schoof@imm.rwth-aachen.de),* RWTH Aachen University, Germany

The aim of this project was to study the effect of transition metal species and the presence of oxygen on the mechanical properties of transition metal (oxy)nitride films, and in doing so to link quantum and continuum mechanics for material design. The growth of these films results in a strongly columnar microstructure, so it is necessary to understand the influence of this texture on mechanical properties. This will enable knowledge-driven materials design on the atomic and microstructural level for macroscopic applications such as protective coatings for polymer extrusion.

Uniaxial compression was thus performed using micro pillars at different angles to the growth direction. Two sets of (V, Al)N samples were used, one manufactured by HPPMS (high power pulsed magnetron sputtering) and one by dcMS (direct current magnetron sputtering). Micro pillars oriented between 0° and 90° to the growth direction were investigated to assess the effect of texture. Furthermore, load rate and pillar diameter were varied while keeping height diameter ratio constant.

For pillars with diameters greater than 0.75 µm, no influence on fracture stress or strain could be observed. Only with smaller diameters was an increase in fracture stress observed. Furthermore, it was shown that different load rates between 0.1 mN/s and 1.0 mN/s have no influence on fracture stress and strain. In pillars with varying grain orientation, different fracture mechanisms were observed depending on the grain alignment. Comparing the critical stresses for these mechanisms with the measured fracture stresses shown that the fracture behavior could be divided into three areas related on the active mechanism and the orientation to the growth direction. In all cases, the specimens produced with HPPMS showed a slightly higher fracture stress than those produced with dcMS. This behavior could be explained by the typical microstructures resulting from the growth process.

E2-10 Study of Corrosion-Resistance Behavior and Tribological Properties of Electrophoretically Deposited Graphene Coatings on Titanium Substrate for Marine Applications*, Madhusmita Mallick (madhusmita1509@gmail.com),* *A. N,* IIT Madras, India

Titanium alloys are widely employed for marine applications due to its excellent properties of high specific strength and corrosion resistance behaviour. However, these alloys face serious biofouling problems and thereby may become susceptible to corrosion attack under extreme marine environment. The chemical inertness, thermodynamically stable and anti-permeability nature of graphene makes it a promising coating material for effective protection of metals against corrosion.

In the present work, the graphene coating was prepared on a titanium substrate through a cost-effective and easily scalable electrophoretic deposition technique (EPD). The surface morphology and microstructure analysis of bare titanium substrate and graphene-coated samples were done by field emission scanning electron microscopy (FESEM). Grazing incidence angle X-ray diffraction (GIXRD) was carried out to identify the crystal structure of graphene coatings. Moreover, phase purity and functional groups of graphene coatings were analyzed by Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) techniques. The tribological performance of bare titanium substrate and graphene-coated samples were investigated. Furthermore, electrochemical studies were carried out to evaluate the anti-corrosion behaviour of graphene-coated samples by Potentiodynamic polarization test. The results revealed that the corrosion current density in Tafel plot analysis was reduced significantly by 72% for a graphene-coated sample as compared to a bare titanium substrate. This improvement in corrosion resistance property of titanium alloys by graphene protective coatings through EPD technique can greatly serve as a suitable anti-corrosive coating material for marine applications. Results will be presented and discussed in detail.

E2-12 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. 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.

E2-13 Hyperelasticity and Viscoelasticity in Thin Organic Semiconductor Coatings*, **Steve Bull (steve.bull@ncl.ac.uk)**,* Newcastle University, UK*; 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.

E2-14 Abrasion Wear Resistance of Low Temperature Plasma Nitrided Inconel 625 Superalloy*, L. Varela, M. Ordoñez,* University of São Paulo, Brazil*; **Carlos Pinedo (pinedo@heattech.com.br)**,* Heat Tech & University of Mogi das Cruzes, Brazil*; A. Tschiptschin,* 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.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room On Demand - Session E3

Tribology of Coatings for Automotive and Aerospace Applications

E3-1 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.

E3-2 Numerical Study of Cracking in Thin Hard Coating Layers Using a Cohesive Phase-Field Model and Experimental Validation*, **Ali Rajaei Harandi (ali.harandi@ifam.rwth-aachen.de)**,* RWTH Aachen, Germany*; S. Rezaei,* Technical University of Darmstadt, Germany*; S. Karimi Aghda, T. Brepols, J. Schneider, S. Reese,* RWTH Aachen University, Germany

Prediction of damage and cracking patterns in hard protective coatings play a vital role in the optimal design of these coating layers. Experimentally, in [1], it is shown that a micro-scale tensile test of a hard coating deposited on ductile substrates is a fast-tracking tool for determining the fracture parameters of such systems. This experimental approach is specifically valid when the first fracture mode is more dominant. On the numerical side, phase-field damage models are utilized, which have attracted much attention among several available methodologies. These models benefit from a robust response and the capability of modeling cracks without introducing any initial crack path. However, the damage field tends to widen based on the internal length-scale parameter. It could be problematic when it comes to simulations on a small-scale and create some boundary effects. To this end, a cohesive phase-field damage model is used. The relevant fracture parameters such as fracture toughness and maximum tensile strength are included in this model, for which the internal length-scale is considered as a purely numerical parameter. Furthermore, due to the specified morphology of the grains in the coating layers, as well as the evolution of damage based on multiple possible damage procedures, it is inevitable to use anisotropic damage models, [2,3]. To include them, a novel orientation-dependent fracture energy function is applied, based on the later reference. Finally, the numerical results considering the crack patterns and the crack density value is compared to the micro-scale tensile test of cubic metastable $V_{0.25}Al_{0.26}N_{0.49}$ coating deposited on the Cu substrate. It is shown in this study, how fracture characteristic parameters such as fracture toughness and maximum tensile strength, as well as the substrate elastic or elastoplastic behavior, will influence the overall damage behavior of the hard coating layer.

[1] B. Völker, C. Du, H. Fager, H. Rueß, R. Soler, C. Kirchlechner, G. Dehm, J.M. Schneider,

How tensile tests allow a screening of the fracture toughness of hard coatings,

Surface and Coatings Technology,

Volume 390,

2020.

[2] S. Reese, T. Brepols, M. Fassin, L. Poggenpohl, S. Wulfinghoff,

Using structural tensors for inelastic material modeling in the finite strain regime - A novel approach to anisotropic damage,

Journal of the Mechanics and Physics of Solids,

Volume 146,

2021.

[3] Shahed Rezaei, Jaber Rezaei Mianroodi, Tim Brepols, Stefanie Reese,

Direction-dependent fracture in solids: Atomistically calibrated phase-field and cohesive zone model,

Journal of the Mechanics and Physics of Solids,

Volume 147,

2021.

E3-3 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

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.

E3-4 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*; S. Berkebile, N. Murthy, J. 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.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room On Demand - Session EP

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces (Symposium E) Poster Session

EP-1 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-2 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-3 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-4 Tribological Properties of Sputter-deposited Mo Films on Polyimide, ***Edyta Kobierska (edyta.kobierska@unileoben.ac.at)***, *S. Hirn,* Montanuniversität Leoben, Austria*; M. Cordill,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria*; R. Franz, 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-5 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. García,* CONACYT - Universidad de Guadalajara, México

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-6 Composite Coating on Cu Prepared by Plasma Electrolytic Aluminating, *C. Zhao, J. Sun, R. Cai,* ***Xueyuan Nie (xnie@uwindsor.ca)***, University of Windsor, Canada*; J. Tjong,* Ford Motor Company, Canada*; D. Matthews,* University of Twente, Netherlands

Metal-ceramic composite coatings were successfully prepared on pure copper by the plasma electrolytic aluminating (PEA) process. The mechanism of PEA processing and the microstructure of the prepared coatings were studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses. It has been revealed that the $Al(OH)_3$ passive film formed on the copper surface was indispensable for plasma discharges. XRD analysis indicated that the prepared coating consists of metallic Cu, Cu_2O, and Al_2O_3. Tribological tests reveal that the PEA treatment significantly increased the wear resistance in dry-sliding conditions, which could be attributed to the high hardness of the prepared coating. The wear mechanism changed from the adhesive wear of the pure copper to abrasive wear of the steel ball after the PEA treatment. Electrochemical tests show that the coated copper has much better performance against corrosion in 3.5 wt.% NaCl solution at room temperature.

Keywords:plasma electrolytic aluminating; copper; wear; electrochemical corrosion

EP-7 A Numerical-Experimental Study of Borided AISI 316L Steel Under Cyclic Contact Loading, ***Daybelis FERNÁNDEZ (ingday1989@hotmail.com)***, *O. DE LA ROSA, G. Rodríguez-Castro, A. Meneses-Amador,* National Polytechnic Institute, Mexico*; A. LÓPEZ-LIÉVANO, A. Ocampo-Ramírez,* Instituto Sanmiguelense, Mexico

Borided AISI 316L steels under cyclic contact loading were evaluated. Boriding was carried out by two powder-pack processes: continuous and interrupted process. surface hardened by the boriding process. Boriding processes were developed at 1173 K for 1 h (continuous process) and 4 h (interrupted process). A Fe_2B monophase layer was obtained by the interrupted boriding, while a FeB/Fe_2B bi-phase layer was formed by the continuous boriding. Cyclic contact tests were performed on a servo-hydraulic testing machine by cyclic loading of a sphere on the borided steel surface. Circumferential cracks because of the applied critical load (monotonic load) were observed at the borided steel surface. Subcritical loads with a frequency of 6 Hz were applied on the borided steel surface to evaluate the evolution of the damage caused. Stress field generated at the borided steel surface because of cyclic spherical contact was obtained by the finite element method. Interrupted boriding process showed a better resistance to cyclic contact loading than the continuous boriding process.

EP-9 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-10 Enhancement in Dry Cutting Performance and Tribological Characteristics of Amorphous Carbon and Bimetal Nitride Coatings Deposited by HiPIMS Technology With Positive Pulses*, David Matthews (d.t.a.matthews@utwente.nl),* University of Twente, Netherlands*; R. Ganesan,* University of Sydney, Australia*; I. Fernandez-Martinez,* Nano4Energy, Spain*; M. Stueber, S. Ulrich,* Karlsruhe Institute of Technology (KIT), Germany*; D. Mckenzie, M. Bilek,* University of Sydney, Australia

High power impulse magnetron sputtering (HiPIMS) technology with positive pulses was employed in the production of a-C, AlCrN and AlTiN coated tungsten carbide inserts for end milling applications. The results reveal positive effects for increasing productivity, improved surface finish and thickness uniformity, as well as enhanceddry cutting performance. Although HiPIMS is a proven PVD technology to deposit dense coatings it is well-known that drawbacks in coating production by HiPIMS include lower deposition rates, higher residual stress and lower adhesion when compared to techniques such as Cathodic-arc and pulsed-cathodic arc. In this work, the advantage of employing positive pulses to modulate ion fluence towards the coating substrate to modify the film properties is presented. Experimental results showed that a minimum threshold pulse duration of HiPIMS voltage and magnitude of HiPIMS current is required to exploit the full advantage of positive pulses. The optimized parameters for positive pulses yield increased coating deposition rates, reduced argon content and improved adhesion properties. The wear resistance of the films has also been substantially improved. Comparative studies on the positive pulse tailored coatings sliding in air and vacuum environments at different speeds elucidated the advantage of applying optimized positive pulse parameters on the wear behaviour of the coatings.

New Horizons in Coatings and Thin Films
Room On Demand - Session F1

Nanomaterials and Nanofabrication

F1-1 Theory and Applications of Inverted Fireballs*, Gerhard Eichenhofer (eichenhofer@4a-plasma.eu),* 4A-PLASMA, Germany*; J. Gruenwald,* G-Labs, Austria

Inverted Fireballs have been proven to be a viable tool for large area surface modifications, especially for coating purposes [1, 2].This novel technology enables energy efficient deposition for various fields of applications.Its suitability for surface modifications in general and for deposition technologies in particular is owed to their very homogeneous plasma potential and their enhanced ion densities. It has been shown that a substantial increase in the degree of ionisation in the deposition plasma is feasible. This work will outline theoretical investigations into inverted fireballs, such as analytical models and particle-in-cell simulations [3-5] and the application of these findings to technologically relevant topics. Details of how these plasma phenomena can be utilisedin possible areas of surface technology, will be shown. Furthermore, it will be demonstrated that inverted FBs exhibit a number of plasma instabilities. However, they can be stabilised over a long period of time, which is necessary for industrial applications. It will also be outlined in this talk where the limitations of fireball research are at the moment and some ideas for future work on pulsed inverted FB deposition will be presented.

F1-2 Pulsed Aerosol Assisted Plasma Deposition: Influence of the Injection Parameters on ZnO/DLC Nanocomposite Thin Films*, Adèle Girardeau (adele.girardeau@laplace.univ-tlse.fr),* LAPLACE, LCC, France*; G. Carnide,* LAPLACE, LCC, IMRCP, France*; A. Mingotaud,* IMRCP, France*; M. CAVARROC,* Safran Tech, France*; M. Kahn,* LCC, France*; R. Clergereaux,* LAPLACE, France

Aerosol-assisted processes enable to deposit thin films, homogeneous [1, 2] or nanocomposite [3, 4, 5,6]. For example, the nebulization of colloidal solutions, *i.e.* liquid solutions containing nanoparticles, in different plasma processes has been widely used for nanocomposite thin film deposition. However, nanoparticles loaded droplets in the aerosol lead to the deposition of aggregated nanoparticles embedded in the matrix.

Recently, a new process of nanoparticles injection has been developed [7]. This method, called reactor-injector of nanoparticles, consists in synthesizing nanoparticles prior to their injection in the plasma in a pulsed injection regime. It enables to form nanocomposite thin films with really small (<10 nm in diameter) and highly dispersed nanoparticles embedded in the matrix [7].

This work aims to study the deposition of ZnO/DLC nanocomposite thin films in a low-pressure RF plasma. The main challenge of this process is to find the best compromise between the parameters for an efficient synthesis of ZnO nanoparticles and an optimal behaviour of low-pressure RF plasmas in a pulsed regime. It is shown that the operating window enables to deposit nanocomposite thin films with an extended range of volume fraction.

References

[1] Hou, X., et al. (2006). Processing and applications of aerosol-assisted chemical vapor deposition. Chemical vapor deposition, 12(10), 583-596.

[2] Palumbo, et al. (2020). Recent advancements in the use of aerosol-assisted atmospheric pressure plasma deposition. Coatings, 10(5), 440.

[3] Palgrave, R. G., et al. (2006). Aerosol assisted chemical vapor deposition using nanoparticle precursors: a route to nanocomposite thin films. Journal of the American Chemical Society, 128(5), 1587-1597.

[4] Mitronika, M., et al. (2020). TiO2–SiO2 nanocomposite thin films deposited by direct liquid injection of colloidal solution in an O2/HMDSO low-pressure plasma. Journal of Physics D: Applied Physics, 54(8), 085206.

[5] Profili, J., et al. (2016). Nebulization of nanocolloidal suspensions for the growth of nanocomposite coatings in dielectric barrier discharges. Plasma Processes and Polymers, 13(10), 981-989.

[6] Fanelli, F., et al.(2014). Aerosol-assisted atmospheric cold plasma deposition and characterization of superhydrophobic organic–inorganic nanocomposite thin films. Langmuir, 30(3), 857-865.

[7] Khan M.L., et al., “Process for the preparation of nanoparticles,” EP 16305977.7, 2016.

F1-3 Design of Functional Nanoporous Ceramic Coatings via Infiltration of Polymer Templates

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Robust and efficient process for synthesis of various composition inorganic coatings with controlled nanoporosity and structure is highly desirable for design of efficient catalytic, purification, and detection systems. Recently, infiltration of a nanoporous polymer template with inorganic precursors using sequential infiltration synthesis (SIS) with inorganic vapor precursors followed by oxidative annealing was proposed as a new and efficient approach to create porous inorganic structures with tunable porosity and composition. The major limitations of the original water-based thermal SIS, though, are the thickness of the patterned structure being limited by vapor penetration depth of the precursors into the polymer template and the SIS material selection restricted by the availability of high vapor pressure precursors. Here, we propose a swelling-based modification to the SIS process that allows to overcome these limitations. We summarize the basics of the multi-step infiltration approach, the structure and properties of the resulting materials, and their functional potential for practical applications. We report ultra-high accessibility of the pores when porous films are prepared via the polymer swelling-assisted SIS. Using a quartz crystal microbalance (QCM) technique, we demonstrate increased solvent absorbing capabilities of highly porous ceramic films as a result of high interconnectivity of the pores in such structures. Our results show that the SIS can be been extended toward preparing conformal coatings, freestanding membranes, and powders consisting of metal or metal oxide nanoparticles embedded in a porous oxide matrix.

F1-4 Improvement of Adhesion between NiTi Alloy and Diamond-like Carbon Filmby Bayesian Optimization

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Surface coating is one of the most interesting methods for improving the mechanical, physical, chemical and biocompatible properties of materials and devices. Fluorine-incorporated diamond-like carbon (F-DLC) has received much attention as a coating material because of outstanding blood compatible properties which suppress fatal failure of the medical devices. However, it is well known that F-DLC thin films exhibit poor adhesion on metallic alloys and delamination or cracks are easy to occur after coating. In order to improve adhesion of F-DLC on metallic alloys, many scientific methods have been reported. Although some of these studies focused on introducing silicon-containing interlayers such as silicon-incorporated DLC (Si-DLC) between metallic alloys and F-DLC thin films to improve the adhesion properties, the film formation conditions of the interlayer that most improves the adhesion are not clear, and the method has not been established for optimizing the film formation conditions. Thus, we considered optimizing the structure of the interlayer using "Bayesian optimization", which is known as one of machine learning. In this study, we optimize the structure of Si-DLC interlayer by Bayesian optimization to apply F-DLC to low blood compatible nickel-titaniumu (NiTi) alloy, which has been attracting attention as a material for medical devices due to superelasticity and shape memory.

The purpose of this study is evaluating the effectiveness of Bayesian optimization for determining optimal structures of interlayers between metallic substrates and F-DLC, and developing high blood compatible NiTi alloy by improving adhesion properties of F-DLC.

Si-DLC and F-DLC were prepared on NiTi substrates using radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) equipment. The adhesion properties between NiTi substrates and DLC thin films were evaluated by the scratch test, and the structures of Si-DLC interlayer were updated successively by Bayesian optimization on the obtained data. Total of 30 Si-DLC interlayers were produced, and the highest adhesion could be improved to about 53 mN, while the lowest adhesion was about 22 mN. The one with the highest and lowest adhesion were deposited on the NiTi stents, and after performing the crimp test and the fatigue test, the surface was observed by Scanning Electron Microscope (SEM). As a result, no delamination was observed in the interlayer derived by Bayesian optimization, whereas delamination occurred in the sample in which structure was not optimized.

Therefore, this study shows that adhesion properties between metallic material and DLC thin film can be improved by Bayesian optimization.

F1-5 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.

[1] V.Yu.Kolosov, A.R.Tholen, *Acta Mater.***48** (2000) 1829-1840.

[2] I.E.Bolotov, V.Yu.Kolosov, *Phys.Stat.Sol.***69a** (1982) 85-96.

[3] B.J.Kooi, J.T.M.DeHosson, *J.App.Phys.***95** (2004), 4714-4721.

[4] J.Kalb et al., *J.Appl.Phys.***98** (2005), 054902

[5] E.Rimini et al, *J.App.Phys*. **105** (2009), 123502.

F1-6 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. Chiarello, E. Selli,* University of Milan, Italy*; A. Ferretti,* ISTM-CNR Lab Nanotechnology, Italy*; M. Ratova, P. 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.

F1-7 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. 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.

New Horizons in Coatings and Thin Films
Room On Demand - Session F2

High Entropy and Other Multi-principal-element Materials

F2-1 Combinatorial Design of High Entropy Alloys: A Rational Approach in Thin Film*,* ***Elise Garel (elise.garel@grenoble-inp.fr),*** *H. Van Landeghem, R. Boichot,* SIMAP, Grenoble-INP, CNRS, France

High entropy alloys (HEAs) have been studied since 2004 for their exceptional mechanical properties. While conventional alloys are composed of one or two main elements plus addition elements, HEAs are designed with five or more principal elements. The development strategy of these alloys usually focuses on the interior region of the composition space. Among them, refractory high entropy alloys (RHEAs) are studied as an alternative to nickel superalloys that could, for instance, be used in aerospace or for energy production.

Improving the properties of a RHEA by the usual method of trial-and-error requires synthesizing and characterizing many different bulk alloys to cover the entire composition space. For five elements, exploring a 5 to 35% molar fraction range, with a variation of 0.1%, would represent 2.43×10^{12} possible samples to make. Thus, using this historical approach, with such a space to explore, new interesting alloys (probably not optimized) would be discovered essentially by applying a rule of thumb.

This study aims at developing a method to systematically explore an entire n-elements composition space with the minimum number of experiments, focusing on the particular quinary alloy Zr-Ti-Nb-Mo-Cr. Linear gradients of composition are synthesized by depositing thin films through a modified confocal Magnetron Sputtering deposition technique, choosing each set of targets so that these gradients pass by at least three points of an augmented centroid mixture design, to guarantee a uniform screening.

In a n-elements space, it has been demonstrated that there are $(3^n-2^{n+1}+1)/2$ possible gradients, that pass several times by each point of the mixture design. For five elements, there are 90 potential samples to deposit. It is then possible, depending on the preference of the experimenter – such as exploring preferentially the centre or the borders of the composition space - to choose a certain number of gradients among all the possibilities. In the case of a five elements RHEA, about 20 samples (meaning 20 experiments) are enough to screen the entire composition space.

All of these deposited alloys are to be characterized (composition, micro-hardness and phases) to build a database that links composition, structure and properties. A Machine Learning approach is tested to evaluate whether or not it is possible to build a reliable predictive model that would allow to define the RHEA compositions that optimize the alloy properties.

Ultimately, samples of optimized compositions would be cast in ingots in order to confirm on bulk samples the properties discovered with the thin film approach.

F2-2 Systematic Investigation of the Impact of Pure Metal Addition on AlCuMgZn Multi Principal Element Alloys*,* ***Johannes Kirschner (johannes.kirschner@tuwien.ac.at),*** *R. Gaschl,* Vienna University of Technology, Austria*; J. Bernardi,* USTEM, Vienna Technical University, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria*; C. Simson,* LKR Leichtmetallkompetenzzentrum Ranshofen, Austria

The design and synthesis of new materials and alloys is a crucial element in various technical areas, from the design of more energy-efficient mobility solutions to the construction of mechanically more robust alloys. Multi-Principal Element Alloys (MPEAs) show great potential as previous studies have shown that certain quaternary and quinary alloys containing approximately equal amounts of their constituents were superior to conventional alloys. The prediction of compatible elements and their optimal composition, especially in the area of light metals, represents a major challenge in this field and up to date, there is a lack of reliable models and concepts.

Multi-component layers (thickness of 10 µm) were co-deposited by magnetron sputtering and thereafter thermally treated to reveal the complex correlation between chemical composition, crystallography, mechanical properties and morphology. Quaternary systems including the elements Al, Mg, Zn and Cu were chosen to prepare samples in different compositions on a single substrate. Special emphasis was given to the increase of the relative Cu content with approximately the same ratios of the other alloying materials. Scanning electron microscopy in combination with energy dispersive X-ray spectroscopy and X-ray diffraction showed that the addition and increase of Cu have immense effects on the crystallographic phase formation. A wide concentration range in the Cu rich regime was observed (Cu content > 65 at%), in which a single phase system was formed. This range is characterized by significant indentation hardness variations and changes in microstructure. The obtained results were compared with the effects of the quantitative variation of the other constituents to evaluate the impact of different metals and metal classes (alkaline earth metals, transition metals, post-transition metals) on the system properties. Furthermore, the effects of the addition of a 5th element on the structure and crystallography of the alloy were investigated. These results establish a better understanding of the correlation between different metals in a complex system and expand the concept of high entropy alloys to the class of light metals to develop low density alloys. They should also provide valuable information for alloy synthesis using traditional methods such as melt synthesis.

Acknowledgements

This project has received funding by the Austrian Research Promotion Agency (FFG): Project PL2N_A, Grant No 865011

F2-3 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. 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.

F2-4 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. 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 is a field in need of new multifunctional materials for corrosive environments. The cell components need to withstand the high potentials and low pH in the cell while simultaneously meeting many 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 carbon addition to multicomponent films deposited by magnetron sputtering. Adding carbon is a known way to overcome the hardness-ductility trade-off [1] and improve the corrosion resistance of thin films, as long as the formation of crystalline carbides is avoided. The Cantor alloy, CrMnFeCoNi, was chosen as a starting point due to the high concentration of weak carbide forming elements. The alloy composition, combined with the high quenching rate during sputter deposition, improves the chances of carbide suppression.

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. Nanoindentation was used to obtain mechanical parameters, while fragmentation tests on polyimide substrates were performed to investigate the crack resistance [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 hardness and crack resistance, and the addition of carbon greatly improved the corrosion resistance. 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.

References:

1. Fritze, S. et al. Sci. Rep. 8, 1–8 (2018).

2. Tavares da Costa, M. V., et al. Surf. Coatings Technol. 370, 374–383 (2019).

F2-5 Structural and Mechanical Properties of AlTiTaZr(-N) Medium Entropy Films (MEF) Obtained by DC Magnetron Sputtering in Dynamic Mode*, 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.

New AlTiTaZr medium entropy films (MEFs) are elaborated by using direct current magnetron sputtering of four pure metallic targets. The films are deposited in various argon-nitrogen gas mixtures on glass, silicon and sapphire positioned in the center and in the target's axis of a rotating substrates holder. Crystallographic structure evolution, as a function of the nitrogen content, is predicted by calculating the phase selection criteria. The theoretical predicted structures are consistent with X-ray diffraction analysis results. Without nitrogen, the films are amorphous, and by increasing the N_2 content in the gas mixture, they are single phased faces centered cubic (FCC). A {200} preferential growth of AlTiTaZr(-N) films is favored in the targets axis position with increased nitrogen flow rate, whereas those in the center position of substrates holder grow preferentially with {111} planes parallel to the substrates surface.

Hardness and Young's modulus are improved with increasing of the nitrogen flow. The highest values were obtained for those in the targets axis position and reach 24.64 GPa and 148.4 GPa for the hardness and the Young's modulus, respectively. These films were annealed at 600 °C and 900 °C in vacuum and their thermal stability is discussed.

(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.

(4) Hsueh, H.-T.; Shen, W.-J.; Tsai, M.-H.; Yeh, J.-W. , , 4106.

(5) Sheng, W.; Yang, X.; Wang, C.; Zhang, Y. , , 226.

F2-6 Mechanical Properties of Multilayered NbMoTaW Alloy Films with Cyclic Gradient Concentration*, Y. Chen,* ***Chun-Yen Chen******(lover0614revol@gmail.com),*** National Taiwan Ocean University, Taiwan

Conventional High-entropy alloy films have been fabricated through sputtering using a target of multi-principal-element materials with equal proportions in chemical compositions. In this study, NbMoTaW alloy films were prepared using a four-gun cosputtering apparatus with four pure-element targets. Moreover, the rotation speeds of the substrate holder were controlled at 1–30 rpm, which resulted in that the films exhibited a multilayer structure stacked with cyclic gradient concentration. The uniformity of the multilayered alloy films was improved with increasing the substrate holder rotation speed. The mechanical properties and crystalline phases of the NbMoTaW alloy films were investigated. The results indicated that the NbMoTaW alloy films prepared with a substrate holder rotation speed of 30 rpm exhibited a single body centered cubic(bcc) phase, a hardness of 12.9 GPa, and a Young's modulus of 287 GPa. The phase evolved into a combination of plural bcc phases as the substrate holder rotation speed was decreased to 1–10 rpm. All the NbMoTaW alloy films exhibited a Young's modulus level of 282–289 GPa. The NbMoTaW alloy films prepared at 10 rpm exhibited a high hardness of 14.1 GPa.

F2-7 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)

F2-8 Phase Formation and Structural Properties of AlSiTaTiZr Multicomponent Thin Film Alloys*, **Felipe Cemin (lipecemin@gmail.com)**, M. Jimenez,* UNICAMP, Brazil*; L. Leidens,* Universidade de Caxias do Sul, Brazil*; R. Merlo,* UNICAMP, Brazil*; C. 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.

In the pursuit of understanding these new materials in the non-bulk, thin film form, we have investigated key parameters leading to film crystallization and phase formation in an AlSiTaTiZr multicomponent system, due to its potential application in the field of high-temperature, oxidation-resistant coating materials. Therefore, metallic films were grown by radio-frequency magnetron sputtering at different deposition conditions 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). The chemical bonds were analyzed by XPS revealing 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. Post-thermal annealing prompts the metallic glass structure into a complex crystalline structure of several coexistent compounds, expected by thermodynamic calculations. Special focus is given to the entropy and enthalpy role on the phase formation and stability.

F2-9 XPS Core-Level Shifts, Local Lattice Distortions and Charge Transfer in HfNbTiVZr Refractory High Entropy Alloy*, **Luis Casillas-Trujillo (luis.casillas.trujillo@liu.se)**,* Linköping University, IFM, Sweden*; B. Osinger, R. Lindblad, D. Karlsson, S. Fritze, K. von Fieandt,* Uppsala University, Angstrom Laboratory, Sweden*; B. Alling,* Linköping University, IFM, Sweden*; U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden*; I. Abrikosov,* Linköping University, IFM, Sweden*; E. Lewin,* Uppsala University, Angstrom Laboratory, Sweden

Ab-initio simulations of HfNbTiVZr high-entropy alloy using density functional theory (DFT) have been combined with experimental studies of the thin film material using X-ray photoelectron spectroscopy (XPS) to investigate lattice distortions, charge transfer and XPS core level shifts in the alloy. The lattice distortions obtained from the DFT simulations show that the size mismatch among the constituent elements is reduced in the alloy, causing a considerable reduction of the assumed lattice distortion effect commonly estimated with metallic radii. We show that this size reduction is due to the charge redistribution caused by the different local chemical environments, which was evaluated using a fixed sphere model that compared the relaxed, non-relaxed, and elemental reference structures. Finally, the theoretical core level shifts (CLS) values calculated from the DFT-simulated high entropy alloy show good agreement with the experimentally observed core level binding energy shifts, as well as peak broadening due to a range of chemical surroundings obtained by XPS measurements of a thin film deposited by sputter deposition.

New Horizons in Coatings and Thin Films
Room On Demand - Session F3

2D Materials: Synthesis, Characterization, and Applications

F3-1 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. Rowley-Neale, C. Banks, P. 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 (<300ºC). 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 (k^0) 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.

F3-2 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. Liao, Y. Wang, H. Zaid, A. Aleman, M. 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.

F3-3 Graphene Deposition on Copper Using Concentrated Solar-Thermal Heating*, Abdalla Alghfeli (alghfeli@g.ucla.edu),* *M. Abuseada, T. Fisher,* University of California at Los Angeles, USA

Manufacturing processes are often highly energy-intensive, even when the energy is primarily used for simple heating processes. This energy tends to derive from local utilities, which currently employ a blend of sources ranging from fossil fuels to renewable wind and solar photovoltaics, among others. When the end manufacturing need is thermal energy, direct solar-thermal capture provides a compelling option, but one that has rarely been employed to date. Here, we report a solar-thermal process using a simulated solar concentrator to demonstrate the ability of such a source to produce a high-value product, namely graphene on copper. Material deposition occurs at a surface and requires knowledge of material science, manufacturing, and heat transfer modeling. In this study, we employ a 10 kW_e concentrated solar source (solar simulator) capable of producing an adjustable high heat flux distribution (up to 4.5 MW/m^2, or 4,500 suns) in order to produce graphene rapidly on copper foil by chemical vapor deposition. The custom-built reactor consists of a xenon short arc lamp (that closely approximates the solar spectrum) placed at a truncated reflector's first focal point to concentrate source radiation with a Lorentzian-like heat flux distribution on the reflector's second focal point. Through the use of a controllable DC power supply and shutter, incident heat flux can be controlled and varied. Copper substrates are placed on a well-insulated mount that allows for varying the substrate's focal position, and hence heat flux distribution. We use the concentrated solar source to study the effect of heating and photocatalysis on the deposition product, and we begin to optimize the process by modeling substrate heat transfer processes that depend highly on optical and local thermal conditions. The process is monitored by optical emission spectroscopy, including an IR camera, pyrometer, and near-IR spectrometer, to determine appropriate gas recipes (flowrate and relative concentrations of methane and hydrogen) and other operating conditions, such as vacuum pressure, that yield high-quality product. The graphene produced through this process is further analyzed with scanning electron and Raman microscopy to assess the uniformity of graphene deposition as well as its quality, which is associated with the intensity ratio between Raman peaks of C-C in-plane vibrations and graphene lattice defects. Upon optimizing the operating conditions, graphene deposition will be extended to a larger and continuous scale through the use of a roll-to-roll solar chemical vapor deposition.

New Horizons in Coatings and Thin Films
Room On Demand - Session FP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-1 Optical, Structural and Morphological Properties of NiO_X Thin Films Obtained by E-Beam*, Jhonathan Castillo (jhonathan.castillo@uabc.edu.mx),* Universidad Autónoma de Baja California, Colombia*; N. Nedev,* Universidad Autónoma de Baja California, Bulgaria*; B. Valdez,* Universidad Autónoma de Baja California, Mexico*; M. Bernechea,* University of Zaragoza, Spain*; M. Mendivil,* Centro de Investigación en Materiales Avanzados (CIMAV, Mexico*; M. Curiel,* Universidad Autónoma de Baja California, Mexico

Non stoichiometric nickel oxide (NiO_x) is a transparent conductive oxide (TCO) that has attracted a lot of attention because of its electrical and optical properties.Most of the available TCOs are n-type semiconductors, while NiO_x is a promising p-type candidate because of its excellent chemical stability and optical transparency. Some potential optoelectronic applications of NiO_x are as a p-type channel in transparent thin film transistors (TFTs) and as a hole transport layer in organic or quantum dot solar cells solar. In this work thin NiO_x films were obtained by thermal oxidation of ~20 nm thick Ni films deposited by electron beam evaporation. The films were deposited on glass substrates with size of 2.5×2.5 cm and n-type <100> silicon wafers. The oxidation process was carried out at 400, 500 and 600°C.

All samples were characterized by transmission electron microscopy, scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, UV-Vis spectroscopy, X-ray diffraction and diffuse reflectance spectroscopy. Results for the obtained NiO_x films will be presented and a discussion of their possible application in TFTs and in solar cells as hole transport layers will be given.

Keywords: NiO_x, e-beam, thin films

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FP-2 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. Lu,* Chinese Culture University, Taiwan*; F. Shieu,* National Chung Hsing University, Taiwan*; H. 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℃ 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-3 On the Grain Size Dependence on Film Thickness*, **Dulmaa Altangerel (dulmaa.altangerel@ugent.be)**, R. Dedoncker, F. Cougnon, D. Depla,* Ghent University, Belgium

A meta-analysis of published data in combination with measurements on Al, Cu, CuO, CrCoFeMnNi, $Ni_{90}Cr_{10}$, TiN, and V sputter deposited thin films, permits to demonstrate that the grain size-thickness correlation can be described by a power law. The exponent depends on the homologous temperature which is defined as the ratio between the deposition and the melting temperature of the studied material. The exponent is close to 0.4 at a homologous temperature between approximately 0.15 and 0.3. Theoretical film growth models that depict an evolutionary overgrowth mechanism obtain the same exponent. Above a homologous temperature of approximately 0.3, a slightly higher exponent is observed which agrees with the general idea that at higher homologous temperatures the grain size is also influenced by restructuring mechanisms occurring during film growth. The exponent becomes substantially lower at low homologous temperatures (<0.15). From a theoretical point of view its value should be close to zero. The aforementioned boundaries of the homologous temperatures corresponds with those observed in published structure zone models which describe the microstructure of physical vapor deposited thin films. The good agreement suggests that the underlying reason for the observed boundaries is the atom mobility. This hypothesis was further investigated by a study on the influence of intentionally added impurities on the power law behavior for Al and Cu thin films. A decrease of the grain size is observed for both materials when the impurity-to-metal flux ratio is increased. No change of the exponent is observed for Al, while for Cu the exponent becomes equal to zero at sufficiently high impurity-to-metal flux ratios.

FP-4 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].

This work was supported by JSPS KAKENHI Grant Number JP17K04989.

[1] S. Shi *et al.* , J. Appl. Phys. 109 (2011) art. no.103508. [2] C. Soci *et al.* , Nano Lett. 7, (2007) 1003-1009.

FP-5 Superior Hydrophilicity in a Magnetron Sputtered Fe-Cr-Ni Thin Film With Nano-Pyramid Surface Structure*, **Pak Man Yiu (pmyiu@mail.ntust.edu.tw)**, J. You, S. Wang, J. Chu,* National Taiwan University of Science and Technology, 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-6 Synergistic Effect of Ultra-thin Ag Film Coupled ITO Sandwich Structures*, **Ying-Jie Gao (www25635179@gmail.com)**, H. Song, W. Wu,* Da-Yeh University, Taiwan

With the fast developments in modern optoelectronic devices including organic light emitting diodes (OLEDs), light-emitting diodes (LEDs), solar cells, and touch screens, the demand of flexible transparent conductive oxide (TCO) is increased. Tin-doped indium oxide (ITO) is most widely adopted because of its high optical transparency and electrical conductivity. For TCO on flexible electronic device, manufacturing challenges such as processing temperature, annealing temperature, total film thickness, and film stress become crucial.

High-power impulse magnetron sputtering, (HiPIMS) technology exhibits a high plasma density and target ionization rate through a duty cycle of less than 5 % and high peak power. Compared with traditional magnetron sputtering technology, the HiPIMS-deposited film has a higher density, adhesion, flatness, and processing temperature below 100 °C. HiPIMS has several advantages for the deposition of TCO structures on polyethylene terephthalate, (PET) and polyethylene naphthalate, (PEN) substrates because of the low heat resistance of the flexible substrate. Due to ITO alone can not fully meet the demand for flexible electronic devices, various materials or structure design have been developed. Among them, the sheet resistance was effectively reduced by stacking the oxide and ultrathin metal film to form a sandwich structure of oxide/metal/oxide (OMO). The ultrathin metal film provides a continuous electronic conduction and the upper and lower oxide layer provide anti-reflection effect and increases transmittance.

In this study, sandwich ITO/Ag/ITO structure have been prepared onto 1.2 mm thick soda lime glass, (SLG) substrates, flexible polymer substrates including PET and PEN using HiPIMS technology after investigating the single layer of Ag and ITO. Through the optical simulation and the thickness optimization, the synergistic effect of ultra-thin Ag film Coupled ITO sandwich structures was studied. The flexible sandwich ITO/Ag/ITO structure in our study gives a sheet resistance of less than 10 Ω/sq, a resistivity of less than 10^{-5} Ω·cm, and an average visible light transmittance of more than 80 %.

Keyword：ITO、HiPIMS、TCO、OMO

FP-7 Development of Hydrogen Barrier Coatings based on Tungsten-doped Alloys*, **Issam Lakdhar (issam.lakdhar@utt.fr)**, A. Alhussein,* Université de Technologie de Troyes (UTT), France*; J. Creus,* LASIE, CNRS-Université de La Rochelle, France

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 [1]. However, the transport and the storage of the smallest chemical element at ambient conditions still a crucial issue because hydrogen can dissolve then permeate in any metallic material and cause its embrittlement and failure (pipelines, tanks).

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, Mo, Ti, Ni and ceramics [2].

This work focuses on the development of hydrogen barriers based on tungsten-alloy thin films (ternary alloys Al-Ti-W/Ti-W-N) and alternative multilayers (Al-Ti-W/Ti-N-W) elaborated with physical vapor deposition technology in presence of plasma environment. 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…). The coating efficiency was evaluated under hydrogen by chemical and electrochemical charging 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[3]. 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 plasma technology, Electrochemical and mechanical properties.

Acknowledgements: The authors would like to thank the co-founder of DERBHY project: the European Union (Fond Européen de Développement Régional)

References:

[1]: P. Emilio and V. de Miranda, Science and Engineering of Hydrogen-based Energy Technologies (2018)

[2]: V. Nemanic, Hydrogen permeation barriers: Basic requirements, materials selection, deposition methods, and quality evaluation, Nuclear Materials and Energy 19 (2019)

[3]: C. Brandolt, L. Noronha, G. Hidalgo, Niobium coating applied by HVOF as protection against hydrogen embrittlement of API 5CT P110 Steel, Surface and Coatings Technology (2017)

FP-8 Structure and Mechanical Properties of ZrB$_{2+x}$ and ZrAlB$_{2+x}$ Hard Coatings

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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.

Authors acknowledge funding from the Slovak Research and Development Agency [APVV-17-0320], VEGA 1/0381/19 and Operational Program Research and Development [project ITMS 26210120010].

[1] B. Alling, H. Högberg, R. Armiento, J. Rosen, L. Hultman, Sci. Rep. 5 (2015).

FP-10 Fabrication of Nanocomposite Thin Films of Metallic Nano Particles in Amorphous Carbon

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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-11 Growth and Characterization of Ga$_2$O$_3$/Ag-Cu /Ga$_2$O$_3$ Multilayers by High Power Impulse Magnetron Sputtering

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High-energy ultraviolet radiation (λ <300 nm) is widely used for surface sterilization of surface, static water, and flowing water. In the past, mercury lamps have always been the only choice for ultraviolet radiation sources, but due to the "Minamata Convention on Mercury", it will be restricted internationally in the future. Therefore, ultraviolet radiation emitting device have become the most potential substitute. The UV device must use transparent conductive electrode materials to prevent electrodes from covered light-emitting elements. However, the most commonly used indium tin oxide (ITO) has a very serious absorption problem at UV. Therefore, reducing the Ultraviolet radiation-absorbing transparent conductive oxide (Transparent Conductive Oxide, TCO) is one of the key technologies to effectively improve component efficiency. Gallium oxide (Ga$_2$O$_3$) has a very wide band gap (4.87 eV) and has excellent transmittance in the shorter wavelength UVC (100~280 nm). However, the wide band gap also led to electrical performance almost insulating in Ga$_2$O$_3$. According to many literature studies, sheet resistance could be effectively reduced by using a multilayer OMO (Oxide/Metal/Oxide) stacking method. Moreover, an ultrathin metal film has a certain degree of transmittance in UV and visible spectrum. Therefore, developing Ga$_2$O$_3$/Metal/ Ga$_2$O$_3$ nano-multilayer film structure as the TCO electrode for the UVC element is necessary.

In this work, the use of HiPIMS co-sputter deposition of Ag-Cu alloy structure reduce the island growth of pure metal thin films and further improve the performance of OMO multilayer film. The dense and continuous ultra-thin metal film improves the optical and electrical properties of the overall structure of the OMO. By fixing the power of Ag and adjusting the current of Cu, various composition of Ag-Cu film was deposit for investigating the influence of the concentration of Cu on the sheet resistance and optical transmittance continuity of the ulta-thin metal film.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G1

Advances in Industrial PVD, CVD and PCVD Processes and Equipment

G1-1 INVITED TALK: Deposition of Functional Nano-Coatings Using Atmospheric Pressure Plasmas*, Daphne Pappas (daphne.pappas@plasmatreat.com)*, *A. Aref, A. Sy,* Plasmatreat USA, Inc., 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.

G1-3 Parametric Analysis of the Selective GTAW Remelting Process for WC-10Co-4Cr Coating by HVOF*, Hortencia Santos (hortencia.noronha@gmail.com)*, Universidade Federal do Pampa, Brazil*; N. Mayhassen,* Instituto Tecnológico de Aeronáutica, Brazil*; A. Miranda, H. SVOBODA,* Universidad de Buenos Aires, Argentina*; A. Oliveira,* Universidade Federal do Pampa, Brazil

Thermal sprayed coatings containing tungsten carbide (WC) are widely used in different industrial applications due to its high hardness, high temperature and wear resistance. As sprayed coatings containing WC usually require a second stage of remelting, after application, to enhance the final properties, which can be made using different heat sources like laser, electric arc, oxi-gas flame or a furnace. Aspects of coating quality like adherence, dilution and level of defects are strongly affected by the heat source and procedure employed. Nevertheless, there is a lack of systematic studies related to these aspects. The objective of this work was to analyze different parameters using GTAW to produce the remelting of WC-Co thermal sprayed coatings obtained by High Velocity Oxi-Fuel (HVOF) process. Samples of carbon steel were coated by HVOF using a WC-Co powder obtaining a coating of 100 microns thickness with a hardness of 1250 HV. Then, the coated samples were remelted using GTAW processes. In each case, the effect of different parameters like power, travel speed and patterns were evaluated. On the refused samples microstructural characterization, microhardness profiles and electrochemical corrosion test were done. There were obtained procedures to remelt the WC-Co coatings with low dilution. The processes produced coatings with hardness values between 1600 and 1800 HV. The resistance to corrosion was similar than the as spray condition. Nevertheless, the integrity of the interphase was strongly improved in both cases.

Acknowledgments

The authors want to acknowledge to RIJEZA-Brasil for providing the coated material and to INTI-Argentina and ITA-Brasil for the wear tests.

G1-4 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.

G1-5 Carbon coating on Three-dimensional Anodically Oxidized Titanium Foam with Hierarchical Nanostructure for Capacitive Deionization Electrode*, J. Huang,* ***Ping-Yen Hsieh (pyhsieh@fcu.edu.tw)****, J. He,* Feng Chia University, Taiwan

Capacitive deionization (CDI) is one of the most promising technique for water treatment and purification. To meet the demand for pursuing high efficiency of desalination, the key component, CDI electrode, requires high chemical stability, high specific surface area, high water wetting ability, and suitable porous structure for ion electrosorption. As opposed to the conventional carbon nanomaterials for CDI electrode, a new design concept is proposed by using facile nanostructure engineering on titanium foam through anodically oxidization and hydrothermal treatment, followed by high-temperature glucose carbonization to develop a carbon film coated titanium dioxide nanostructured porous electrode (CTPE). Further, the feasibility of using such novel electrode for CDI performance was evaluated. The experimental results show that successful preparation of a carbon film coated titanium dioxide nanostructure on titanium foam can be facilitated to obtain CTPE. With the carbon film served to passivate surface and provide low impedance interface, it enhances ion transmission capacity and improves electrochemical stability. By taking the synergistic effect of abovementioned characteristics, the efficiency of salt electro-sorption/desorption performance was enhanced significantly based on the cyclic voltammetry results. Finally, under an optimal CDI cell operation condition, the CTPE can reduce sodium chloride water solution with its conductivity from 748 µS/cm to 627 µS/cm, corresponding to the adsorption NaCl amount of 0.54 mg/cm^3. Overall, the proposed CTPE can be considered a promising material for CDI application.

G1-6 Digital Twin PVD Coater Matsight - State-of-the-Art and Future Outlook*, Adam Obrusnik (obrusnik@plasmasolve.com)**, P. Zikan, M. Kubecka,* PlasmaSolve s.r.o., Czechia

In most fields of industry, CAE (computer-aided engineering) is the go-to tool for designing a new system or a process. Recent scientific advancements and the evolution of high-performance computing also enabled predictive simulation of industrial PVD processes, substantially reducing the effort invested to trial-and-error. As a provider of industrial PVD CAE, we report on the development of MatSight - a user-friendly “digital twin” software that will enable in-house user-friendly CAE of PVD systems and processes. We discuss the numerical strategies and physical assumptions which enable the underlying simulation. The presentation aims to provide relevant use cases and success stories for PVD CAE but it also aims to discuss the challenges encountered during the development and present limitations of PVD simulation.

G1-7 Oxygen-Controlled Crystal Structures and Properties of SnO_2 Infrared Transparent Conducting Films*, Liangge Xu (xuliangge@aliyun.com)**, L. Yang,* Harbin Institute of Technology, China*; J. Zhu,* Key Laboratory of Micro-systems and Micro-structures Manufacturing, China

Tin oxide (SnO_2) has been widely explored for various applications due to its excellent n-type semiconductor properties, low resistance, and high optical transparency in the visible range. However, few studies on the preparation of SnO_2 films using high power pulsed magnetron sputtering have been reported. Oxygen content is a critical parameter in the practice of SnO_2 thin films by high-power pulsed magnetron sputtering. the average free range of Sn atoms is usually much smaller than O atoms. SnO_2 films deposited in a pure Ar atmosphere are likely to be oxygen-deficient and form O vacancies. and such oxygen vacancies will cause lattice distortion, which will affect the mobility of charge carriers in the SnO_2 film. Therefore, oxygen is the main factor affecting the electrical conductivity of SnO_2 films.

In this paper, the reaction mode of high-power pulsed reactive magnetron sputtering at different oxygen partial pressures and the crystal structure and infrared transparent conductive properties of SnO_2 films prepared at 600°C were investigated. The crystal structures and properties of infrared transparent SnO_2 films deposited by high-power pulsed magnetron sputtering at different oxygen partial pressures from 10 to 24 sccm were investigated. For the SnO_2 films deposited with 10~14 sccm oxygen partial pressure, the reaction mode is dominated by the metallic mode, and the polar unsaturated (101) plane is the preferred orientation of the film crystals. For SnO_2 films deposited with oxygen partial pressures of 16 to 18 sccm, the reaction mode is dominated by the transition mode, and the (110) plane shows a preferred orientation. In the deposition process with oxygen partial pressure greater than 18 sccm, the reaction proceeds in the poisoning mode. As the oxygen partial pressure increases, the carrier concentration decreases to 2.335×10^{15} cm^{-3}; the mobility increases to ~15 cm^2/Vs, and the IR transmittance at 4 µm increases. At the same time, the electrical properties of the prepared SnO_2 films deteriorate due to the oversupply of O_2, with resistivity up to 5.029×10^2 Ω•cm^2.

G1-8 INVITED TALK: 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.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G2

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications

G2-1 INVITED TALK: 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 α2 phase. The γ phase has a low oxygen uptake, can act as a barrier against oxygen and has better mechanical properties than the α2 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.

G2-3 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

The Additive Manufacturing (AM) of metals promises disruptive changes in a host of manufacturing industries. While the field has been advancing at a rapid pace over the past years, resulting surface states remain a particularly unyielding obstacle to a wide range of applications. Powder particle sizes in the tens of micrometres impose similarly sized features on AM surfaces, with obvious negative impacts on mechanical performance or dimensional precision.

Electrolytic plasma polishing (EPPo) is a finishing method used for the polishing, cleaning, deburring, smoothing of metals and alloys. In contrast with other finishing techniques requiring careful control of directionality, such as mechanical polishing or laser-based methods, EPPo natively effects the surface as a whole. Among other geometry-independent approaches, such as electropolishing or chemical etching, EPPo stands out with its 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 AM particularly well, with few or no constraints put on piece design as well as 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 analysis of the process could enable the automated fine-tuning of parameters through direct feedback. To help realize this, comprehensive analyses in the frequency domain of the electrochemical cell current response were conducted and shown to give real-time information on the balance between the different reactions and physico-chemical phenomena at play. Additionally, plasma light emission and gas evolution were analyzed to inform interpretation and the role of the different process parameters.

Extensive ex situ analysis of the surfaces was performed in terms of morphology and composition. Very superficial dealloying (~10nm) could be demonstrated in the case of Ni-Cr steels which, along with the overall roughness decrease, is believed to drive moderate improvements in corrosion resistance 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, a metric particularly pertinent to the finishing of AM pieces and their large-scale surface roughness.

G2-4 PEO Coatings for Adhesive Bonded AA6060 Components*, **Dominic Shore (dominic.shore@manchester.ac.uk)**,* The University of Manchester, UK*; J. Avelar-Batista Wilson,* BCW Manufacturing Group Ltd, UK*; A. Matthews, A. Yerokhin,* The University of Manchester, UK

Adhesive bonded aluminium components have become increasingly important to the automotive industry, where lightweight structures are imperative to performance and vehicle efficiency. Since the mid-20th century, conventional anodizing processes have been applied to aluminium components subject to adhesive bonding, to increase bond durability and corrosion resistance. However, conventional anodizing generally uses strongly acidic electrolytes which have a significant environmental impact. Anodizing procedures are generally multi-stage processes which can be resource intensive and time consuming. This study looks into application of Plasma Electrolytic Oxidation (PEO) as an alternative to conventional anodizing techniques for the preparation of aluminium parts for bonded structures. PEO is a promising emerging coating technique for the production of oxide coatings with excellent tribological performance and corrosion resistance. It offers an alternative route for the production of well adhered oxide coatings where weak alkaline electrolytes can be utilised in place of the highly acidic electrolytes associated with conventional anodizing processes. PEO has the further potential to reduce the number of additional treatments prior to and after the anodizing stage, offering scope for savings in resources and time.

In this investigation, experiments were carried out to produce PEO coatings on the alloy AA6060-T6 using different electrolyte compositions and power/polarity regimes, to develop coatings with differing characteristics for comparison. Detailed analyses of the microstructure, chemical and phase composition of these coatings was carried out using methods including SEM, EDS, GDOES and XRD. The adhesive strength of coatings was assessed using mechanical tests including tensile lap-shear testing. Analysis of the fracture behaviour and the ultimate strength of the adhesive joints was considered along with the observed physical/compositional characteristics of the different coatings to determine the suitability of PEO coatings for bonding applications and to achieve an understanding of the important parameters influencing the joint strength when bonding PEO coated AA6060-T6. The coatings were further investigated using electrochemical techniques such as EIS and subjected to accelerated corrosion testing along with investigations into the abrasive wear of the coatings to determine their overall suitability for automotive applications. It is intended that the findings of this study will be of interest for potential industrial applications and will also contribute to the general understanding of the mechanical properties of PEO coatings.

G2-5 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.

[1] P. C. M. Hamdani , R.N. Singh, “Co3O4 and Co- Based Spinel Oxides Bifunctional Oxygen Electrodes,” Int. J. Electrochem. Sci., vol. 5, pp. 556–577, 2010.

[2] P. W. Menezes et al., “High-Performance Oxygen Redox Catalysis with Multifunctional Cobalt Oxide Nanochains : Morphology-Dependent Activity,” ACS Catal., vol. 5, pp. 2017–2027, 2015.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G3

Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

G3-1 Enhancing the Performance of Rake and Flank Surface Textured Ceramic Tool Filled With Solid Lubricants*, Sathiya Narayanan Nagarajan (sathyasairam89@gmail.com)*, *S. Venkata Sai Prabhu, S. G, A. G, S. N,* Sastra Deemed University, India

Non-hazardous, toxic-free, allergic-free and less cost-orientated methods are expected by the industries and the industrial workers for the better working-environment. In this work, an effort is made to achieve this expectation by integrating the concept of surface texturing and extended self-lubrication for machining grey cast iron materials. Cross-chevron and line textures were fabricated on the tool's rake and flank faces using Nd: YAG laser texturing machine. An untextured ceramic tool (UT), cross-chevron and line textured tool (TT) and solid lubricants (MoS_2 and Graphite) and SAE 40 oil mixed chemical solutions filled textured tool (STL) are considered for machining under dry conditions. The particles' average size was observed to be 1400 nm and 1590 nm for MoS_2 and graphite solid lubricants, whereas the polydispersity index (PdI) found to be 0.903 and 0.977 respectively. The solid lubricants' PdI values indicated that the particle samples were larger in size distribution and polydisperse. The experimental results observed with the reduced main cutting force, feed force, average friction co-efficient for semi-solid lubricant filled texture tool than other considered tools.

G3-2 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. Korenyi-Both, S. Midson, M. 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.

G3-3 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.

G3-4 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.

Surface Engineering - Applied Research and Industrial Applications
Room On Demand - Session G4
Pre-/Post-Treatment and Duplex Technology

G4-1 INVITED TALK: 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.

The work was partly supported by the Cooperative Research Program in the ISIR, Osaka University, 20191261 and Kyoto University Nano Technology Hub by the MEXT, Japan.

[1] C. B. Samantaray and R. N. Singh, Int. Mater. Rev. **50** (2005) 313.

[2] Y. Zhang et al., Phys. Rev. **B** 73 (2006) 144115.

[3] Y. Hattori et al., ACS Appl. Mater. Interfaces **8** (2016) 27877.

[4] T. Burton et al., J. Propul. Power. **30** (2014) 690.

[5] M. Noma et al., Jpn. J. Appl. Phys. **53** (2014) 03DB02.

[6] T. Higuchi et al., Surf. Coat. Technol. **377** (2019) 124854.

[7] C. Ronning et al., Diamond and Relat. Mater. **6** (1997) 1129.

[8] K. Nose et al., Appl. Phys. Lett. **83** (2003) 943.

[9] E. Broitman, Tribology Lett. **65** (2016) 23.

G4-3 Notable Difference between Rapid-Thermal and Microwave Annealing on Ge pMOSFETs*, Fu-Yang Chu (xxmoon666@gmail.com),* *K. Chang-Liao,* National Tsing Hua University, Taiwan*; D. Ruan,* National Tsing Hua University, China*; S. Yi,* National Tsing Hua University, Taiwan

Effects of rapid-thermal-annealing (RTA) and microwave annealing (MWA) on GeOx interfacial layer (IL) and HfO_2 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/cm_2 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.

G4-4 Characterization of Tungsten-doped InZnO Thin Films with Plasma Treatment for Conductive-bridge RAM Applications*, Chih-Chieh Hsu (cchsu.06g@g2.nctu.edu.tw),* National Chiao Tung Universiy, Taiwan*; P. Liu, K. Gan, D. Ruan, Y. Chiu, S. Sze,* National Chiao Tung University, Taiwan

In this study, the impact of plasma treatment on InWZnO (IWZO) CBRAM was reported.In order to improve the characteristics of IWZO CBRAM device, we use oxygen remote plasma to surface-treat the IWZO layer. Oxygen plasma can slightly suppress oxygen vacancies in IWZO. The set voltage of the device becomes more uniform and smaller, which is beneficial for low power operation. The a-IWZO CBRAM shows the excellent memory performance, such as high switching endurance (up to3 ´ 10^3 cycles) and overshoot current decrease. Without high temperature is used in the process, which would be suitable for memory in flexible substrates.

Surface Engineering - Applied Research and Industrial Applications
Room On Demand - Session G5
Hybrid Systems, Processes and Coatings

G5-1 INVITED TALK: Frontiers of Surface Engineering for Ultra-low Friction and Wear*, Ali Erdemir (erdemir8184@gmail.com),* Texas A&M University, 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.

G5-3 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)

G5-4 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).

G5-6 Thermal Stability of Passivated Oxygen Vacancy in Indium Gallium Zinc Oxide with Supercritical Fluid Cosolvent Oxidation, Post Annealing or Oxygen Plasma Treatment*, Chia-Yu Lin (mandylin21107@gmail.com), P. Liu,* National Chiao Tung University, Taiwan*; D. Ruan,* National Chiao Tung University, China*; Y. Chiu, K. Gan, C. Hsu,* National Chiao Tung University, Taiwan*; S. Sze,* National Chiao Tung University, USA

In this report, the thermal stability of oxygen vacancy in indium gallium zinc oxide (IGZO), which was passivated by supercritical fluid (SCF) cosolvent oxidation, post annealing or oxygen plasma treatment, has been investigated in detail. With X-ray photoelectron spectroscopy (XPS) analysis, it can be found out that the oxygen vacancy passivated by SCF treatment exhibits better thermal stability than other oxidation treatment. Besides, the IGZO treated with different treatment has been used as the channel material for thin thin-film transistor device. Similar with the XPS result, the device with SCF treatment shows excellent reliability and uniformity even within high temperature ambient.

Surface Engineering - Applied Research and Industrial Applications
Room On Demand - Session G6
Application-Driven Cooperations between Industry and Research Institutions

G6-1 Hard Protective Coatings Inside Narrow Tubes and Cavities in Aircraft Engine Components*, J. Crespo Villegas, 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.

G6-2 Prediction of Loss of Barrier Properties in Cracked Thin Coatings on Polymer Substrates Subjected to Tensile Strain*, **Marcus Vinícius Tavares da Costa (marcus.tavares@angstrom.uu.se)**, E. Gamstedt,* Uppsala University, Angstrom Laboratory, Sweden

The layered structure of carton containers for food and beverage packaging is one of the most widely used products in our daily life which allows the transportations while keeping the food protected. This design has been around for decades, but more sustainable solutions are needed to replace aluminium barrier layers with thinner and more environmentally friendly coatings. Recent developments in thin film deposition over large areas of polymer substrate have sparked the interest of food packaging producers in thin brittle coatings of nanometre thick of various compositions in the package structure. Such coatings can be impermeable and therefore enhance the barrier properties of the packages as a whole [1]. However, when these coatings are implemented in the manufacture process, cracking in the coating is almost inevitable since the package materials are deformed in the converting process, and hence the barrier properties are impaired. A mechanism-based model to predict the loss of barrier properties during deformation in the manufacturing process could potentially serve as a tool in developing improved packaging.

In this presentation, we will tackle this question by showing how the fracture behaviour of coatings on polymers substrates is affected by uniaxial tensile deformation, and subsequently how a key barrier property for beverage packaging, namely the oxygen transmission rate (OTR), is affected by the fractured coating. This is done quantitatively by numerical modelling. The modelling is dependent on reliable experimental characterization published previously [2, 3]. The specimens for this study case were produced by roll-to-roll atomic layer deposition of metal oxides, with thickness values between 4 and 20 nanometers on poly(ethylene terephthalate) substrate films. The advantages and disadvantages of the model will be addressed, as well as its accuracy.

References

[1]P. Fayet, C. Neagu, K. Gamstedt, Mechanics-driven material design for optimized barrier films, Proceedings of the AIMCAL Web Coating and Handling Conference, Naples, USA, 2015.

[2]M.V. Tavares da Costa, J. Bolinsson, R.C. Neagu, P. Fayet, E.K. Gamstedt, Experimental assessment of micromechanical models for fragmentation analysis of thin metal oxide coatings on polymer films under uniaxial tensile deformation, Surface and Coatings Technology. 370 (2019).

[3]M.V. Tavares da Costa, E.K. Gamstedt, Energy-release rates and opening of cracks in thin barrier coatings on polymer substrates subjected to tensile loading, Engineering Fracture Mechanics. 235 (2020) 107151.

G6-3 PALMS - Plasma Additive Layer Manufacture Smoothing*, **Tomasz Brzezinka (tomasz.brzezinka@wallworkht.com)**, J. Housden, A. Fox,* Wallwork Cambridge Ltd, UK*; N. Laugel, A. Matthews, A. Yerokhin,* 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 remains a significant hindrance to more wide-spread industrial use. The aerospace and medical industries, where the surface finish of components is highly critical, are particularly attentive to the issue. We have developed PALMS (Plasma Additive Layer Manufacture Smoothing), an innovative cost-effective macro-polishing solution based on electrolytic plasma technology. The use of electrolytic plasma polishing, with its fast and uniform material removal, makes for a particularly effective method of finishing components. The method is moreover largely unaffected by complex geometries, a key advantage for an AM finishing method. AM parts are treated in less than 90 minutes with highly reproducible resulting surface states, leaving a uniform, smooth micro-finish (R_a<0.1µm), and considerably improved aesthetics and mechanical performance.

This collaboration, involving multiple industrial partners within the framework of the PALMS project and coordinated by Wallwork with academic support from the University of Manchester, recently led to a published account of some of the development achieved (Yang et al. Additive Manufacturing 2020, vol. 34 p. 101204). Strategies for successful PALMS application to further case studies, such as hot stamping tools or AM demonstrators will be discussed here, and the resulting surface performance presented.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session GP

Surface Engineering - Applied Research and Industrial Applications (Symposium G) Poster Session

GP-1 Corrosion Induced Diffusion Pathways in Thin Film Materials Investigated by Atom Probe Tomography*, **Oliver Hudak (oliver.hudak@tuwien.ac.at)**,* CDL-SEC, TU Wien, Austria*; E. Aschauer,* TU Wien, CDL-SEC, Austria*; V. Dalbauer,* FAU Erlangen, Germany*; L. Shang, O. Hunold, M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Felfer,* FAU Erlangen, Germany*; H. Riedl,* 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-2 Engineered Phase Differences between HiPIMS Power and Substrate Bias for Improved Mechanical Properties of Titanium Nitrides*, **Ying-Xiang Lin (qw36100@gmail.com)**, W. Wu,* Da-Yeh University, Taiwan

In order to enhance the hardness, density, and adhesion of the deposited film, a substrate bias was normally applied during the deposition to attract ions to the substrate to increase the bombardment of the Ar^+ on the film. However, an excessively ion bombardment also causes an extremely high compressive residual stress of the film and leads to peel off. Therefore, adjusting the substrate bias voltage to obtain a proper ion impact to the film is an important factor in the process. High-power pulsed magnetron sputtering (HiPIMS) is an advanced technology of conventional magnetron sputtering. The plasma density of HiPIMS is three levels higher than conventional magnetron sputtering due to its high ionization rate. Therefore, a high amount charged particles are generated in the HiPIMS process. Applying a DC bias voltage in HiPIMS process helps these charged particles reach the substrate, but a high amount charged particles also cause the bias fail instantaneously. Meanwhile, two group high-energy ions of gas and target were observed when the pulse is turned on and off, respectively. Therefore, adjusting the phase differences between HiPIMS power and substrate bias becomes critical in a HiPIMS deposition process. However, the effect of applying synchronized and phase different bias on the film deposition has not been detail discussed.

Ti films have high mechanical strength and excellent corrosion resistance and are often used as an interface layer for TiN deposition to enhance adhesion. In this study, different phase difference bias of HiPIMS deposited Ti and TiN layer was individually investigated. A DC substrate bias was also used for comparison. The plasma composition in front of the target and substrate was individually analyzed by optical emission spectroscopy (OES), and it was found that Ti^{2+} and Ar^{+} increased significantly at the substrate after applying DC bias and pulsed bias. According to the XRD, SEM and AFM results, the grain size and surface roughness of Ti and TiN decreased when a DC bias was applied. The enhanced (002) plane was observed when a synchronous pulse bias was applied. Finally, the corrosion resistance of Ti/TiN was analyzed to determine the best substrate bias condition for HiPIMS process.

Keywords: HiPIMS, TiN/Ti, Phase difference pulse bias, Substrate bias

GP-3 Thermally Spayed Coatings with Integrated Sensor Systems for Tribological Load Surfaces*, **Annett Dorner-Reisel (a.dorner-reisel@hs-sm.de)**,* Schmalkalden University of Applied Sciences, Germany*; W. 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, 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

(b) protection of the sensor during tribological loading during practical application of the metallic components

(c) receiving proper electric signals from embedded sensors

Thermally sprayed WC-NiCr and Cr3C2-NiCr coatings with approximately 250 µm thickness were deposited on steel substrates. Flat piezoelectric sensors were embedded. Tribological behaviour of thermally sprayed coatings without and with sensor embedding was tested. The Palmqvist fracture toughness was measured and data are correlated to the wear behaviour and the electric signals from the coatings.

GP-4 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. Chang-Liao, D. Ruan, S. Yi,* National Tsing Hua University, Taiwan*; F. 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-5 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-6 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-7 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 $2.81 \times 10^{-3\%}$. Key words: silicon nanowires (SiNWs), Electroless Metal Deposition (EMD), inorganic solar cell

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

Room On Demand - Session H1

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

H1-1 INVITED TALK: 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.

H1-3 Development of In-situ Liquid Cell Transmission Electron Microscopy for Quantifying Temperature-Dependent Thin Film and Nanostructure Processing*, Serin Lee (serinlee@mit.edu),* Massachusetts Institute of Technology, USA*; N. Schneider,* Renata Global, USA*; J. Park,* Princeton University, USA*; S. Tan, F. Ross,* Massachusetts Institute of Technology, USA

Over the last several years, the technique of liquid cell TEM(LC-TEM) has been developed for imaging liquid samples in TEM with good spatial and temporal resolution. LC-TEM enables us to complete the triangle of structure-properties-processing of materials under controlled conditions of temperature, biasing, and liquid composition. Temperature control is particularly important as it is a key parameter in the operation of battery materials and the kinetics of electrochemical processes such as corrosion and etching, as well as being a useful variable in understanding the physics of nanostructure evolution. Here, we will discuss the effect of temperature on the evolution of dendrite formation from metal ions in solution, because this is a widely found morphology that has significant relevance to battery electrode stability and materials synthesis. First, we build a robust model to calculate the equilibrium concentration of chemical species in the liquid medium under electron beam irradiation as a function of temperature. The model includes the complete radiolysis reaction set for the full sent of chemical species in the initial solution. The model also includes the temperature-dependent radiolysis reaction parameters. We use Arrhenius behavior for the reaction rates and G values (rates of generation of the primary products due to beam irradiation). We use this model to predict how temperature affects the radiolysis-driven equilibrium concentrations of the species. Next, we expand the model so that it can be applied to understand temperature-dependent kinetics of nanostructure evolution, by considering the diffusion and depletion of precursors. This involves modification of the Stokes-Einstein equation with temperature-dependent viscosity to calculate the diffusion length. This complete model provides an opportunity to understand how radiolysis species behave at different temperatures under the combined effect of parameters such as the important experimentally controllable variables for liquid cell experiments: dose rate, initial concentration of the solution, pH, and aeration. We will show the results of testing this model by comparison of calculated results with experimental observations on nanoparticle generation from silver nitrate solution, dendrite growth trajectories, and the beam-induced etching and growth of metal thin films at different temperatures. We are excited by the opportunities presented by LC-TEM to develop and test a robust model that enables the temperature to be used quantitatively to probe the physics of nanostructure evolution and for a range of practical processing applications in energy storage, corrosion, and catalyst synthesis.

H1-4 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.

H1-5 Cold Sprayed Cr-coating on Optimized ZIRLO™ Claddings: An Atom Probe Tomography Study of the Cr/Zr Interface and its Microstructural and Chemical Evolution after Autoclave Corrosion Testing*, Andrea Fazi (fazi@chalmers.se),* *H. Aboulfadl, H. Andrén, M. Thuvander,* Chalmers University of Technology, Gothenburg, Sweden

As-produced Cr-coated Optimized ZIRLO™ cladding material fabricated with the cold-spray deposition process is studied. Atom probe tomography is used to investigate the nature of the cold sprayed Cr-coating/Optimized ZIRLO™ bonding interface and the heat affected zone produced by the coating deposition on the Zr-substrate. A 10–20 nm thick intermixed bonding region is observed at the interface between coating and substrate. The chemical composition of this region suggests that this layer originated from a localized melting of a thin volume of the outermost former surface of the substrate. Chromium, diffusing from the coating into the Optimized ZIRLO™ substrate during the deposition process, is found segregating at grain boundaries at up to a few hundred nanometres distance from the interface. The same material is also analysed after autoclave corrosion testing to examine the microstructural and chemical evolution of the previously mentioned intermixed bonding region. Nucleation of $ZrCr_2$ intermetallic phase is discovered at the interface, inside the intermixed layer. Cr-rich regions are observed penetrating a few hundreds nanometres beyond the interface into the substrate, possibly along grain boundaries or sub-grain boundaries.

H1-6 INVITED TALK: 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 **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).

References :

[1] S Merabtine, F Zighem, D Faurie, A Garcia-Sanchez, P Lupo, AO Adeyeye, Nano letters 18 (5), 3199-3202 (2018).

[2] S Merabtine, F Zighem, A Garcia-Sanchez, V Gunasekaran, M Belmeguenai, X Zhou, P Lupo, AO Adeyeye, D Faurie, Scientific reports 8 (1), 13695 (2018).

[3] D Faurie, F Zighem, P Godard, G Parry, T Sadat, D Thiaudière, P-O Renault, Acta Materialia 165, 177 (2019)

H1-9 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 ^oC 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.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

Room On Demand - Session H2

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

H2-1 Advanced Characterization Techniques for Zinc Based Coatings on Steel Varying from Microstructure Investigation to Mechanical Testing*, Houssem Eddine Chaieb (houssem-eddine.chaieb@mines-paristech.fr),* Mines ParisTech, PSL Research University, Tunisia*; V. Maurel, K. Ammar, S. Forest, A. Koster,* Mines ParisTech, PSL Research University, France*; F. Nozahic, J. De Strycker,* ArcelorMittal Global R&D Gent, Belgium*; J. Mataigne,* ArcelorMittal Global R&D Maizières, France*; A. Tanguay,* LMS, Ecole Polytechnique, Paris-Saclay University, France*; E. Héripré,* MSSMat, CentraleSupélec, Paris-Saclay University, France

Zinc based coatings on steel are widely used in different fields ranging from construction to the automotive sector. The main quality of this type of coatings is their high resistance to corrosion. The addition of other alloying elements like aluminum and magnesium to the coating's composition enhances the corrosion resistance of the coatings and is associated with a modification of their mechanical properties.

The purpose of this work is to highlight some original characterization techniques that allowed to investigate the microstructure and the mechanical properties of some grades of Zn-Al-Mg coatings.

SEM observations, EBSD characterizations and FIB analyses were carried out both at deformed and non-deformed states. This allowed to diagnose the microstructural aspects of the coatings and to link them to the deformation and damage mechanisms. In-situ tensile tests and determination of strain fields were performed at different length scales. At a mesoscopic length scale, optical microscopy yields measurement of strain localization and associated failure probability down to a spatial resolution of about 100 µm, without any modification of the coating surface. Lithography technique was used within the SEM in-situ tensile test to deposit a double patterned gold grid on the coating's surface which allowed to capture strain at a global scale and at a finer scale, down to a spatial resolution below 2 µm. At this finer scale, detailed failure mechanisms have been analyzed through a direct comparison of local grain orientation, slip and twinning, and initiation of crack. The global scale was used to prescribe measured displacement field as a boundary condition for a Finite element analysis of the polycristal, including grain orientation and precise morphology of grain boundaries obtained by EBSD. The correlation between local straining and damage is finally discussed.

H2-2 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. Raskin,* Université Catholique de Louvain, Belgium*; J. 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.

H2-3 Intrinsic Mechanical Properties of Moderate Temperature Processed Cvd Amorphous Silicon Oxide (Sio_2) and Oxynitride (Sio_XN_Y) Thin Films*, Maxime Puyo (puyo@chimie.ups-tlse.fr),* *C. Lebesgue, K. Topka,* Université de Toulouse, France*; B. Diallo,* Univ. Orléans, France*; R. Laloo, V. Turq, H. Vergnes, D. Samelor, F. Senocq, B. Caussat,* Université de Toulouse, France*; N. Pellerin, C. Genevois,* Univ. Orléans, France*; C. Vahlas,* Université de Toulouse, France

Silicon oxides (SiO_x) and silicon oxynitrides (SiO_xN_y) films are frequently encountered as protective coatings to isolate devices and surfaces from air or aggressive media[1]. Several studies highlight the influence of both the structure and the chemical composition of such materials on their properties. Young modulus (E) and hardness (H) values are notably linked to the nature and the density of the material network and are strongly impacted by changes in stoichiometry[2]. For coatings, such modifications can also affect the adhesion to the substrate[3]. Characterizing the above mechanical properties is of importance, since it allows to monitor subsequent film functional properties and performances as a function of the processing conditions.

Herein, we focus on sub-micrometer SiO_x and SiO_xN_y thin films processed on Si wafers by state-of-the-art, scalable, thermal chemical vapor deposition (CVD) processes which are well adapted to coat thermosensitive substrates with complex 3D geometry.Oxidation by oxygen or ozone of tetraethyl orthosilicate (TEOS), eventually substituted with nitrogen-rich precursors, such as tris(dimethylsilyl)amine (TDMSA), for SiO_xN_y films, has been utilized to achieve lower deposition temperature. Films stoichiometry and composition were characterized; hydration of the network spans from 4 to 20 at.%H depending on the precursors and processing conditions.

Mechanical characterization of such films can be highly challenging, especially in the cas of important E mismatch between the film and the substrate and for very thin layers[4]:depending on the penetration depth, the substrate mechanical properties are likely to affect the measurement, resulting in the characterization of a film-substrate system instead of the intrinsic film properties. Consequently, E and H have been evaluated by nanoindentation using Oliver and Pharr method and several models[5,6] proposed in the literature have been used to extract the intrinsic film properties E_f and H_f. For SiO_x films, the calculated value of E_f was around 45 GPa; which is consistent with that reported for hydrated SiO_x[2]. Investigation on SiO_xN_y is underway with the aim of revealing how the intrinsic film properties evolve with the processing conditions due to influence of the latter on the film chemical composition and network structure.

[1] K. Bawane *et al.*, *Corros. Sci.*, **2020**, 166, 108429

[2] H. Mei *et al.*, *Acta Mater.*, **2019**, 178, 36

[3] D.S Wuu *et al.*, *Surf. Coat. Technol.*, **2005**, 197, 253

[4] A. Kumar and K. Zheng, *Int. J. Appl. Mech.*, **2010**, 2(1), 41

[5] M. Martyniuk *et al.*, *Proc. of SPIE*, **2005**, 5798, 216

[6] A.M. Korsunsky and A. Constantinescu, *Mater. Sci. Eng., A*, **2006**, 423, 28

H2-4 New Models and Advancement in Measuring the Elastic Behaviour of Thin Films using Impulse Excitation Technique

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The deposition of thin films is developed more and more to meet the industrial and society needs. Coatings present a great solution to protect a material and giving it multiple functionalities. The elasticity behavior of these films is the mean issue to be controlled in order to enhance their performance (e.g. hardness, wear resistance, oxidation resistance, etc.).

The goal of our research work 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 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.

The methodology used is based on a multi-scale approach for mono and multilayer films. The correlation between microstructure, texture, and the properties of the coating was established after performing experiments (Film deposition, IET measurements, Nanoindentation, XRD, etc.) and analytical developing using Abaqus and Mathematica software. These analyses allowed us to develop new models to get Young's and shear moduli of films and understand the relationship between the deposition parameters, the physicochemical properties, the microstructures and the elastic constants of the materials [1-5].

Keywords: Coatings, Elastic constants, Multilayers, Anisotropy, Microstructure, Texture, Micromechanical models, Impulse Excitation Technique, Magnetron sputtering.

Acknowledgements: The authors would like to thank the co-founders of CEMAV and CERA projects: Grand-Est region and the European Union (Fond Européen de Développement Régional)

References:

[1] E. Zgheib, A. Alhussein, M.F. Slim, K. Khalil, M. Francois, Elastic behavior of anisotropic coatings sputter-deposited at oblique incidence, International Journal of Mechanical Sciences (2020) 106050.

[2] M.F. Slim, A. Alhussein, E. Zgheib, M. François, Acta materialia 175 (2019) 348 – 360.

[3] E. Zgheib, A. Alhussein, M.F. Slim, K. Khalil, M. François, Mechanics of materials 137 (2019) 103143.

[4] M.F. Slim, A. Alhussein, F. Sanchette, B. Guelorget, M. François, Thin solid films 631 (2017) 172-179.

[5] M.F. Slim, A. Alhussein, A. Billard, F. Sanchette, M. François, Journal of Materials Research 32(3) (2017) 497-511.

H2-5 Influence of the Bonding Nature on the Fatigue Resistance of Cr-based Thin Films

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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.

References:

[1] X. Luo, B. Zhang, G. Zhang, Fatigue of metals at nanoscale: Metal thin films and conductive interconnects for flexible device application, Nano Materials Science. 1 (2019) 198–207.

H2-6 Development and Application of a Multifunctional Nanoindenter: Coupling to Electrical Measurements and Integration in-situ in a Scanning Electron Microscope

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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;...

References:

1. H. Nili, K. Kalantar-Zadeh, M. Bhaskaran, S. Sriram, Prog Mater Sci. 58 (2013).

2. S. Comby-Dassonneville, F. Volpi, M. Verdier, Sensors and Actuators A: Physical, 294, 185-193 (2019)

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

H2-7 X-Ray Photoelectron Spectroscopy Analysis of Electronic Band Structure for MIM Capacitor Interfaces*, **Son Hoang (son.hoang@emdgroup.com)**, T. Ngo, E. Januar, M. McBriarty, A. Lee, C. Clavero,* Intermolecular Inc., a subsidiary of Merck KGaA, 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

H2-8 INVITED TALK: 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.

H2-10 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.

H2-11 Improving the High Temperature Hardness of Nanocrystalline Copper through Tungsten Nanoparticles*, N. Rohbeck, T. Edwards, E. Huszár, L. Pethö,* ***Xavier Maeder (xavier.maeder@empa.ch)**, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, 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.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session H3

Characterization of Coatings and Small Volumes in Harsh Environments

H3-1 INVITED TALK: 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.

H3-3 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.

H3-4 Characterization of Selective Solar Absorbing Coatings Under Operating Conditions*, C. D'Alessandro, **Antonio Caldarelli (antonio.caldarelli@na.isasi.cnr.it)**, D. De Maio, E. Gaudino,* UniNA and CNR - ISASI, Italy*; M. Musto,* UniNa - Univeristà degli Studi di Napoli "Federico II", Italy*; D. De Luca,* UniNA and CNR - ISASI, Italy*; E. Di Gennaro,* UniNa - Università degli Studi di Napoli "Federico II", Italy*; R. Russo,* CNR - ISASI, Italy

Thermal energy is an important fraction of the worldwide energy that is annually demanded, and it mainly used to produce industrial process heat, such as high pressure steam. Evacuated flat collectors, thanks to the high vacuum insulation, can respond to the mid-temperature (100 °C – 250 °C) heat request without concentration. The Selective Solar Absorber (SSA) is the key component of the solar collector: it should efficientlyconvert the incident solar irradiation into heat for the transfer fluid. Thanks to the high-vacuum insulation, the thermal radiation is the main loss mechanism that limits the panel efficiency. Solar absorptance and thermal emittance of the SSA are the radiative properties that, in first approximation, define the overall efficiency of the evacuated panel. Typically their evaluation is made at ambient temperatureand comes from optical analysis, such as FT-IR Spectroscopy and Optical Reflection Spectroscopy. Unfortunately at the operating temperature,the radiative properties can differ from the optical analysis performed at room temperature..In this work we describe a calorimetric emissiometer and the related procedure aimed at measuring the spectrally averaged absorptivity and thermal emittance under operating conditions (direct illumination and high vacuum insulation). The presented system has been validated with a commercial absorber under SUN and LED illumination. It has been used to perform calorimetric tests of novel SSAs designed to work at different operating temperatures [1] and other innovative absorbers. We will present the temperature dependence of radiative properties for several SSAs obtained using different substrates and different multilayer structures.

The system can detect variation in absorpted or emitted power of the order of 1% and it is a powerful tool to measure the SSA properties as function of temperature. It can be also adopted to perform thermal stress tests, i.e. keeping the SSA at a temperature higher than the stagnation temperature under the Sun irradiation by using a well calibrated LED system[2]. This allowsto estimate the possible coating degradation over the lifetime of the collector.

[1] D. Demaio et al . *"Multilayer design and deposition for efficient thermal energy conversion in high vacuum flat solar thermal panels"*submitted to this conference

[2] D' Alessandro, C. et al *"Low Cost High Intensity LED Illumination Device for High Uniformity Laboratory Purposes"*Preprints 2020, 2020060322 (doi: 10.20944/preprints202006.0322.v1).

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session HP

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes (Symposium H) Poster Session

HP-1 Expanding the Information and Increasing the Reliability of XPS Analysis*, **Donald Baer (don.baer@pnnl.gov)**,* Pacific Northwest National Laboratory, USA*; K. Artyushkova,* Physical Electronics, USA*; C. Easton,* CSIRO, Australia*; M. Engelhard,* Pacific Northwest National Laboratory, USA*; A. Shard,* National Physical Laboratory, UK

Because of the importance of surfaces, interfaces, and thin films in many areas of science and technology, use of X-ray Photoelectron Spectroscopy (XPS) has grown exponentially for the past two decades. One impact of this rapid increase is that many analysts have limited experience or detailed knowledge of the method. This has led to two interrelated issues. First there is an increase of inaccurate or incorrect analyses of XPS data reported in journal publications. An examination of six months of XPS data in three quality journals indicated that 30% of the reported analyses had significant misleading errors and another 30% had the potential to significantly impact the conclusions. The error rate was even greater for papers reporting fitting of spectra. The second challenge is that much of the data analysis is conducted in the most simplistic manner and does not take full advantage of the information that XPS can provide regarding layered structures, including thickness determination and uniformity. Multiple efforts are needed, some underway, to address these two challenges. Raising community awareness of the issues and opportunities is a critical first step. The error rate assessment also identified the types of errors occurring, providing analysts with information of common problems. A survey of AVS members indicated that guides, tutorials, protocols, and standards could help the community. To that end, a collection of XPS guides and introductions to various aspects of XPS has been prepared and published in Journal of Vacuum Science and Technology A. These papers address a range of topics required for quality XPS including preparation and planning, instrument setup and data collection, quantitative data analysis and curve fitting and depth information. These papers both provide guidance for minimizing errors and suggest the full range of information that might be extracted. Guides aimed at the use of XPS for specific systems such as polymers, catalysts, nanoparticles, and epitaxial films provide application specific guidance extending beyond the most common analysis approaches. Increasingly XPS analyses may involve modeling of signals expected from complex surface structures, including ultrathin films, epitaxial layers, and nanoparticles using programs such as SESSA, Multiquant and QUASES. Other pathways to advancing XPS include using high energy X-rays (HAXPES), an expanding range of environmental conditions (NAP-XPS), reporting data according to the FAIR data principles, the development of expert systems that codify and apply the hundreds of years of XPS experience, and the application of AI for enhancing data analysis and recognizing faulty data.

HP-2 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. 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-3 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-4 Sub-50 nm X-ray Diffraction Reveals Nanoscale Residual Stress and Microstructure Distributions across the Cutting Edge Area of a TiN Coating on WC-Co*, Michael Meindlhumer (Michael.Meindlhumer@oeaw.ac.at)*, *N. Jäger, S. Spor,* Montanuniversität Leoben, Austria*; M. Rosenthal,* ESRF Grenoble, France*; H. Hruby,* eifeler-Vacotec GmbH, Düsseldorf, Germany*; J. Keckes, C. Mitterer,* Montanuniversität Leoben, Leoben, Austria*; R. Daniel, J. Keckes, J. Todt,* Montanuniversität Leoben, Austria

The nanoscale microstructural and residual stress gradients across hard coatings on cutting tools are of high scientific and industrial interest. Here, cross-sectional X-ray nanodiffraction with a beam size of 35×25 nm^2 was used to retrieve structural and mechanical gradients in the cutting edge area of a ~2 µm thick TiN coating deposited by cathodic arc evaporation on a WC-Co substrate. Scanning small-angle X-ray scattering microscopy (SAXSM) is presented and utilized for the first time to investigate the nanoscale defect density in the cutting edge area. At the cutting edge, interface-like planar domains of high scattered intensity were indicated, while a gradual increase of the SAXS intensity at the rake face was correlated with pores found by scanning electron microscopy. Furthermore, the coating's <111> fibre texture axis orientation correlates with the substrate's surface normal, showing abrupt orientation changes across the former mentioned interface-like structures. The planar regions next to the edge exhibit gradual and constant stress profiles with anisotropic defect build-ups on the flank and rake faces, respectively. Directly at the edge, nonlinear lateral and cross-sectional compressive residual stress gradients ranging from ~0 to −3 GPa were observed, which together with the interface-like planar domains may represent a reliability issue during operation.

HP-5 e-Poster Presentation: Nanoindentation Analysis as a Two-Dimensional Tool for Mapping the Mechanical Properties of Complex Microstructures*, Nicholas Randall (nicholas.randall@alemnis.ch)*, *J. 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-6 Microstructural Influences on the Fracture Properties of CrN Coatings*, Rainer Hahn (rainer.hahn@tuwien.ac.at)*, *S. Rosenecker,* CDL-SEC, TU Wien, Austria*; T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* TU Wien, CDL-SEC, Austria

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-9 Thin Film Characterization Utilizing Broad Ion Beam Specimen Preparation and FESEM*, Natasha Erdman (erdman@jeol.com)*, *N. Inoue,* JEOL USA Inc, USA

Examination of materials cross sections often provides essential information about the crystal structure, layer or film thicknesses, existence of voids or cracks and other properties that might impact materials performance and reliability. Cross-sectional observation is especially essential in thin film technology, to examine layer thickness, deposition integrity (voids/adhesion), as well as film growth and crystallographic orientation. Currently various methods are used to prepare specimen cross sections for scanning electron microscope (SEM) observation. Mechanical methods of cutting and polishing are widely used, particularly for metallographic sample preparation. However, mechanical polishing presents several problems: a) in composite materials with different hardness values, the polished surface becomes uneven as the softer components are cut faster and more easily than the harder components; b) in soft materials, particles of hard abrasive can be buried in the material being polished; c) in materials with voids, the edges of the voids can stretch and deform; e) for metals, due to the strain caused by mechanical polishing on the polished surface, the information about the crystal structure by means of electron back-scatter diffraction (EBSD) becomes difficult or impossible to obtain; f) fine features like hairline cracks and small voids can get smeared shut and will not be recognized as such.

This paper presents utilization of broad ion beam instrument (JEOL CP polisher) for cross-sectional preparation of various thin film/substrate combinations. This table top instrument utilizes Ar ion beam to produce large area cross-sections of materials, with the ability to employ cryogenic (LN2) temperatures to address beam sensitive and eutectic metal systems. Moreover, the use of FE-SEM equipped with in-lens detectors and high sensitivity backscatter detecotr allows observation of the resulting samples to investigate nanoscale features, including voids, grain boundaries and layers. Additionally, EDS and EBSD can be utilized to provide additional characterization of the thin film specimens in terms of compositional variations and crystallographic orientation.

We will present examples of Zn thin films - depending on the film composition these may require cryogenic preparation to preserve film integrity. Additionally we would present examples of other materials - anodized films, evaporated metal thin films, solar films, etc.

Topical Symposia
Room On Demand - Session TS1
Anti- and De-icing Surface Engineering

TS1-1 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. 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.

TS1-2 Improving the Efficiency of Electro-Thermal De-Icing Systems With Icephobic Coatings*, Jack Brierley (emxjpb@nottingham.ac.uk)*, *X. Hou, B. Turnbull, W. Sun,* University of Nottingham, UK

Active ice protection systems implemented in aerospace are incredibly power-hungry, but necessary safety feature. Applying icephobic coatings is a potential zero-energy passive solution to this problem. This study explores the viability of icephobic coatings to work alongside a thermal de-icing system to guide this field of research into designing a hybrid energy-saving solution. A coating that reduces ice adhesion strength passively is synergised with an electro-thermal de-icing system to make it more energy-efficient. Studies on the effects of surface roughness,coating thickness (Sylgard 184) and the implementation of thermally conductive fillers (silicon carbide fibres), have been carried out in the present work, to highlight a pathway for this combined solution: a hybrid system of an active heating system that is enhanced, and not limited by, an icephobic coating. The influence of surface treatment using 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (POTS), a self-assembling monolayer to reduce the surface energy of the aluminium was also investigated. The inclusion of silicon carbide fibres in the PDMS coating provided a 5-fold reduction of energy consumption for de-icing was observed compared to pure polymer alone.The control of coating thickness was also a critical issue for both the ice adhesion and the energy consumption in de-icing. The design of an icephobic coating to focus on its specific operational environments is essential.

TS1-3 Icephobic Coatings by Thermal Spraying as Surface Engineering Technique*, Heli Koivuluoto (heli.koivuluoto@tuni.fi)*, Tampere University , Finland*; R. Khammas, V. Donadei,* Tampere University, Finland

Icing causes challenges and serious problems in different industrial sectors e.g., in aviation, energy and construction as well as logistics. Increasingly, surface engineering offers various solutions to solve these challenges. However, still more sustainable solutions are needed and for this, thermal spraying as one of the surface engineering techniques opens a novel approach to produce icephobic coatings. These surfaces can act as potential passive anti-icing solutions in arctic environments. Thermal spraying technology makes it possible to produce coatings with a wide range of materials including metals, metal alloys, ceramics, composites, and polymers. Feedstock materials are fed to the thermal spray gun, where these are melted, heated, or accelerated towards a substrate or component surface to form a coating. Additionally, the material selection, coating structure and properties can be tailored with a thermal spray processing method where coating formation is based on either thermal or kinetic energy. Thermally sprayed icephobic coatings are typically polymer or composite based coatings with multifunctional characteristics e.g., wetting performance, slipperiness and protection against different wearing and corrosion conditions. These coating solutions can be divided into three categories such as thermally sprayed solid icephobic coatings (TS-SIC), thermally sprayed slippery liquid infused porous surfaces (TS-SLIPS) and thermally sprayed lubricated icephobic coatings (TS-LIC). These coating designs possess low to medium-low ice adhesion values measured with the centrifugal ice adhesion test (CAT). For the tests, ice was accreted in the icing wind tunnel (IWiT) at Tampere University (TAU) in ICE Laboratory.

Generally, it can be noted that the lower ice adhesion leads to the higher icephobicity. Thermally sprayed icephobic coatings have shown their potential to avoid the icing of the components and minimize the adhesion between ice and the coating surfaces.

TS1-4 Limitations of Anti-icing Materials for Aeronautic Applications*, Paloma Garcia (garciagp@inta.es),* National Institute of Aerospace Technology, Spain*; J. Mora,* Isdefe, Spain*; 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.

TS1-5 Fluorination of Aluminum Surfaces as a General Strategy to Induce an Effective Anti-Icing Response*, Carmen López Santos (mclopez@icmse.csic.es), V. Rico, J. Mora, P. Garcia,* University of Seville, Spain*; A. Agüero Bruna,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; A. González-Elipe, C. López-Santos,* Instituto de Ciencia de Materiales de Sevilla (CSIC-USE), Spain

Icephobicity and anti-icing response of common materials used in aviation, such as Al6061, depends on different factors, such as surface morphology or chemical state. This work presents a systematic study of the wetting and anti-icing properties of aluminum surfaces that are modified by different procedures. Firstly, it is found that surface roughness modification by nanosecond pulsed IR laser treatments may induce a superhydrophobic behavior that also conveys an effective anti-icing response. An enhanced effect in wetting and anti-icing responses is observed for rough aluminum surfaces covered with porous Al_2O_3 layers providing a dual roughness surface microstructure. Then, we show that the anti-icing behavior can be highly improved by the surface functionalization of these aluminum surfaces with fluorine containing compounds or layers. The applied methodologies encompass the deposition of fluorinated polymeric coatings (CFx) prepared by plasma enhanced chemical vapor deposition, the infusion of a low surface tension slippery liquid (Krytox) or the surface grafting of fluorocarbon molecules (perfluorooctyltriethoxysilane, PFOTES).

A comparative analysis of the wetting, water condensation and anti-icing properties (freezing delay time and ice accretion in a wind tunnel) of these three fluorine modified surfaces have serve to determine the factors contributing to the observed good anti-icing performance and long term stability of metal fluorinated surfaces. This analysis takes into account the influence of roughness parameters, the chemical state of the surface and the mobile character of the fluorocarbon molecules to promote an efficient anti-icing response. A general methodology to develop fluorinated metal surfaces with an effective anti-icing behavior is proposed (1,2).

1.-V. Rico et al., Hydrophobicity, Freezing Delay, and Morphology of Laser-Treated Aluminum Surfaces, Langmuir 35 (2019) 6483–6491

2.- V. Rico et al., Robust anti-icing superhydrophobic aluminum alloy surfaces by grafting fluorocarbon molecular chains, Applied Materials Today 21 (2020) 100815

Acknowledgments: Authors thank the EU through the H2020-FETOPEN-2018-2020 program (899352), AEI-MICINN (PID2019-110430GBC21, PID2019-09603RA-I00) and Junta de Andalucía (PAIDI-2020 through P18-RT-3480 and US-1263142) for financial support.

Topical Symposia

Room On Demand - Session TS2

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

TS2-1 The Industrially Deposited W-B-C Coatings from Segmented Target*, Michael Kroker (kroker@physics.muni.cz), P. Matej, P. Souček, L. Zábranský, V. Buršíková,* Masaryk University, Czechia*; V. Sochora, M. Jílek,* SHM, Czechia*; P. Vašina,* Masaryk University, Czechia

The coatings composed of transition metal (Me = Mo, W, Ta, Nb, …), boron, and carbon are promising candidates for next-generation hard protective coatings. The experimental studies are reporting a combination of high hardness and increased fracture resistance for Mo-B-C and W-B-C coatings, which are deposited using sputtering techniques at laboratory conditions. Such properties favor the use of Me-B-C coatings in the industry, where the demand for replacing the hard but brittle state-of-the-art ceramic coatings is significantly increasing.

For this study, the W-B-C coatings were sputter-deposited by non-reactive magnetron sputtering using an industrial system provided by the company SHM, Czech Republic. The system utilizes as a sputter source a cylindrical rotating segmented target composed of metal, boron carbide, and graphite segments. As an industrial standard, the planetary table capable of multi-axis rotation of substrates was used to simulate the batch coating of the tools. The depositions were carried out in both stationary regime and single-axis rotation regime to understand the differences between laboratory-like and industrial preparation of the coatings.

The properties of the W-B-C coatings were studied over a broad range of their chemical composition. Despite the coatings were mostly amorphous, they still exhibited high hardness (up to 30 GPa) and elastic modulus (up to 450 GPa). The coatings deposited in the rotation regime exhibited multilayered character due to different transport pathways of the light (B,C) and heavy (W) elements. Detailed analyses of their mechanical properties proved their superior fracture resistance compared to current ceramic based protective coatings. Low internal stress in the coatings together with good adhesion enabled to deposit sufficiently thick coatings on the test samples and tools used in forming applications. The application relevant testing was performed at the end-customers of SHM in the Czech Republic.

This research is conducted within the FV30262 project, which is funded through TRIO program of the Ministry of Industry and Trade with financial support from the state budget of the Czech Republic.

TS2-2 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,* Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Germany*; J. Julin,* Institute of Ion Beam Physics and Materials Research, 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.

TS2-3 Chemical Shift in W-B-C Systems: Experiments and Modeling*,* ***Jaroslav Ženíšek (jzenisek@mail.muni.cz),*** Masaryk University, Czechia*; P. Ondračka,* RWTH Aachen University, Germany*; P. Souček,* Masaryk University, Czechia*; D. Holec,* Montanuniversität Leoben, Austria*; M. Stupavská,* Masaryk University, Czechia*; J. Schneider,* RWTH Aachen, Germany*; P. Vašina,* Masaryk University, Czechia

This work discusses and reviews the generally accepted assumptions commonly used in the XPS bonding analysis of different materials. These are in the presented case applied to amorphous W-B-C materials with different compositions. We focus ourselves on the chemical shift of 4f electronic states of W atoms. In the W-B-C systems, the formation of binary W–B and W–C bonds leads to a shift in core-level to lower and higher binding energies, respectively, of W 4f core electrons due to the differences in the Pauling electronegativity of W, B and C. For the theoretical verification of this assumption we generated three amorphous W-B-C atomic models of different compositions (W:B:C ratios), calculated the W 4f core electron binding energies from *ab initio* methods and compared them with the measured XPS profiles of deposited W-B-C with the same W:B:C ratios. The atomic models reproduced the behaviour of the deposited systems in terms of XPS profiles. In the next step, we used the models to analyse the relationships between the W 4f electron binding energies and the local atomic environments of W atoms. It was found that the relative W 4f peak positions depend on the B/C ratio in the system, as was expected and as is commonly assumed in the bonding analysis. However, the relative amount of W and its density fluctuations in the volume of the unit cell on the other hand, which is usually omitted in the bonding analysis, also led to a chemical shift of the W 4f peak. Therefore, several series of amorphous W-B-C coating were deposited in a way to obtain amorphous coatings with compositions allowing to separate the effect of B/C ratio and the amount of W on the W 4f peak positions. The experimental positions of the W 4f peaks confirmed the theoretical predictions and have shown that general simplified assumptions based on electronegativity of elements need to be taken with care for precise chemical analysis of the bonding in W-B-C coatings.

TS2-4 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. 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].

References:

[1] *"Superior high-temperature oxidation resistance of magnetron sputtered Hf–B–Si–C–N film"*, P. Zeman, S. Zuzjakova, P. Mares, R. Cerstvy, M. Zhang, J. Jiang, E.I. Meletis, J. Vlcek, Ceram. Int. **42**, 4853 (2016).

[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).

TS2-5 Application of the Heat Balance Integral Method to the Growth Kinetics of Nickel Boride Layers on Inconel 718 Superalloy*,* ***Alan Daniel Contla-Pacheco (acontlap1400@alumno.ipn.mx),*** Instituto Politecnico Nacional, Mexico*; M. Keddam,* Laboratoire de Technologie des Matériaux, Faculté de Génie Mécanique et Génie des Procédés, Algeria*; L. Lartundo-Rojas, M. Ortega-Avilés, I. Mejia-Caballero, I. Campos-Silva,* Instituto Politecnico Nacional, Mexico

The nickel-based superalloys are designed to meet industrial requirements to withstand higher temperatures during the long-term service. They have wide applications in the aerospace, marine, nuclear, and petrochemical industries due to their excellent oxidation and corrosion resistance. However, because their high nickel content, these alloys are susceptible to abrasive, erosive and adhesive wear damage. Boriding process is considered as an efficient method for improving the tribological properties of nickel-based superalloys. These superalloys were successfully borided by using different methods without impairing corrosion and oxidation resistance. Among the boriding processes, the powder-pack boriding is a highly effective and low-cost method to produce hard nickel borides with outstanding properties.

From a kinetic viewpoint, the growth kinetics modeling is very substantial to select the optimum values of boride layers' thicknesses matching the practical use of nickel-based superalloys in terms of wear conditions.

The Heat Balance Integral Method (HBIM) is an alternative to investigate the boriding growth kinetics of nickel-based superalloys. This approach, originally applied for analyzing thermal problems, is based on numerical resolution of a system formed by differential algebraic equations (DAE) under certain assumptions.

In the present work, new results about the growth kinetics of nickel boride layers on an Inconel 718 superalloy was estimated considering a diffusion model based on the HBIM. The boron diffusion coefficients in nickel boride layers were estimated in the temperature range of 1123 - 1223 K at different exposure times. In addition, the layers were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and Berkovich indentation techniques to determine the phases formed on the surface, the microstructure and the chemical composition across the depth of the layer-substrate, and the distribution of the hardness, respectively.

TS2-6 Influence of the Diffusion Annealing Process in the Corrosion Susceptibility of Cobalt Boride Layer Immersed in Hank's Solution*, A. Delgado-Brito,* ***Ivvone Mejia-Caballero (ivvone_mejia@hotmail.com),*** Instituto Politecnico Nacional, Mexico*; M. Palomar-Pardavé,* Universidad Autonoma Metropolita-AZC, Mexico*; J. Martinez-Trinidad, I. Campos-Silva,* Instituto Politecnico Nacional, Mexico

The corrosion susceptibilities of the borided CoCrMo alloy exposed to the diffusion annealing process (condition I) and the borided CoCrMo alloy (condition II) immersed during 7 days in Hank's solution were evaluated. Firstly, the CoCrMo alloy was exposed to the powder-pack boriding process (PPBP) during 5 h at 1273 K, to obtain a biphasic layer (CoB-Co_2B) with a total thickness around 30 µm. Then, the diffusion annealing process (DAP) was performed in the borided CoCrMo alloy during 2h at 1273 K in an inert argon atmosphere to obtain a 30 µm of monophasic Co_2B layer. The potentiodynamic polarization technique was used to evaluate the corrosion resistance (R_p) using the linear polarization technique (LPR) and the corrosion current density (j_{corr}) from the Tafel extrapolation technique. In addition, the corrosion resistance estimated from conditions I and II were compared with the CoCrMo alloy (reference material). The results showed, in the 7th day of immersion in the Hank's solution, that the condition I (~357 kΩ cm^2) exhibited corrosion values ~24 times higher than those obtained by the condition II (~15 kΩ cm^2) reaching values close to the reference material (~385 kΩ cm^2). The corrosion behavior of the borided CoCrMo alloy exposed to the diffusion annealing process was attributed to: i) the presence of the monophasic Co_2B layer on the surface of the borided CoCrMo alloy, ii) the redistribution of Cr and Mo after the process, which increased the content of these elements at the surface of the borided alloy and iii) the inhibition of the B_2S_3 and $CrPO_4$ species, which has a detrimental effect on the corrosion behavior at the surface of borided CoCrMo alloy. Finally, the effect of the diffusion annealing process (condition I) reduced the corrosion susceptibility of the cobalt boride layer around 7% in comparison to the value of 96 % estimated for the borided CoCrMo alloy (condition II).

TS2-7 Pulsed-DC Powder-Pack Boriding: Growth Kinetics of Boride Layers on AISI 316 L Steel and Inconel 718 Alloy, ***Erick Japhet Hernandez-Ramirez (ehernandezr1601@alumno.ipn.mx)***, *I. Campos-Silva, J. Rosales-Lopez, A. Contreras-Hernandez, E. Valdez-Zayas, I. Mejia-Caballero, J. Martinez-Trinidad,* Instituto Politecnico Nacional, Mexico

The conventional powder-pack boriding process (PPBP) is a surface hardening treatment, which results in the formation of boride layers to enhance the mechanical and chemical properties of the materials. Particularly, in the PPBP, the growth kinetics of the boride layers depends basically on the boriding temperature, the exposure time, and the content of the powder mixture (B_4C, SiC and KBF_4), using temperatures for the process in the range of 1123 to 1223 K with long exposure times (4 to 12 h).

Facing this problem, several studies have developed an alternative process to reduce exposure times in the formation of boride layers at the surface of various steels and alloys, using a direct current field in the powder-pack boriding process (PBDCF). During the process, the current flux between the electrodes follows the direction of the conventional current (from positive to negative), however, the migration of the boron atoms, on the surface exposed to the cathode, is opposite to the normal direction of diffusion, consequently, the growth of the boride layer is slower than that exposed to the anode.

Based on the aforementioned, this study develops a novel treatment called pulsed-DC powder-pack boriding (PDCPB). This treatment employs a DC power supply coupled to an electronic programable control device (EPCD) to generate timed cyclic polarity changes on the flux of ionized boron atoms. The effect of the pulsed DC current field provides a homogeneous boron diffusion during the PDCPB, which promotes the growth of similar boride layer thicknesses on both surfaces (anode and cathode) exposed to the direct current field. The PDCPB treatment was performed on the AISI 316 L steel and Inconel 718 alloy at temperatures of 1123 - 1223 K with different exposure times for each temperature. The powder mixture consisted of B_4C, SiC and KBF_4, supplying a current input of 5 A and polarity inversion cycles of 10 s.

Finally, the growth kinetics of the boride layers, in both materials, was established using a diffusion model that considers two mass balance equations at the growth interfaces, considering that the boride layers obey the parabolic growth law. The boron diffusion coefficients in the boride layers, were expressed as a function of the experimental temperatures using the Arrhenius relationship to estimate the boron activation energies. The results showed that the boron activation energies, estimated for the boride layers, decreased drastically (17% for the borided AISI 316 L steel and 31% for the borided Inconel 718 alloy) compared to those obtained for the conventional powder-pack boriding process.

TS2-8 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; *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

Authors acknowledge funding from the Slovak Research and Development Agency [APVV-17-0320], VEGA 1/0381/19 and Operational Program Research and Development [project ITMS 26210120010]

TS2-9 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, Sweden; *F. Klimashin,* Linköping University, Sweden; *G. Greczynski,* Linköping University, Sweden; *P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan; *I. Petrov,* University of Illinois, USA, Linköping University, Sweden; *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.

TS2-10 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. Svensson,* Detector Group, European Spallation Source ERIC, Sweden*; L. Robinson,* Detector Group, European Spallation Source ERIC,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.

TS2-11 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*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. 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.

References

[1] C. Fuger, V. Moraes, R. Hahn, H. Bolvardi, P. Polcik, H. Riedl, P.H. Mayrhofer, MRS Com. (2019) 1–6.

[2] V. Moraes, C. Fuger, V. Paneta, D. Primetzhofer, P. Polcik, H. Bolvardi, M. Arndt, H. Riedl, P.H. Mayrhofer, Scr. Mater. 155 (2018) 5–10.

[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.

TS2-12 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. 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$\sqrt{m}$. Furthermore, we critically evaluate the comparability of distinct micromechanical testing techniques assessing the fracture behavior also with respect to the residual stress state.

[1] V. Moraes, H. Riedl, C. Fuger, P. Polcik, H. Bolvardi, D. Holec, P.H. Mayrhofer, Sci. Rep. (2018).

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

TS2-13 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.

TS2-14 Design of Under/Overstoichiometric Superhard $TaB_{2\pm x}$ Films

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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.

Authors acknowledge funding from the Slovak Research and Development Agency [APVV-17-0320], VEGA 1/0381/19 and Operational Program Research and Development [project ITMS 26210120010].

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

TS2-15 Vacancies and Related Substoichiometry in Magnetron Sputtered Transition Metal Diboride Thin Films

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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 $W(Ta)B_2$.

TS2-16 INVITED TALK: Boron-containing Metallic-glass Coating: Unique Properties and Various Applications

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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.

TS2-18 XPS Analysis of TiB_x Thin Films

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We report on comprehensive analysis of TiB_x thin films by x-ray photoelectron spectroscopy. Films were grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target in Ar discharge. By varyig the deposition parameters, the film composition could be tuned over the wide range $1.34 \le B/Ti \le 3.0$, as determined by elastic recoil detection analysis (ERDA) and Rutherford backscattering spectrometry (RBS). By comparing spectra over this wide range of compositions, we can draw new conclusions about how to interpret XPS spectra of TiB_x. By careful spectra deconvolution, the signals from Ti-Ti and B-B bonds can be resolved from those corresponding to stoichiometric TiB_2. The intensities of the off-stoichiometric signals can be directly related to the B/Ti ratio of the films. Furthermore, we demonstrate a way to obtain consistent and quantum-mechanical accurate peak deconvolution of the whole Ti 2p envelop, including plasmons, for both oxidized and sputter-cleaned samples. Due to preferential suttering of Ti over B, the film B/Ti ratio is best determined without sputter etching of the sample surface. This allows compositional determination, assuming extensive levels of oxygen has not penetrated below the sample surface. Fully dense films can be accurately quantified for at least a year after deposition, while under-dense samples do not give reliable data if the O/Ti ratio on the un-sputtered surface is ≥ 3.5. Titanium sub-oxides detected after sputter etching is also indicative of too much oxygen penetrating the sample, and quantification by XPS should not be trusted.

TS2-19 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. Chang,* National Tsing Hua University, Taiwan*; S. Hung, C. Wang,* National Taiwan University of Science and Technology, Taiwan*; J. Duh,* National Tsing Hua University, Taiwan*; J. 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.

TS2-20 Effects of Stoichiometry and Individual Layer Thickness Ratio in the Quality of Epitaxial CrB_x/TiB_y Superlattice Thin Films*, **Samira Dorri (samira.dorri@liu.se)**, N. Ghafoor, F. Eriksson, J. Palisaitis, B. Bakhit, L. Hultman, J. Birch,* Linköping University, IFM, Thin Film Physics Division, Sweden

Studies of single crystal artificial superlattices (SL) have been instrumental to understand hardening mechanisms at the nano-scale in transition metal (TM) nitride and carbide multilayers. The lack of such fundamental studies for TM diborides is the motivation for this study of CrB_x/TiB_y (0001) SLs, grown epitaxially onto Al_2O_3 (0001) wafer substrates by direct current magnetron sputtering from compound diboride targets. Growth conditions for obtaining well-defined SLs with good interface quality are found at a sputter gas pressure of 4 mTorr Ar and a substrate temperature of 600 °C. 1-µm-thick SL films deposited with modulation periods Λ between 1 and 10 nm, and $\Lambda = 6$ nm SLs with TiB_y-to-Λ layer thickness ratios Γ ranging from 0.2-0.8 are characterized by means of HRTEM, STEM, EDX, EELS, XRD, ToF-ERDA, RBS, and XPS. It is found that SLs with $\Lambda = 6$ nm and Γ in the range of 0.3-0.4 exhibit the highest structural quality. The effects of Γ and the stoichiometries (B/TM ratio) of the CrB_x and TiB_y layers on the distribution of B in the SL structures are highlighted. We show that by increasing the relative thickness of TiB_y, the crystalline quality of SLs starts to deteriorate due to B segregation in over-stoichiometric TiB_y layers, resulting in narrow epitaxial SL columnar growth with structurally-distorted boron-rich boundaries. An increase in relative thickness of under-stoichiometric CrB_x on the other hand, enhances the SL quality and hinders formation of boron-rich boundaries. Detailed structural analyses, mechanical properties with hardness, and stress as well as possible solutions for further improved SL definition will be presented.

TS2-21 INVITED TALK: Boron-based Thin Film Materials for Future Neutron Technologies 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 than existing neutron sources, which will enable faster neutron scattering experiments on new materials using new techniques. For best utilization of the brightness, novel thin film based neutron-optical components, such as neutron mirrors and area detectors, are being developed. The Thin Film Physics division at Linköping University aims at developing novel thin film concepts enabling future neutron technologies.

Together with ESS, affordable ^{10}B -based thin film neutron converter coatings have been developed that allows for eliminating the present unsustainable use of the rare isotope ^3He 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. We have shown that $^{10}B_4C$ thin films can be grown by magnetron sputter deposition with properties that fulfill the requirements of mechanical and chemical stability as well as being radiation hard, while maintaining a high volume density of ^{10}B. For example1µm thick films with residual stress as low as 0.09 GPa can be grown by DC magnetron sputtering and by employing HiPIMS it is possible to lower the substrate temperature to ~100°C which is useful for sensitive substrates. This $^{10}B_4C$ thin film technology is proven superior to ^3He-based detectors and is chosen for most of the foreseen detectors for scattering, reflectometry, as well as time-of-flight inelastic spectroscopy at the ESS.

Novel solid-state neutron detector designs, requiring neutron converter filling of narrow high-aspect ratio wells and trenches in semiconductor surfaces, require conformal coverage CVD methods. We have recently shown that conformal coatings of BC_x in wells with aspect ratios as high as 10 000:1 are possible using triethylborane, $B(C_2H_5)_3$ as precursor. This allows for future ^{10}B-based solid state neutron detectors with sensor pixels in the range of 10x10 µm^2 (rather than the present ~cm^2).

Nanometric metallic multilayers act as neutron mirrors and are key to guiding neutrons from source to experiment. By combining incorporation of ^{11}B in the multilayers with temporal ion-assistance modulation during sputter deposition, we obtain a significant reduction of interface width which, in turn, leads to significantly improved neutron reflectivities. For example in Ni/Ti:^{11}B multilayer mirrors reflectivity increased by 43% using this technique, implying up to 10x higher neutron flux throughput and significantly increased spectral range of future neutron guides.

TS2-23 Thermal and Mechanical Properties of $(W,Zr)B_{2-z}$ Coatings Deposited by RF Magnetron Sputtering Method*, **Justyna Chrzanowska-Giżyńska (jchrzan@ippt.pan.pl)**, R. Psiuk, P. Denis,* Polish Academy of Sciences, Poland*; Ł. Kurpaska,* National Centre for Nuclear Research, Poland*; T. Mościcki ,* Polish Academy of Sciences, Poland

W-Zr-B films with different stoichiometric ratio Zr/W were deposited by RF magnetron sputtering on silicon and tungsten carbide substrates. The coatings were deposited from plasma spark sintered targets using one-inch sputtering cathode. The impact of zirconium content on the film mechanical and thermal properties were investigated. Nano-indentation test was performed to analyze the hardness, Young modulus and subsequently flexibility of the films. It is shown that α-WB2 magnetron sputtered coatings alloyed with zirconium content 0 ⍰ 24 at% are superhard and in all investigated compositions possess similar hardness. In the same time Young modulus is decreasing about 10% what make deposited films more flexible. Obtained W-Zr-B films represent a new class of coatings which are simultaneously superhard H = 43±3 GPa, exhibit high values of the hardness and effective Young's modulus E* ratio H/E* >0.1, elastic recovery We > 60%. The results of thermal studies i.e. thermal shocking, annealing in vacuum and TGA show that deposited coatings are thermally stable at least to 800 °.

Topical Symposia
Room On Demand - Session TS3
In-Silicio Design of Novel Materials by Quantum Mechanics and Classical Methods (jointly sponsored by ICMCTF and AQS)

TS3-1 INVITED TALK: 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.

TS3-3 Prediction of Composition, Crystalline Structure and Microstructure of Sputtered Multi-Component Coatings by a Virtual Machine*, **David Böhm (david.boehm@tuwien.ac.at)**,* Vienna University of Technology, Austria*; T. Schrefl,* Danube University Krems, Austria*; A. Eder,* MIBA High Tech Coatings GmbH, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria

To be able to predict the composition and the structural properties of multi-component thin films deposited by magnetron sputtering a so-called Virtual Machine (VM) was designed. The VM is an interactive ray tracing software that simulates film growth by a line-of-sight model, also taking into account the decay of the flux density of the particles due to gas phase scattering.The VM is initiated with a 3D model of a real sputter system which includes the static arrangement of multiple targets and the substrate and eventual obstacles, as well as dynamics like e. g. rotating substrate holders. Then the composition, the microstructure and the crystallographic phases with their associated XRD patterns are calculated for the simulated film. On each sampling point a composition is calculated over several time steps associated with an adjustable temperature which can be different for each step enabling the correlation of the real temperature distribution during the coating experiment. Depending on the material and the applied simulation parameters e.g temperature or coating rate models of grain growth and island formation are applied.With this information and a library of binary phase diagrams the corresponding crystallographic phase can be calculated and displayed per time step. The XRD patterns are calculated from the crystallographic phases and summed over all time steps. This procedure allows to construct a diffractogram which can be compared to the diffractogram of an accordingly produced sample. Another way to display the data is to stack the appearing composition and phases over all time steps. Such a phase stack is equivalent to an EDX line scan performed on a metallurgical cross section from the substrate to the surface of the coating. Several phase stacks can be compared with an element mapping of the cross section. Since surfaces and volume diffusion are not yet considered, only immiscible multilayer systems can be investigated at present. On the basis of examples the above mentioned comparisons are presented.

TS3-4 Atomistic Modelling of Diffusion in Quasi-amorphous Nanocomposite Coatings*, **Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at)**, D. Holec,* Montanuniversität Leoben, Austria

TiN-based materials are widely established as protective coatings for cutting tools. Grain interiors (single crystal regions) could serve as reservoirs for functional species, e.g. Al or V, which provide effective lubrication and wear protection at high temperatures by diffusing to the coating surface where they form a protective oxide scale (Al) or a lubricious oxide to reduce friction (V). The microstructure of real coatings has a polycrystalline or nanocomposite nature. Here, the intergranular region consists of quasi-amorphous (amorphous materials interfaced with TiXN, X=Al, V) tissue which serves as a diffusion highway for transporting species from bulk to the coating surface.

While approaches exist for estimating diffusivity in crystalline materials, the situation is much less explored in the case of (quasi-)amorphous materials. In this contribution, we will report on our recent progress in addressing issues related to the atomistic modeling of mass transport. To do so we employ complementary computational investigations to determine elementary point-defect migration mechanisms in crystalline as well as amorphous materials and subsequently their relative rates. Molecular dynamics (MD), which traces the motion of each particle contained in the system by numerically solving Newton's equations, coupled to the accuracy of density functional theory (DFT) to describe interatomic forces, is the most reliable computational tool to calculate atomic jump rates as a function of temperature. We will present the DFT-based "5-frequency model" allowing us to calculate the diffusion coefficient in the crystalline fcc material. Furthermore, we also demonstrate that pressure has a notable impact on the diffusivity of V, Al, and Ti in TiN. Next, we show how to approach both crystalline and amorphous materials by employing the Green-Kubo relation together with a detailed analysis of diffusion pathways as provided by MD.

TS3-5 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. 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 initio* 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.

TS3-6 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).

TS3-7 Strength, Transformation Toughening and Fracture Dynamics of Rocksalt-structure $Ti_{1-x}Al_xN$ ($0 \le x \le 0.75$) Alloys*, **Davide Sangiovanni (davide.sangiovanni@liu.se)**, F. Tasnadi, M. Oden, I. 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.

Topical Symposia

Room On Demand - Session TS4

Photocatalytic and Superhydrophilic Surfaces

TS4-1 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.

TS4-2 Double Perovskite $LaFe_{1-x}Ni_xO_3$ Coating Urchin-like Golden Nanoparticles to Enhance Water Splitting Reaction*, Hsiang-Wei Tsai (flylittlewei@gmail.com)*, *Y. Su,* National Cheng Kung University (NCKU), Taiwan

$LaFe_{1-x}Ni_xO_3$ (LFNO) has attracted considerable attention. Ni^{3+} is in the low spin state (t^6_{2g}, e^1_g) and the conduction band is formed by the hybridization of Ni^{3+} e_g orbitals and O^{2-}2p orbitals. Since the t_{2g} band is full and e_g electrons form the delocalized $\sigma*$band, it has no localized moments and exhibits Pauli para-magnetism above 50K. In this research, I used the 0.00 mol, 0.01 mole, 0.03 mole, 0.05 mole, and 0.07 mol Ni concentrations to dope into the $LaFeO_3$. As a fundamental understanding, the bonding strength between surface TM (transition-metal) 3d and O 2p states is considered to be the major factor that determines the intrinsic OER activity. The bonding strength between catalyst and adsorbate is predicted by the $E-E_f$ parameter (relative to the E_f), where the larger $E-E_f$ value, the greater the bonding strength because the larger $E-E_f$ indicates a low energy 3d state of TMs and would produce higher hybridization between the TM 3d and O 2p states due to the shortened energy distance. The d-band center close to the E_f can enable strong bonding between adsorbed oxygenated species and surface TMs, which promotes electron transfer and thus boost OER activity.

Furthermore, another my attempt is to improve the localized surface plasmon resonances with sea-urchin-like Au nanoparticles fabricated. Au–Ag alloy Nus (Nano urchin structure) are novel metal nanoparticles that have been employed as a SERS active substrate. Moreover, an individual Au–Ag alloy Nus exhibit a high density of nanotips, which could dramatically increase its surface area and bring more active sites, further enhancing its catalytic properties. The photocatalytic water-splitting into H_2 and O_2 is a direct solar-to-chemical energy conversion technology and has become a research hotspot globally. Photocatalytic H_2 production usually goes through a route that photoexcited electrons reduce the protons in solution to hydrogen atom chemisorbed on the catalyst surface and then desorbed into H_2. Finally, $LaFe_{1-x}Ni_xO_3$ is combined with sea-urchin like Au nanoparticles to be as the hetero-junctional photocathode. Due to LSPR, porous structures, and mixed secondary-phase, the water-splitting process is augmented under visible-light irradiation.

TS4-3 Effect of Tungsten-Substitution on the Structure and Photocatalytic Properties of Anatase TiO_2 Thin Films Deposited on Polymer by PECVD*, William Ravisy (william.ravisy@cnrs-imn.fr)*, Université de Nantes, France*; B. Dey, S. Bulou, P. Choquet,* Luxembourg Institute of Science and Technology, Luxembourg*; N. Gautier,* Université de Nantes, France , France*; A. Goullet,* Université de Nantes, CNRS, France*; M. Richard-Plouet, A. Granier,* Université de Nantes, France

Whereas most coating techniques require a high-temperature step in order to crystallize TiO_2 as the anatase phase, it has been shown that crystallized TiO_2 could be deposited at T≤130°C with a Plasma-Enhanced Chemical Vapour Deposition (PECVD) process, without further thermal treatment and thus allowing the use of thermally sensitive substrates.[1] These films exhibit a potentially high surface area, due to a columnar morphology, with anatase crystallization, which are two necessary features for efficient photocatalysis. However, photocatalytic activity is still limited by the value of TiO_2 band gap in the UV domain, allowing absorption of only 10% of the solar spectrum and hence restricting its efficiency as photocatalyst.

Among other possibilities to enhance properties of the TiO_2 thin films, substituting Ti with an alliovalent cation such as tungsten is expected to increase oxygen vacancies and shift the band gap energy toward higher wavelengths and ultimately to induce absorption in the visible range.[2][3]

In this work, W-substituted TiO_2 thin films have been deposited on Si and polymer substrates by Low-Pressure Low-Temperature PECVD. Titanium Tetraisopropoxide (TTiP) and Tungsten(V) Ethoxide were injected in a 400W radiofrequency inductively coupled oxygen plasma. W concentration was tuned by varying the flowrate of tungsten ethoxide carrier gas (O_2) or container temperature. All the 250nm-thick films were characterized by Raman and X-Ray Photoelectron Spectroscopy, X-Ray Diffraction, SEM and TEM to investigate their composition and nanostructure. The film growth was monitored by in situ spectroscopic ellipsometry. Photocatalytic activity was studied by measuring methylene blue decomposition in aqueous solution.

W concentrations were measured ranging from 1 to 14 at% and it was found that tungsten precursor was partly oxidized in the plasma phase from oxidation state V to VI. In the thin films, the columnar morphology is retained and anatase is still found although in quantities diminishing with W concentration. Moreover, preferential orientation of anatase growth is also impacted by the substitution with W cations. Finally, it was found that photocatalytic activity was significantly improved by tungsten substitution, especially at low amounts (<10%at).

[1] Li et al.*Appl Surf Sci***2019**, *491*, 116–122

[2] Kubacka et al. *Catal. Today***2009**, *143* (3), 286–292

[3] Ratova et al. *Coatings***2013**, *3* (4), 194–207

TS4-4 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*; A. Hernandez-Gordillo, M. Bizarro,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; J. Medina,* Instituto de Ciencias Aplicadas y Tecnologias, Universidad Nacional Autonoma de 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.

Topical Symposia

Room On Demand - Session TS5

Thin Films on Polymer Substrates: Flexible Electronics and Beyond

TS5-1 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.

TS5-2 Functionalised Copper Nanoparticle Catalysts for Electroless Copper Plating on Textiles*,* ***Golnaz Taghavi Pourian Azar (ac8637@coventry.ac.uk),*** *A. Cobley,* Coventry University, UK

The MATUROLIFE project utilises two disciplines of materials science and design to meet the needs of older adults to lead independent lives through design-driven Assistive Technology (AT). Metallised conductive textiles are potentially an enabling technology for AT allowing better and more discreet integration of electronics into clothing, footwear, and furniture.

Electroless copper plating can be regarded as an enabling technology for electronic textiles, due to the uniform deposition with consistent thickness, simplicity, and relatively low cost. This procedure is a useful approach to produce electrically and thermally conductive fabrics that are flexible to be utilised as smart textiles. However, the choice of catalyst is crucial to activate the surface and generate nucleation sites for the copper ions to deposit on. The most widely used catalyst is a palladium/tin colloid, however, the use of palladium makes the process expensive. Therefore, alternative and inexpensive metals such as silver and copper have been recently investigated to catalyse the electroless copper plating reactions.

In this study, different catalysts based on Cu nanoparticles (functionalised by various organic molecules) have been utilised for electroless copper plating of textiles. The catalysts were characterised using Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), and X-ray Photoelectron Spectroscopy (XPS). The efficacy of different catalysts was determined by characterising electroless copper-plated textiles in terms of mass gain (after plating), the coatings coverage, and deposits morphology using Scanning Electron Microscopy (SEM). In addition, the sheet resistance of the plated textiles was measured using a four-point probe.

It was found that the degree of coverage of fibres by copper coatings and the resulted conductivities are strongly dependent on the applied catalyst. The results revealed the important role of functionalising molecules on the performance of Cu nanoparticles as a catalyst. Using the best-performing organic molecule in functionalisation of Cu nanoparticle catalyst resulted in coatings with complete coverage and consequently high electrical conductivity being favourably comparable to the coatings catalysed with a Pd catalyst.

The authors would like to thank the European Union for funding this work via the H2020 NMBP project 'MATUROLIFE' (Grant No. 760789).

TS5-3 Low-temperature Plasma Enhanced Atomic Layer Deposition of ZnO and Al_2O_3 Thin Films for Applications in Flexible Electronic Devices*,* ***Jhonathan Castillo (jhonathan.castillo@uabc.edu.mx),*** Universidad Autónoma de Baja California , Colombia*; N. Nedev,* Universidad Autónoma de Baja California , Bulgaria*; B. Valdez,* Universidad Autónoma de Baja California, Mexico*; N. Hernandez,* Instituto Politécnico Nacional (IPN), Mexico*; E. Martinez,* Centro de Investigación en Materiales Avanzados (CIMAV) , Mexico*; M. Curiel,* Universidad Autónoma de Baja California , Mexico*; M. Mendivil, M. Martinez,* Centro de Investigación en Materiales Avanzados (CIMAV), Mexico

Thin films of zinc oxide (ZnO) and 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 in order to obtain atomically saturated layers. The films were grown on ITO/Glass, quartz, p-type silicon and polyethylene terephthalate (PET) substrates. X-ray photoelectron spectroscopy (XPS) revealed a high purity of the obtained films. The optical constants and thicknesses of the grown layers were determined by spectroscopic ellipsometry, while the roughness was measured by atomic force microscopy. High transmittance, above ~90%, was measured by UV-Vis spectroscopy. Electrical characterization was carried out using Keythley 4200 Semiconductor Characterization System. ZnO and Al_2O_3 films were used to fabricate transparent thin film transistors (TFT) on ITO/Glass substrates by means of photolithography.The thickness of the ZnO (n-type semiconductor) was 60 nm, while the thickness of the gate oxide (Al_2O_3) was varied (25, 50 and 100 nm). Aluminum with thickness of 200 nm was used as a gate electrode and source and drain contacts.

The films obtained showed excellent optical, structural, compositional, morphological and electrical properties, what make them promising candidate for electronic and optoelectronic applications, which require low temperature processes.

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

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TS5-4 Roll-to-Roll Reactive Ion Etching of Nanoscale Features in Si for Next Generation Flexible Electronics*,* ***Ziam Ghaznavi (z.ghaznavi@eandr.com),*** Emerson and Renwick Ltd., USA*; N. Butcher, J. Crowther,* Emerson and Renwick Ltd., UK

Roll-to-Roll (R2R) processing has garnered significant research interest from industry in recent years due to its potential ability to simultaneously address throughput and cost requirements for next generation flexible electronics and the Internet of Things (IoT). However, a complete ecosystem of R2R tools including patterning, deposition, and etch is needed in order to facilitate the transition of device fabrication from wafer-scale to the continuous regime. Many prospective applications also require nanoscale control and repeatability for yield management which necessitates thorough characterization of each process step and an in-depth understanding of the underlying physics of these R2R tools compared to their wafer-scale counterparts particularly during pattern transfer i.e. etching. This work demonstrates progress towards process development and control on an exemplary semiconductor device fabrication scheme utilizing Emerson & Renwick's Genesis R2R platform. Specifically, we successfully demonstrate etching nanoimprinted patterns of nanopillars into Si in a continuous R2R fashion with submicron resolution. Process verification details include quantifying etch uniformity, directionality and material selectivity at varying web speeds. Furthermore, we discuss the systematic characterization of the constituent processes and equipment by intelligent Design of Experiment (DOE) allowing for process parameter tuning to meet desired etch targets.

TS5-5 HiPIMS Metallization of Polymers: Titanium on PEEK*, Aarati Chacko (aarati.chacko@empa.ch),* *K. Thorwarth, R. Crockett, U. Müller, H. 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.

TS5-6 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. 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. 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. 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^{2}psi 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.

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

TS5-7 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. Barud,* Universidade de Araraquara, Brazil*; R. Carvalho,* Pontifícia Universidade Católica do Rio de Janeiro, Brazil*; A. Cebrian,* UNESP, Brazil*; A. Barreto,* PUC-Rio, Brazil*; F. Maturi,* UNESP, Brazil*; R. Silva,* Chalmers University Technology, Sweden*; C. Legnani,* Universidade Federal de Juiz de Fora, Brazil*; S. 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 1.8x10^{-2}cm^2/Vs, threshold voltages of -7.6V and low leakage current up to 50V.

Topical Symposia

Room On Demand - Session TSP

Topical Symposia (TS) Poster Session

TSP-1 Transparent nc-Z_rB_2/a-BN Films for Protection of Optical Devices*, Philipp Kiryukhantsev-Korneev (kiruhancev-korneev@yandex.ru),* *A. Kozlova, K. 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)

TSP-2 Novel AuAgSI Thin Film Metallic Glasses With Outstanding Electrical and Mechanical Properties*, Lisa-Marie Weniger (lisa-marie.weniger@stud.unileoben.ac.at),* *O. Glushko, C. Mitterer,* Montanuniversität Leoben, Austria*; J. Eckert,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Gold based thin film metallic glasses (TFMGs) on polymer substrates combine the high elastic strain limit, low electrical conductivity and superior chemical properties of noble metallic glasses with the flexibility of polymers. This work systematically investigates the novel AuAgSi system to gain fundamental knowledge about thin film metallic glasses as well as tune the composition towards optimized electrical and mechanical properties.

$Au_{85-x}Ag_xSi_{15}$ TFMGs were deposited by magnetron sputter deposition on polymer substrates from the respective three elemental targets. Different compositions with x varying between 0 and 85 at% were fabricated and compared to Au and AgSi. Film thicknesses ranging between 12 nm and 1000 nm were deposited to investigate possible size effects within this system. The amorphous state was confirmed by X-ray diffraction; additionally, time-dependent measurements were performed to prove stability of the TFMGs. The three-component films with Ag contents between 20% and 60% were amorphous and stable over the observed period of two months. In contrast, AgSi and AuSi as well as $AuAg_{10}Si_{15}$ and $AuAg_{70}Si_{15}$ were crystalline. Moreover, the binary systems were unstable showing spontaneous phase separation or even film delamination with time.

In case of crystalline metals, the resistivity of a thin film drastically increases for thickness below 10-20 nm. Contrary to this behavior, metallic glasses like AuAgSi exhibit a constant resistivity over a wide range of film thicknesses. The investigated AuAgSi TFMGs have a lower resistivity than crystalline gold with thicknesses below 13 nm. Additionally, a negative coefficient of resistance was found within this system, which could prevent overheating in potential microelectronics applications these TFMGs.

Mechanical properties of AuAgSi TFMGs were systematically characterized by monotonic tensile tests combined with in-situ resistance measurements. The critical strain, at which cracks are generated and propagate homogeneously, is at least 3% for all amorphous compositions and even higher for film thicknesses below 25 nm. Scanning electron microscopy characterization revealed a fracture morphology characteristic for metallic glasses with two distinct types of shear bands. The high elastic strain limit of the investigated TFMGs results in excellent bending fatigue properties. After 50,000 cycles with an effective bending strain of 1.25%, AuAgSi TFMGs did not exhibit any damage, whereas massive fatigue damage was induced in the crystalline Au sample. This outstanding cyclic performance makes AuAgSi TFMGs a promising candidate for flexible microelectronic devices.

TSP-3 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*; J. Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan*; P. Yiu,* National Taiwan University of Science and Technology, Taiwan

Fe-based thin film metallic glasses (TFMGs) with different atomic compositions 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 a 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, 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.

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