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.

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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!

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].

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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.

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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

[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.

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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.

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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]

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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.

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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

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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 ≥ y ≥ 0.40) alloys, the decomposition pathway was investigated with an emphasis on the formation of Ti_4AlN_3 (MAX phase) in thin films via solid state reactions [4] .

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

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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!

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**

Author Index

Bold page numbers indicate presenter