**Monday Morning, May 20, 2024**

**Plenary Lecture**  
Room Town & Country A - Session PL-MoM

**Plenary Lecture**

**Moderator:** Johanna Rosen, Linköping University, Sweden

8:40am **PL-MoM-3 Engineering 2D MXene Surfaces for Functional Films and Coatings, Yury Gogotsi**, Drexel University, USA  
**INVITED**

MXenes (carbides, nitrides, oxy_carbides and carbonitrides of early transition metals) are a very large family of 2D materials. They have a chemical formula of $M_{n+1}X_nT_x$, where $M$ is a transition metal (Ti, Mo, Nb, V, Cr, etc.), $X$ is either carbon and/or nitrogen ($n=1$, $2$, $3$ or $4$), and $T_x$ represents surface terminations ($O$, $OH$, halogens, chalcogens). The large variety of structures and compositions, availability of solid solutions on $M$ and $X$ sites, and control of surface terminations offer a plethora of materials to produce and investigate.

Combining their plasmonic properties with ease in aqueous processing, high electronic conductivity (over 20,000 S/cm), biocompatibility, and excellent mechanical properties, which exceed other solution-processable 2D materials, MXenes have the characteristics enabling numerous applications.

Inherent to their 2D structure, the charge carriers responsible for MXene’s optical responses and electronic transport are very close to the surface that has an exceptional ability to undergo reversible chemical and electrochemical reactions to add or change surface terminations. MXenes can be applied to a variety of surfaces to provide electronic and ionic conductivity, control optical properties in a wide range of wavelengths, produce electrochromic films, and even achieve a low friction coefficient. Polymers, paper, and fabrics coated by MXenes from aqueous or organic solutions acquire unique surface properties. The properties of MXene coatings can be optically or electrochemically modulated. Many technological advances can be enabled by these chemically and optically responsive conductive coatings.

References


Monday Morning, May 20, 2024

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM1-1-MoM

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

Moderators: Damien Faurie, Université Sorbonne Paris Nord, France; Barbara Putz, Empa, Switzerland

10:00am CM1-1-MoM-1 Exploring Nanostructure Behavior and Ordering Dynamics Through Advanced Electron Microscopy, Lilian Vogl, University of California at Berkeley, USA; P. Schweizer, Lawrence Berkeley Lab, University of California, Berkeley, USA; J. Michler, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; A. Minor, University of California at Berkeley, USA

Characterizing the property-structure relationship and unraveling mechanism on atomic level is not only key for the development of novel nanostructures but also helps to improve the performance of materials on the bulk-scale. In situ electron microscopy enables the direct observation of how nano-objects respond to external stimuli, such as mechanical loading or heat treatment. For instance, the significant impact of a disordered crystal structure on the mechanical properties has been widely observed in bulk-alloys. However, the investigation of ordering characteristics in semiconducting and metallic nanostructures (thin films, nanowires) has largely been unexplored. Considering the large surface area to volume ratio of nanostructures, it is expected that local variance within the crystal lattice would have an amplified effect. Therefore, studying the precise characteristics of local ordering in nanostructures becomes all the more important to better tailor their behavior.

By using our unique small-scale model systems of alloyed nanowires, we investigate the transition from the disordered state to intermetallic phases by in situ heating experiments. With increasing degree of ordering, microdomains are observed showing characteristic long-range periodicity. Visualized by 4DSTEM, such local ordering induces strain at the order-disorder domain boundary. For metallic nanowires, the size effect of “smaller is stronger” has been established, showing that nanostructures have superior mechanical properties compared to their bulk counterpart. Now, alloyed nanowires offer the opportunity to further optimize the mechanical response by tuning the ordering degree. In situ mechanical testing (including the acquisition of stress-strain curves) of single-crystalline nanowires with different degree of ordering demonstrate the slip-to-twinned transition. While solid-solution nanowires deform via twinning, ordered ones show distinct slipping mechanism.

But ordering isn’t limited to its pivotal role in alloyed systems. In the case of designing semiconducting thin films, in addition to composition, short-range ordering (SRO) can be utilized to adjust the band gap. The presence of preferential neighbors in the range of 1-2 unit cells in an otherwise random lattice induces diffuse intensity distributions in the diffraction pattern which can be visualized by energy filtered 4DSTEM. In order to manipulate the short-range ordering within the thin films, they undergo heating or irradiation, inducing atoms to exchange positions and thereby altering the local ordering.

10:40am CM1-1-MoM-3 Autonomous Health Tracking in Self-Reporting MAX and MAB Phases, Peter Pöllmann, S. Lellig, D. Bogdanowski, A. Navid Kashani, M. Hans, Materials Chemistry RWTH Aachen University, Germany; P. Schweizer, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; D. Holzapfel, C. Azina, P. Zill, Materials Chemistry RWTH Aachen University, Germany; D. Przemetkofer, Department of Physics and Astronomy, Uppsala University, Sweden; S. Kolosvári, P. Polcik, Plansee Composite Materials GmbH, Germany; J. Michler, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; J. Schneider, Materials Chemistry RWTH Aachen University, Germany

Materials health defining mechanisms including chemical changes induced by annealing and oxidation have been tracked via contact-based in-situ resistivity measurements. The resulting changes in structure and composition have been analyzed by scanning transmission electron microscopy (STEM), selected area electron diffraction (SAED), high-energy X-ray diffraction (HEXRD), as well as differential scanning calorimetry (DSC) and related to the resistivity data. From this comparison, it is evident that Cr-Al-Mo (Mo/Cr-Al (n=1-2)) exhibit autonomous self-reporting behavior as it was demonstrated that structural and chemical changes, influencing materials health, can be readily tracked by contact-based in-situ resistivity measurements in an application-relevant temperature regime.

Furthermore, a proof of concept for contactless materials health monitoring has been demonstrated for the first time. This contactless resistance measurement was benchmarked with respect to contact-based resistivity measurements as well as the methods mentioned above to probe structure and composition. It was shown that phase changes, decomposition, and oxidation can be tracked contactless. The proposed method can hence be utilized in the future to track the remaining lifetime of complex-shaped, fast-moving components enabling efficient and therefore more sustainable component utilization.

11:00am CM1-1-MoM-4 Correlation of Laser-Reflection and Thermionic Emission of Thermally Loaded Coatings Under UHV Conditions, Lukas Wimmer, Vienna University of Technology, Austria; C. Bienert, R. Schiffler, PLANSEE SE, Austria; C. Eisenmenger-Sittner, Vienna University of Technology, Austria

In (ultra) high vacuum conditions the evaporation of materials at high temperatures is an important issue, which may significantly reduce the lifetime of thin coatings. To analyze the behavior of film evaporation at high temperatures, the surface evolution has been monitored in-situ using thermionic remission and a laser reflection setup. The temperature during the investigations was regulated by a pyrometer on a designated spot via direct resistive sample/substrate heating. The identified correlation between these two signals showed the capabilities of the measurement system and technique to develop new materials for high temperature applications, such as thermal barrier or thermionic emission coatings.

Within this study different oxide coatings have been analyzed, based on reactive magnetron sputtered ZrO2 and Y2O3 films on tungsten substrates. Depending on the thermal stability of the respective materials, the coatings of various thickness were tested at temperatures in the range of 1200-1800°C, while keeping the total pressure below 10-5 Pa. Even though the thermionic emission of the oxide coatings provides information regarding the coating breakdown, the reflection signal is more decisive. The reflection signal shows a strong dependence on the thickness of the “transparent” oxide coatings, allowing to obtain close information on the film evolution. For instance, the evaporation rate of ZrO2 at 1700°C was determined to be approx. 10 nm/h for pressures below 10^-5 Pa. The combination of the reflection signal and thermionic emission on the other hand allows an observation of the chemical stability of the film. The investigated oxide coatings thereby maintain their chemical composition throughout the high temperature process and eventually evaporate completely.

11:20am CM1-1-MoM-5 Bill Sproul Award and Honorary ICMCTF Lecture: When Stressed Condensed Matter Reveals Its Ultimate Secrets: Thin Film Growth Dynamics Probed by Real-Time Diagnostics, Gregory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; K. Solanki, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; M. Kaminski, Karlsruhe Institute of Technology (KIT), Germany; A. Michel, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; A. Vlad, A. Resta, A. COATI, Synchrotron SOLEIL, France; B. Krause, Karlsruhe Institute of Technology (KIT), Germany; D. Babonneau, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Town & Country C - Session CM4-1-MoM

Simulations, Machine Learning and Data Science for Materials Design and Discovery
Moderator: Davide G. Sangiovanni, Linköping University, Sweden

10:00am CM4-1-MoM-1 High-Throughput Rapid Experimental Alloy Development (HT-READ), Kenneth Vecchio, University of California at San Diego, USA

The development of high-throughput materials development strategies in the thin-film field have moved forward more quickly than bulk material high throughput strategies, primarily due to the need in bulk materials to account for microstructure effects on properties.In addition, the current
bulk materials discovery cycle has several inefficiencies from initial computational predictions through fabrication and analyses. Much of the information and knowledge generated existed in isolated data silos making integrated approaches more challenging. This was the motivation for the 2011 Materials Genome Initiative, which sparked advances in many high-throughput computational techniques related to materials development. However, computational techniques ultimately rely on experimental validation. Furthermore, bulk materials are generally evaluated in a singular fashion, relying largely on human-driven compositional choices and analysis of the volumes of generated data, thus also slowing validation of computational models. Thus, increasing the rate of materials experimentation is fundamental to improving materials research, and requires parallelizing, automating, and miniaturizing key steps in experimental materials research, including computation, synthesis, processing, characterization, and data analysis.

To overcome these limitations, we developed a High-Throughput Rapid Experimental Alloy Development (HT-READ) platform and methodology that comprises an integrated, closed-loop material screening process inspired by broad chemical assays and modern innovations in automation. Our method is a general framework unifying computational identification of ideal candidate materials, fabrication of sample libraries in a configuration amenable to multiple tests and processing routes, and analysis of the candidate materials in a high-throughput fashion. An artificial intelligence agent is used to find connections between compositions and material properties. New experimental data can be leveraged in subsequent iterations or new design objectives. The sample libraries are assigned unique identifiers and stored to make data and samples persistent, thus preventing institutional knowledge loss. This integrated approach paves the way for truly compositionally-accurate and microstructurally-informed bulk materials development in a highly accelerated manner. This overall strategy has enabled our group to achieve the ability to design, fabricate, and fully characterize more than 800 bulk alloy samples per year with a single researcher.

10:40am CM4-1-MoM-3 Fundamental Investigation for Film Quality Prediction Based on Zone Model in Magnetron Sputtering. Kohei Kuroshima, I. Ikeda, Osaka Vacuum, Ltd., Japan; Y. Gotoh, Department of Electronic Science and Engineering, Kyoto University, Japan; M. Iguchi, S. Sugimoto, Osaka Vacuum, Ltd., Japan

There are diagrams for film structures that are closely related to film properties, called the structure zone model. Thornton’s model[1] uses a pressure for one axis, so the model may vary depending on the sputtering apparatus. Anders[2] argued the structure zone diagram (SZD) for the films deposited under presence of energetic particles. In the SZD, the axes are the normalized energy of the particles incident on the substrate, E*, and the generalized temperature, T*.

Although it is said that this model cannot be used to predict film structure at points on the E*-T* plane, a trial to predict the structure on the SZD was done in this study. We focused on magnetron sputtering and calculated E* using only the kinetic energy when sputtered particles are incident on the substrate, and with measured substrate temperature, and verified whether Anders’ SZD could be applied. We developed a sputter particle transport simulation software and calculated E*. This simulation includes the thermal motion effect of the process gas.[3]. For validation, two common types of magnetron sputtering equipment were used to deposit film samples at several combinations of sputtering pressure (0.3–4.0 Pa), target-to-substrate distance (50–100 mm), and substrate temperature (RT–450 °C). The input power was constant at 300W DC. We observed the surface and cross section of the samples by Scanning Electron Microscope (SEM). It was confirmed whether the structure of the film deposited with the condition which is represented by a certain point on the SZD was consistent with the structure represented by the ZONE.

As a result, under the conditions corresponding to the film structures of ZONE 1 and ZONE 2 on the SZD, the SEM images of the film had the near the boundaries of the zones.

Following SZD, we are developing a new diagram which exhibits film properties instead of film structure.[4]. A part of this work was supported by Kyoto University Nano Technology Hub in "Nanotechnology Platform Project" and "Advanced Research Infrastructure for Materials and Nanotechnology Project" sponsored by MEXT, Japan.

References

11:00am CM4-1-MoM-4 Are ML Potentials Useful to Understand Deformation and Fracture of Ceramics?, Nikola Koutna, S. Lin, TU Wien, Austria; L. Hultman, Linköping University, Sweden; P. Mayerhofer, TU Wien, Austria; D. Sangiovanni, Linköping University, Sweden

Theoretical understanding of atomic-scale mechanisms underlying deformation and crack growth in ceramics enables rational design of alloys, superlattices, or nanocomposites with optimized combination of hardness and toughness. Simulations represent an important counterpart to experiment, being relatively inexpensive and allowing to impose well-defined loading conditions, thus making fair comparisons within one material class. Certain comprehension of how ceramics behave subject to mechanical loads can be achieved by ab initio methods, however, experimentally-relevant predictions require a combination of finite-temperature effects and large-enough models to consider extended crystallographic defects. In this talk I will discuss the exciting and rapidly growing field of machine-learning interatomic potentials (MLIPs) for molecular dynamics and how these can be used to study the onset of fracture. Transition metal diborides and MAB phases (i.e. atomically-thin laminates of ceramic/metallic-like layers) will serve as model materials to showcase a possible training strategy for the MLIP development and challenges upon up-scaling beyond length scales of ab initio reach. Furthermore I will present simulations of crack initiation in TbB2, as well as the formation of ripplcations in Ta4AlB7, and other MAB phases under certain loading conditions will be interpreted in the light of experimental data available via collaborators. The ML potentials will turn out to be quite useful.

11:40am CM4-1-MoM-6 Transformation Plasticity and Fracture in MB: (M=Ti, Ta, W, Re) Diborides via Ab-Initio and Machine-Learning-Potential Molecular Dynamics. Shuyue Lin, TU Wien, Institute of Materials Science and Materials Engineering, Austria; T. Leiner, Montanuniversit.te Leoben, Leoben, Austria; Z. Chen, Austrian Academy of Sciences, Austria; R. Janknecht, TU Wien, Institute of Materials Science and Technology, Austria; F. Tasnadi, Linköping University, Sweden; Z. Zhang, Austrian Academy of Sciences, Austria; L. Hultman, Linköping University, Sweden; P. Mayerhofer, TU Wien, Institute of Materials Science and Technology, Austria; D. Holec, Montanuniversit.at Leoben, Austria; D. Sangiovanni, Linköping University, Sweden; N. Koutna, TU Wien, Institute of Materials Science and Technology, Austria

In this contribution we employ ab-initio molecular dynamics (AIMD) and machine learned interatomic potential molecular dynamics (ML-MD) simulations to elucidate trends and typical patterns in the mechanical response of transition metal diborides. Four representative diboride systems, MB2, are selected, with M from the group IV (Ti), V (Ta), VI (W), and VII (Re) of the periodic table. The AIMD simulations serve to find finite-temperature equilibrium lattice parameters of the chosen diborides and to estimate their tensile and shear response at the atomic scale. The thereby produced ab initio dataset is used to fit and validate machine-learning interatomic potentials for ML-MD (within the moment tensor potential, MTP, formalism), providing a basis to study deformation behavior at the nanoscale. By controlling the phase structure (the AlB2, WB2, and ReB2-prototype phase), supercell size (few to dozens of nm3), and imposing well-defined loading conditions (tensile or shear deformation with various loading conditions and/or unit cells), our ML-MD simulations allow assessing similarities as well as fundamental differences between the studied diborides. Considering a nanoscale model with a pre-indent on the surface, we go one step further and discuss ML-MD predictive power and limitations in the light of experimental results for an indented TiB2 thin film.

12:00pm CM4-1-MoM-7 Machine-Learning Potential for Accurate Predictions of Elastic Properties in Amorphous W-B-C, Pavel Ondraca, J. Ženiček, Masaryk University, Czechia; G. Noyok, RWTH Aachen University, Germany; D. Holec, Montanuniversit.at Leoben, Austria; P. Vászina, Masaryk University, Czechia

Amorphous tungsten boron carbide is a prospective material for protective coatings, with superior ductility and crack resistance[1], and yet the subtle
.details of its atomistic structure and origin of its excellent mechanical properties are still unclear. Due to the small sizes of representative models and limited timescales of \textit{ab initio} molecular dynamics based on density functional theory, it is difficult for this standard methodology to reliably predict structural and mechanical properties of amorphous W-B-C. Such predictions lead to strongly anisotropic mechanical properties and large uncertainties in the results. We solved the issues by fitting interatomic potentials [2] in a general nonlinear atomic cluster expansion (ACE) form [2] to this material system using an active learning approach to sample the amorphous configuration space and the D-optimality criterion and MaxVol algorithm to efficiently construct the training set [3]. The potential was trained for the W content between 10 and 60 at. % and C:B ratios between 4:1 and 1:4. Subsequently, we employed a melt & quench procedure to generate amorphous structural models containing more than 10000 atoms which yielded an isotropic mechanical response and revealed trends with respect to the system composition, density and quenching rates. The thus obtained values of \textit{Young's} modulus were successfully validated against experimental data.


**Protective and High-temperature Coatings**

**Room Town & Country D - Session MA3-1-MoM**

**Hard and Nanostructured Coatings I**

**Moderators:** Marcus Günther, Robert Bosch GmbH, Germany, Rainer Hahn, TU Wien, Institute of Materials Science and Technology, Austria, Stanislav Havír, University of West Bohemia, Czechia, Fan-Yi Ouyang, National Tsing Hua University, Taiwan

10:00am **MA3-1-MoM-1 Nitride and Carbide Layers: Point Defects, Interfaces, Mechanical Properties, Daniel Gall**, RensselaerPolytechnic Institute, USA

**INVITED**

We explore transition metal nitride and carbide compounds and multilayers using a combination of epitaxial layer growth, first-principles calculations, and measurements of lattice parameters and mechanical properties. 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 based-centered monoclinic stoichiometric MoN. Epitaxial WCx layers exhibit a cubic phase that is stabilized by carbon vacancies but phase competition involving hexagonal and orthorhombic WxC and amorphous carbon lead to an epitaxial breakdown. Epitaxial MoCx shows a similar phase competition between cubic $\beta$-MoC($111$) and hexagonal $\beta$-MoC($10001$) as a function of CHx content in the processing gas. In contrast, epitaxial TiC is phase pure over a large composition range as the cubic phase is stabilized by the entropy of random C-vacancies for $x > 1$. However, carbon interstitials and small clusters are energetically unfavorable leading to amorphous C segregation for $x > 1$, as detected by photoelectron and Raman spectroscopies. This causes a decrease in the elastic modulus and hardness from 462 and 31 GPa for stoichiometric TiC to 201 and 13.5 GPa for $x = 1.8$. Epitaxial TiC$_x$N$_{1-x}$ ($001$) layers show a nearly composition independent elastic modulus but a hardness that decreases approximately linearly from 31 to 21 GPa with increasing $x = 0.0-1.0$. TiN-Ti multilayers exhibit a 5-30% superlattice hardening effect, reaching 34 GPa for an epitaxial layer with a 6 nm lattice period.

10:40am **MA3-1-MoM-3 The Influence of the Carbon Source on the Mechanical and Electrical Properties of Magnetron-Sputtered Titanium Carbonitride Coatings, Juliana Kessler**, Uppsala University, Angstrom Laboratory, Sweden

Titanium carbonitride coatings were investigated for use in electrochemical cells. Here, contact resistance should be minimal while maintaining mechanical strength and a fairly good corrosion resistance. Similar to titanium carbides, an increased carbon content leads to the formation of an amorphous carbon-a(C) phase resulting in nanocrystalline grains of titanium carbonitride surrounded by an a-C matrix. Fine-tuning the microstructure of titanium carbonitride films contact resistance can minimise contact resistance as it is largely determined by surface properties such as hardness and formability, which in turn vary with the amount and structure of the a-C phase. Depending on the carbon source used during the sputter process, the microstructure of the deposited films changes. The aim of this work is to compare the formation of a-C during sputter deposition using two different carbon sources: graphite and methane. Films were either deposited by co-sputtering from a Ti- and a graphite target under a TiN$_x$ target, or by sputtering solely from a Ti target under N$_x$ and CH$_x$ gas flow. For each process films of different carbon content were deposited and analysed using XRD, XPS, SEM, and Raman spectroscopy. Additionally, properties such as hardness, resistivity, and contact resistance were also investigated. Results show that the carbon concentration of the films varies from 10-24 at.%. Using XPS and XRD, it was found that the films contain NaCl-type Ti(C,N) and an amorphous carbon (a-C) phase. For different carbon concentrations Ti(C,N) shows a varying lattice parameter between 4.26 to 4.32 Å. Furthermore, an increasing overall carbon content causes an increased amount of a-C phase, which has a significant effect on the properties of the films. Comparing the a-C content of films with a similar overall carbon content suggests that carbon is more effectively incorporated in Ti(C,N) grains when using methane as a carbon source. The hardness of the films varied between 12 and 35 GPa and it was found to be dependent on the carbon content, where a lower carbon content corresponded to a reduced hardness. The peak hardness of 35 GPa was found for the film with the highest carbon content deposited using methane as a carbon source. In terms of contact resistance, the lowest values (below 10mΩ) were found for titanium carbonitride coatings with small amounts of a-C, which outperformed both titanium carbide and nitride reference coatings.

11:00am **MA3-1-MoM-4 A Strategic Design Approach Controlling the B-Solubility in Transition Metal Nitride-Based Thin Films, Rebecca Janknecht**, K. Weiss, N. Koutra, Institute of Materials Science and Technology, TU Wien, Austria; E. Ntemou, Department of Physics and Astronomy, Uppsala University, Sweden; P. Poliček, S. Kolozsvári, Plansee Composite Materials GmbH, Germany; D. Primethöfer, Department of Physics and Astronomy, Uppsala University, Sweden; R. Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria; R. Hahn, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Limited B-solubility in fcc-TiN poses significant challenges to the applicability of Ti-B-N-based hard coatings. In particular, excess B tends to segregate at the grain boundaries instead of being fully incorporated in the fcc lattice. Although increasing the B content enhances mechanical properties such as hardness, forming excess amorphous grain boundary phases can significantly reduce fracture toughness. Compared to TiN, we observed an increase of 10 GPa in hardness (up to 36.9±1.8 GPa) but a decrease in fracture toughness of roughly 25 % (down to 2.1±0.1 MPa*mm$^{0.5}$). Assisted by ab-initio DFT calculations, we previously demonstrated that additional Ti (to deviate from the TiN–TiB tie-line) is required fully incorporated in B or Al to stabilize B-rich amorphous phases. Here, we expand this research by adjusting the metal sub-lattice through Ti-, Cr-, Al- or Zr-addition to a Ti-B-N compound target (50 at.% Ti, 40 at.% N, and 10 at.% B). Our study highlights the key-role of kinetics in non-reactive deposition processes to overcome the thermodynamic limits of B-solubility in TiN. Through changing the stoichiometry by knowledge-based metal addition, we propose a general strategy to enhance the B solubility in transition metal nitride-based thin films.

11:20am **MA3-1-MoM-5 The Influence of Bilayer Periods and Ratios on Mechanical and Tribological Properties of TiN/MoN Superlattice Thin Films, Z. Gao, J. Buchinger, R. Hahn, TU Wien, Institute of Materials Science and Technology, Austria; Z. Chen, Z. Zhang, Austrian Academy of Sciences, Austria; Paul Mayrhofer**, TU Wien, Institute of Materials Science and Technology, Austria

Transition metal nitrides are commonly used in hard and protective coating industry, but still limited by low intrinsic fracture toughness. Encouraged by the previous study that superlattices (SLs) could remarkably improve strength and ductility, in this study, some TiN/MoN SL thin films are sputtered on (100) MgO substrates. These SLs are with bilayer periods (A) of 2–23 nm and a bilayer ratio ($E_{MoN}/E_{TiN}$) of 1.1, 1.05, 1.1, 1.2, and 1.2.7. This work is aimed to explore the influence of bilayer periods and ratios, and the ratios on TiN/MoN superlattice. All SLs – independent of bilayer period, bilayer ratio, and nitrogen content – present a rocksalt structure, with high-order satellite peaks during X-ray diffraction. But a weak tetragonal $\beta$-Mo$_{53}$N signal is also detected for the SLs with $A = 7.3$ nm
The overall stress and the layered stress of the coatings were measured using the laser curvature method and the average X-ray strain (AXS) combined with nanoindentation methods [3-5], respectively. By using the energy-balance model and the concept of EDT [1,2], the stress and energy relief efficiency of the multilayer architecture could be estimated.


Functional Thin Films and Surfaces
Room Town & Country A - Session MB4-MoM

10:00am MB4-MoM-1 Influence of Plasmonic Coupling and Size Effect on Photocatalysis of MoS$_2$/Au Hybrid Nanostructures for Water Splitting. Yi-Hseuh CHEN, J. Ruan, NCKU, Taiwan

Hydrogen energy is a clean and sustainable form of energy for our environment, serving as a viable alternative energy source that can be used without the production of greenhouse gases. Utilizing solar energy to split the water and generate hydrogen in the presence of photocatalysts is a promising and economic approach to address the current energy and environmental crisis. MoS$_2$ has been recognized as the most efficient photocatalyst for hydrogen evolution among non-noble metals. In particular, MoS$_2$ nanosheets exposed lots of active sites for the attachment of proton and later reduction reactions, and the efficiency is better than nanoflowers or bulk morphology. However, the absorption wavelength of MoS$_2$ nanosheets is almost within the UV region, in addition to the challenge of high electron/hole pairs recombination rate. Visible light accounts for 95% of sunlight and UV light occupies only 5%. It is vital for photocatalysts to efficiently harvest visible light and avoid exciton recombination. The absorption of visible light is able to cause strong localized surface plasmon resonance (LSPR) of gold nanoparticles (AuNPs), which has been widely investigated to promote light absorbance. Nevertheless, the desired dispersion patterns of AuNPs for the optimization of plasmonic resonance are less achievable. As an approach to maximize the amount of energy absorbed from the sunlight, we aim to design and fabricate hybrid particles composed of AuNPs and MoS$_2$ nanosheets with the control of coupling effect among AuNPs and the size of AuNPs. We have successfully grown MoS$_2$ nanosheets directly on the (111) planes of gold nanoparticles to form the core-shell structure with controlled thicknesses. Furthermore, the extent of enhancement of plasmonic coupling for gold nanoparticles with different diameters, i.e. 16 nm and 38 nm has been verified. Through the achieved adjustment of edge-to-edge distances among AuNPs and the size of AuNPs, the required condition for the best plasmonic resonance to absorb visible light is able to be clarified and thus optimizes the hot electron transition from AuNPs to MoS$_2$, which critically enhances desired hydrogen production.

10:20am MB4-MoM-2 Sputter Deposition of Hexagonal Boron Nitride Films, Minseuk Seo, L. Baya Aji, Lawrence Livermore National Laboratory, USA; Y. Tseng, S. Kim, Stanford University, USA; Y. Zhou, L. Wan, C. Kim, B. Wang, T. Heo, L. Zepeda-Ruiz, Lawrence Livermore National Laboratory, USA; S. Chu, Stanford University, USA; S. Kucheyev, Lawrence Livermore National Laboratory, USA

Hexagonal boron nitride (hBN) films are attractive for several emerging related applications. Extensive previous research has focused on the growth and properties of either ultrathin hBN films with thicknesses up to a few TiN or CrN films. The synthesis of wafer-scale hBN films with controlled thickness above ~10 nm with desired properties remains a challenge. Here, we present results of our ongoing systematic study of polycrystalline hBN films with thicknesses in a wide range of 50-6000 nm deposited by various variants of reactive magnetron sputtering with a radiofrequency (RF) driven discharge. We describe how the plasma...
Advancing 2D Materials for Future Electronics: Selective Synthesis, Transferring Processes, and Device Integration, Ching Yuan Su, National Central University, Taiwan

Two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMDs) have attracted significant attention due to their exceptional electrical properties, holding promise for next-generation nanoelectronics. However, integrating 2D materials into IC devices presents challenges, including precisely controlled synthesis methods, defect-free transfer processes, and back-end-of-line (BEOL) device integration. In this talk, I will discuss advancements in selectively seeding growth of high-quality 2D materials on insulating substrates using a new precursor and advanced process. Additionally, an efficient and reliable method for the wafer-scale transfer of graphene and other 2D materials, ensuring integrity and cleanliness, will be presented. Finally, I will highlight the concept of a heterogeneously integrated 3D-IC, combining a 2D-field-effect transistor (FET) with high-performance memory, showcasing the potential for BEOL and monolithic integration of 2D-based 3D-ICs.

Room Temperature Highly Efficient NO2 Gas Sensors Based on MoSe2-WS2 Nanocomposite-Filled Porous Si, S. Kodan, Indian Institute of Technology Roorkee, India; A. Kumar, National Council of Educational Research and Training (NCERT), India; Ramesh Chandra, Indian Institute of Technology Roorkee, India

We report on the room temperature NO2 gas sensing characteristics of a novel molybdenum disulfide-tungsten disulfide (MoSe2-WS2) nanocomposite thin film that was formed on a porous silicon substrate (PSi). Employing the DC magnetron sputtering technique, the thin film was carefully deposited on the PSi, which had been prepared through an electrochemical anodization setup. Our investigation utilized X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) to delve into the sensing film’s phase, microstructure, atomic composition, and elemental bonding. The superhydrophobic nature of the as-deposited thin film was confirmed through the sessile droplet water contact angle method. This innovative sensor showcased impressive room temperature performance, with a rapid response/recovery time of 22 seconds/42 seconds and remarkable sensitivity, registering at 82.7% for a 100-ppm concentration of NO2. The enhanced sensing capabilities can be attributed to several factors, including the augmented surface area resulting from the composite formation, the abundance of reaction sites facilitating efficient interaction with NO2 molecules, the individual catalytic effects of MoSe2 and WS2, and the establishment of a heterojunction between MoSe2 (n-type) and WS2 (p-type). Furthermore, the choice of the PSi substrate played a pivotal role in achieving an enhanced response by safeguarding the sensor surface against deleterious humidity effects. The sensing mechanism during adsorption and desorption cycles is elucidated by examining the charge transfer process and potential barrier variations in the formed MoSe2-WS2 nanocomposite heterojunction.

Reduced Electrocatalytic potential of Nitrate to Ammonia through MoS2 Deposited Carbon Felt based Flexible Electrode, Prateek Sharma, C. Liao, Y. Chang, D. Huang, W. Hsu, J. Huang, Y. Lai, Ming Chi University of Technology, Taiwan

The increasing need, for environment friendly and energy efficient methods to remove nitrate from water has prompted the investigation of inventive electrocatalytic techniques. This work highlights an approach to convert nitrate into ammonia at low potential using carbon felt coated with Molybdenum disulfide (MoS2) nanosheets as a flexible electrode. The layered structure of MoS2, with exposed edge sites, provides active catalytic sites for the reduction reactions. This enhances the catalytic activity compared to other materials, contributing to more efficient nitrate ion degradation, making it a potential candidate for sustainable water treatment. MoS2 can be deposited on flexible substrates, such as carbon felt, creating flexible electrodes. The flexible nature of the MoS2-deposited carbon felt electrode enhances the catalytic activity, allows for easy integration into existing water treatment systems, providing adaptability and scalability for practical applications. This research contributes towards the formation of efficient MoS2 nanosheets as catalyst material for the advancement of electrocatalysis for sustainable water treatment but also underscores the significance of flexibility of electrodes in enhancing the adaptability and efficiency of the nitrate to ammonia conversion process. The findings presented in this conference aim to foster discussions and collaborations towards the development of energy-efficient and environmentally friendly technologies for nitrogen removal from water sources.

Keywords: Nitrate ion reduction, Electrocatalysis, Flexible electrode, Electrodeposition, MoS2 nanosheets

Trigraphy and Mechanics of Coatings and Surfaces Room Palm 1-2 - Session MC1-1-MoM

Friction, Wear, Lubrication Effects, and Modeling I

Moderators: Manel Rodriguez Ripoll, AC2 Research GmbH, Austria, Michael Chandross, Sandia National Laboratories, USA

10:00am MC1-1-MoM-1 Fragile Films, Angela Pitenis, UC Santa Barbara, USA

Invited

Solid lubricants (e.g., gold, molybdenum disulfide, graphite, and polytetrafluoroethylene) effectively protect sliding surfaces by creating weak interfacial layers that dissipate energy during sliding. In biology, cells secrete fragile yet protective mucin gel networks that function like mechanical fuses by shear-thinning under critical shear stresses and rapidly recovering to provide load support. Taking inspiration from biology, many groups over the past several decades have functionalized surfaces with weak gel layers or brushy films, although these methods can be time-consuming and costly. In this work, we deliberately polymerized gels near oxygen-rich environments and oxygen-permeable surfaces to create polymer-depleted surface gel layers. This inexpensive process can easily produce gel surfaces that mimic the gradient structure of natural mucin gel networks.

11:40am MB4-MoM-3 Advancing 2D Materials for Future Electronics: Selective Synthesis, Transferring Processes, and Device Integration, Ching Yuan Su, National Central University, Taiwan

Invited

Two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMDs) have attracted significant attention due to their exceptional electrical properties, holding promise for next-generation nanoelectronics. However, integrating 2D materials into IC devices presents challenges, including precisely controlled synthesis methods, defect-free transfer processes, and back-end-of-line (BEOL) device integration. In this talk, I will discuss advancements in selectively seeding growth of high-quality 2D materials on insulating substrates using a new precursor and advanced process. Additionally, an efficient and reliable method for the wafer-scale transfer of graphene and other 2D materials, ensuring integrity and cleanliness, will be presented. Finally, I will highlight the concept of a heterogeneously integrated 3D-IC, combining a 2D-field-effect transistor (FET) with high-performance memory, showcasing the potential for BEOL and monolithic integration of 2D-based 3D-ICs.
networks protecting cells across biological sliding interfaces (e.g., cornea-eyelid). We characterized the thickness of the surface gel layer on our synthetic gels using micro rheology and micro- and nanoindentation techniques. We conducted in vitro biotribological testing of soft gels (with and without surface gel layers) against human corneal epithelial cells to model device-tissue interfaces (e.g., soft contact lens sliding against the cornea). Our results suggest that surface gel layers are more effective at reducing frictional forces and mitigating the removal of natural mucus gels, and hold promise for inexpensive yet informed routes for designing gel-based biomedical devices and coatings.

10:40am MC1-1-MoM-3 Wear-Performance and Durability of in-Situ-Deposited Carbon Tribofilms Derived from Instrinsically Strained Cycloalkane Molecules as Lubricant Additives, Z. Al Hassan, H. Wise, T. Martin, Y. Liu, Y. W. Chung, Northwestern University, USA; S. Berkebile, US Army Research Laboratory, USA.

Wear-protective coatings on tribo-component surfaces are usually applied via vapor deposition methods. Once worn, they can only be restored through component disassembly. In our study, we explored in situ carbon tribofilm deposition using instrinsically strained cycloalkane molecules. These molecules, when dissolved in lubricants, can induce tribopolymer formation under stress and temperature at asperities. Our previous work on cyclopropane-carboxylic acid (CPCA) as an additive in polyalphaelophin and dodecan demonstrated the successful deposition of micro-thick carbon tribofilms in 15 minutes during pin-on-disc testing with a ten-fold reduction in wear. New results show that even after the removal of PCPs from the lubricant, these tribofilms continue to provide wear protection for up to 20 hours. Infrared surface examination using filamentary spectroscopy helps us unravel the underlying mechanism for such extended durability of these carbon tribofilms. This research suggests a unique approach to providing unlimited replenishment of wear-protective layers.

11:00am MC1-1-MoM-4 Lubricant Interaction of Tribactive CrAlMoCuN Coatings in Steel Contacts, K. Bobzin, C. Kalscheuer, Max Philipp Möbius, Surface Engineering Institute - RWTH Aachen University, Germany.

Conventional lubricants are designed for wear and friction reduction in steel-to-steel contacts. Rising power densities require enhanced wear resistance of machine components. This can be achieved using hard CrAlN coatings, although their chemical inertness limits interaction with lubricants. Therefore, Mo and Cu are incorporated into CrAlN coatings, promting tribico-chemical interaction with lubricants. Mo can interact with sulfur to create MoS2 tribofilms. Cu acts catalytically for this reaction and can enhance tribofilmon formation for Fe-P, and a-C. In most applications like gear boxes, bearings or chain drives, it is economically and technologically challenging to coat all components. Therefore, this study focuses on coating-steel contacts. Three CrAlMoCuN coatings and one CrAl reference were deposited using physical vapor deposition (PVD). Coating characteristics, such as morphology determining thickness, chemical composition, indentation hardness, surface roughness and compound adhesion. All coatings, along with an uncoated reference, were tribologically investigated using a pin on disk (PoD) tribometer. As substrate, the chain pin steel SCR8Cr4 was used, quenched and tempered to H = (52±1,5) HRC. The PoD parameters were an initial contact pressure of \( p_{\text{HO}} = 1,400 \text{ MPa} \), a relative velocity of \( V_{\text{rel}} = 0.1 \text{ m/s} \), and a temperature of \( T_{\text{amb}} = 70 \text{ °C} \). 100Cr6 steel was used as counterpart and Polyalphaelophin (PAO) as lubricant. PAO was highly additized with sulfur and phosphorous. Tribofilms were investigated using energy dispersive spectroscopy (EDS) and Raman spectroscopy. All CrAlMoCuN systems showed lowered coefficients of friction compared to both references indicating the formation of MoS2 containing tribofilms. This correlates with a significantly reduced total wear volume.Via EDS, Cu-enriched lubricant residues were found on the uncoated counterparts in the CrAlMoCuN system, indicating the interaction of Cu with the lubricant in the tribological contact for the first time. The results show high potential of CrAlMoCuN coatings for lubricated machine element applications.

11:20am MC1-1-MoM-5 Enhancing the Tribological Properties of Ti6Al4V Alloy through Duplex Plasma Nitriding and MoS2 Coating, Kai Le, W. Wang, J. Yang, Y. Liu, S. Xu, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China.

In this study, an innovative dual surface treatment combining plasma nitriding with MoS2 coating is introduced to enhance the tribological properties of Ti6Al4V alloy, a material widely used in aerospace, medical and marine fields. The combined of increasing surface hardness through plasma nitriding and reducing friction through MoS2 coating represents a comprehensive solution to the inherent of Ti6Al4V alloys, such as high friction and wear. Meanwhile, the influence of the surface roughness and hardness of nitride substrate on the tribological properties are also investigated, aiming to extend the service life of the MoS2 coating. The results demonstrate that a relatively rough substrate helps retain lubricant and creates a strong and durable tribofilm, which is critical for extended performance. Although increasing hardness is beneficial to the anti-wear and load-bearing capacity of the Ti6Al4V alloy, an excessively hard substrate cannot prolong the lifetime of MoS2 coating. The sample with an appropriate subsurface hardness exhibits the better lifetime of the MoS2 coatings. It highlights the importance of a synergistic approach in surface engineering, especially for materials such as Ti6Al4V alloy, where each aspect plays a key role in the overall tribological behavior. Effective control of these factors can greatly improve the durability and efficiency of such alloys in harsh operating environments. In conclusion, the research suggests that duplex plasma nitriding and MoS2 coating treatment method offers an effective strategy for improving the performance of Ti6Al4V alloys, and optimizing the surface texture and mechanical properties of nitride Ti6Al4V can significantly enhance the service life of coatings. By solving the critical issues of alloy surface hardness, texture and lubrication, this approach marks a significant advance in applications where improving durability and reducing wear are critical.

11:40am MC1-1-MoM-6 Modern Analytical Methods for Characterizing Wear Surfaces and Subsurfaces, Thomas Scharf, The University of North Texas, USA.

It is now common to employ focused ion beam (FIB)-SEM and subsequent TEM characterization techniques to study site-specific deformation structures. In this talk, I will highlight more underutilized diffraction and imaging techniques, such as Precession Electron Diffraction (PED)-TEM, Transmission Kikuchi Diffraction (TKD)-SEM, as well as 3-D FIB serial sectioning to interrogate subsurface structural evolution during sliding wear. First, new insights into solid lubrication mechanisms in directed energy deposition (DED) metal matrix composites (Ni/TiC/graphite) reveal that the improved tribological behavior is due to the in-situ formation of a low interfacial shear strength amorphous carbon tribofilm that is extruded to the surface through refined Ni grain boundaries. 3-D FIB serial cross-sectioning inside the worn surfaces of these composites revealed that the tribological stresses in the subsurface extrude the graphitic, primary carbon towards the surface through intergranular separation of refined nanocrystalline Ni grains. Second, surface and subsurface structural evolution during sliding wear of an in situ nitrided DED titanium alloy, Ti-35Nb-7Zr-5Ta (TNZT), was studied by cross-sectional TEM coupled with PED. Corresponding precession-orientation imaging phase maps were used to determine the orientation and percentage of α and β-Ti in the worn nitrided TNZT. The maps revealed that the nanocrystalline grains of soft/compliant β are much smaller (10-100 nm) than hard/stiff α grains (>100 nm). Wear reduction is due to the combination of the above phases and increase in the alignment of (0002)-textured coarser α grains along the sliding direction with absence of texture in the highly refined β grains. Lastly, I will show how coupled cross-sectional TKD-SEM can interrogate the microstructural evolution in a Co-Cr alloy sliding on a Ta-W alloy.

Plasma and Vapor Deposition Processes Room Palm 5-6 Session PP6-MoM

Microfabrification Techniques with Lasers and Plasmas Moderators: Carles Corbella, George Washington University, USA, Valentina Dinca, National Institute for Laser, Plasma, and Radiation Physics, Romania

10:00am PP6-MoM-1 Laser Bipprinting: From the Breast Tumor Microenvironment to Migration in Wound Healing Assays, Doug Chrisey, Tulane University, USA.

Laser bioprinting can be additive (depositing cells) and subtractive (etching) and both have power to study the micro-physiological behavior of heterogeneous tissue constructs in vitro. The use of a UV laser in both these scenarios is shown to be very powerful and this presentation will show results over this wide range of applications. The most enriched cell types in the breast tumor microenvironment are cancer cells, cancer-associated fibroblasts, and tumor-associated macrophages. To recapitulate the cellular dynamics of the breast tumor microenvironment in vitro, the most abundant cell types need to be incorporated. Laser direct write bioprinting offers a precise, gentle, and reproducible method to print disparate cell types in user-defined geometries. Herein, we develop novel laser direct write cell printing protocols – first as a customizable generalized framework, which is then adapted to print homotypic and heterotypic cellular dynamics of the breast tumor microenvironment in vitro.
cancer-stromal arrays, and human macrophages. We demonstrate the ability to fabricate in vitro heterogeneous constructs for studying cell-cell signaling in healthy and diseased microenvironments, as well as the capability to print human immune cells with high fidelity to pave the way for bioprinting immunocompetent tissue models going forward. Traditional in vitro scratch assays lack standardization due to poor control over wound geometry and fail to account for cell proliferation. Here, we developed a novel scratch assay that enables precise control over wound geometry using CAD/CAM laser photoablation and takes cell proliferation into consideration using a simple reaction-diffusion based mathematical model. We demonstrated that diffusivity in precisely photoablated cell layers serves as a more accurate measure of cell motility than the rate of gap closure. Further, we biologically validated this assay using cells harvested from patients and patient-derived xenografts to gain insights into the influence of the presence stromal cells on metaplastic and non-metaplastic triple negative breast cancer metastasis.

10:40am PP6-MoM-3 Plasma-Assisted Nanofabrication of Advanced Nanoplasmonic Surfaces for SERS Applications, Uros Cvelbar, Jozef Stefan Institute, Slovenia

In the realm of plasmonic detection, pivotal for applications such as food and water quality monitoring, theranostics, and virus and toxin analysis, Surface Enhanced Raman Scattering (SERS) stands out as a powerful technique. Employing vibrational spectroscopy and surface nanoengineering, SERS leverages metallic nanoparticles to enhance signals through the confinement effect of the electromagnetic field, creating intense 'hot spots' near nanoscale metal surfaces. The morphology and arrangement of plasmonic nanomaterials crucially influence the formation of hot spot networks. This presentation focuses on our recent research in the plasma-assisted fabrication of advanced nanoplasmonic surfaces, showcasing nanocarbon structures, metal-oxide nanotrees, and coupled nanogold. Utilizing various plasma setups, including low-pressure and atmospheric pressure, we demonstrate their versatility, reliability, and fast, one-step processing. These surfaces excel in detecting cancerogenic toxins at ppb levels, ultrafast recognition of trace chemicals, and even bacterial DNA detection with nanogram sample amounts. The talk underscores the significant potential of plasma-assisted nanofabrication in advancing nanoplasmonic surfaces for a broad spectrum of analytical applications.

References:

11:20am PP6-MoM-5 New Designed PDMS Microtopography Using Laser Methods for Modulating in Vitro Cell Behaviour and Bacteria Growth, Valentina Dinca, INFLPR, Romania; C. Corbella, George Washington University, USA.

Nowadays, reducing complications after breast implant surgery, as well as enhancing implant integration and performance by modulating the foreign body response (FBR) still represents a fundamental challenge. Therefore, influencing FBR by tailoring the surface/interface physical characteristics of the material, independent of surface chemistry, can provide an important outcome in implantology. The present study reports new polydimethylsiloxane (PDMS)-based shell interfaces featuring honeycomb-like wells microtextures for modulating fibroblasts and immune cell function and hindering biofilm formation towards creating a pro-healing environment. These textures were achieved through replication on a large scale using molds obtained by an innovative laser-based 3D fabrication assisted by a grayscale mask process. The specifically designed honeycomb-sequestering wells topography altered the fibroblast adhesion, and collagen fibers alignment and reduced macrophages' inflammatory activity as compared to smooth substrates. Additionally, the microstructured surface was capable of hindering the macrophage fusion process after 7 days, and decreased the retention of Gram-positive and Gram-negative microbial strains. Overall, our results suggested that the structured PDMS surface led to an altered fibroblast's response and a reduced macrophages' inflammatory activity, turning the present study into a novel approach for obtaining an attenuated in vitro FBR response to silicone through the development of honeycomb-like topography prosthetic implant surfaces. One notable benefit of utilizing this design is achieving consistent features across large surface area, rather than relying on hazard patterns, which can significantly advance the understanding and controlling a wide range of cellular lineages behaviour towards topography in the field of implants.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-1-MoM
Coatings for Batteries and Hydrogen Applications I
Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, Chen-Hao Wang, National Taiwan University of Science and Technology, Taiwan.

10:00am TS1-1-MoM-1 New Coating Methods for New Electrolyzer Technologies for PEM Electrolyzer and AEM Electrolyzer, Thomas Kolbusch, Coetema, Germany

The author describes in his talk the scale up process for PEM electrolysers regarding coating technologies. The first part of the talk shows the need for
scale up in the green hydrogen market due to the huge amount of green hydrogen which has to be produced till 2030 and 2050 to reach net zero targets. For this industrial standardization of coating processes are needed as soon as possible. Here the upscale process of reproducible and reliable roll 2 roll equipment are shown and getting over the limiting factors like dimension instability of membrane materials and multi layer coating applications of rare materials like iridium.

The second part describes the boundaries of today's coating methods describing the parameters needed to be optimized. The background on one of the standard methods today, slot die coating is described here in detail with some theoretical background on slot die coating technology and an overview on developments for intermittent slot die coatings. The third part of the talk describes a new digital fabrication method for electrolyzers and shows the opportunity for the overall green hydrogen market using digital fabrication methods, reducing the carbon footprint of coating equipment for PEM electrolyzer.

10:40am TS1-1-MoM-3 Dual Doped Two-dimensional Carbon Supported Single Atomic Iron for Oxygen Reduction Reaction in Alkaline Exchange Membrane Fuel Cells. Afandi Yusuf, F. T. D. Wijaya, H. Hsin-Chih, C. Wang, National Taiwan University of Science and Technology, Taiwan

Single atom catalysts (SAC) represent an intriguing option due to their ability to unlock the latent catalytic potential in oxygen reduction reaction (ORR). Nevertheless, the endurance of individual atomic entities is confronted by numerous impediments, encompassing the dissolution of metallic species, metal agglomeration, and the deactivation of catalytically active sites. A crucial factor in enhancing stability lies in the judicious selection of a compatible support catalyst capable of fostering strong metal-support interaction (SMSI).

Carbon is widely utilized as a catalyst support material owing to its favorable electronic conductivity and the ability assume diverse dimensional configurations, ranging from 0D to 3D. Additionally, the carbon support facilitates additional customization, such as the introduction of Chalcogen or PtNi atom groups through doping, leading to enhanced catalytic activity.

In this work, we successfully fabricated a two-dimensional porous nanosheet electrocatalyst designed to enhance the Oxygen Reduction Reaction (ORR) in Anion-Exchange Membrane Fuel Cells (AEMFCs). This catalyst featured single atomic active sites of Iron supported by a Nitrogen-Phosphorus co-doped Carbon material, aimed at reducing catalyst cost and thereby increasing the accessibility of the fuel cell for commercial applications. The electrochemical performance of the material was exemplified by the MDP-4-Fe-800 sample, demonstrating an onset potential of 0.97 V, an L_{298} of 0.86 V, and a L_{298} of 5.5 mA/cm² under alkaline conditions, surpassing that of commercial Pt/C under the same conditions. Moreover, the material exhibited notable stability after 30,000 cycles, experiencing only a marginal 0.39 mA/cm² in L_{298} and 30 mV decrease in both onset and L_{298}. While MDP-4-Fe-800 did not outperform the single-cell performance of commercial Pt/C, it displayed commendable activity, generating a power density of 244.8 mW/cm².

11:00am TS1-1-MoM-4 Grazing Magnetron Sputtering of CuO-MoO₃ Electodes for Hydrogen Production. J. Castro, D. Cavaleiro, University of Coimbra, Portugal; M. Lima, University of Minho, Portugal; A. Cavaleiro, Sandra Carvalho, University of Coimbra, Portugal

The world energy grid faces a big issue in transit forward clean energy. Enlarging the possibilities to advance in cleaning the energy grid, humanity has made bids in several technologies, contemplating using Hydrogen as a clean drive. Reducing the carbon footprint through affordable and sustainable production has made bids in several technologies. For this industrial standardization of coating processes are needed as soon as possible.

Here the upscale process of reproducible and reliable roll 2 roll equipment are shown and getting over the limiting factors like dimension instability of membrane materials and multi layer coating applications of rare materials like iridium.

Electrolyte applications of rare materials like iridium.

11:20am TS1-1-MoM-5 Bimetal Phosphide (NiCoP)/Graphitic Carbon Nitride(g-C₃N₄) Composites for Hydrogen Evolution Reaction in Alkaline Electrolyte. Yu-Hsuan Kao, National Cheng Kung University, Taiwan; S. Wong, Southern Taiwan University of Science and Technology, Taiwan; J. Huang, National Cheng Kung University, Taiwan; Y. Shen, Hierarchical Green Material (HGM) Research Center, Taiwan

In order to address the growing energy crisis and environmental concerns, the development of hydrogen energy through electrochemical water splitting into hydrogen represents a viable solution. The hydrogen evolution reaction (HER) during water splitting is multi-electron transfer process that requires catalysts to proceed at appreciable rates. Noble metals have been widely used for water splitting due to their low Gibbs free energy; however, their high cost limits their availability and hinders commercialization. To address this challenge, we conducted a study on HER in alkaline electrolytes with the aim of developing highly efficient and durable electrocatalysts. The efficiency of HER in an alkaline environment is determined by a delicate balance among three crucial factors: the energy required to dissociate water molecules, hydrogen adsorption (θH), and the prevention of hydrogen adsorption (θH₂), often referred to as the poisoning of active sites.

Graphitic carbon nitride (g-C₃N₄) has been extensively studied due to its two-dimensional layered structure and high nitrogen content. However, its poor conductivity limits its application in the field of HER. Therefore, we modified transition metal phosphide on g-C₃N₄ to enhance its conductivity and increase the number of active sites. Additionally, it has been mentioned in previous studies that nickel and cobalt atoms can promote the reaction kinetics of HER in the first and second steps, respectively, thus improving the efficiency of HER in an alkaline electrolyte. Therefore, we synthesized NiCoP/g-C₃N₄ composites in different weight percent to replace the platinum electrode in a 1.0 M KOH electrolyte.

We used Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM) to determine the structure of NiCoP/g-C₃N₄. In addition, Linear Sweep Voltammetry (LSV) and Tafel slope were employed to confirm the electrochemical performance of NiCoP/g-C₃N₄. In HER. The results demonstrate that we successfully synthesized g-C₃N₄ and NiCoP/g-C₃N₄ electrocatalysts using a wet chemical method and calcination. Furthermore, the electrochemical results indicate that the addition of 10 wt% NiCoP to g-C₃N₄ significantly improves and exhibits excellent performance in HER in an alkaline electrolyte, reducing the overpotential from 560.7 mV to 338.9 mV and decreasing the Tafel slope from 197.2 mV/dec to 89.6 mV/dec. Then we will use in-situ TEM and in-situ Raman analysis to confirm the contribution and role of the NiCoP alloy on g-C₃N₄ in the hydrogen evolution reaction.

11:40am TS1-1-MoM-6 Hybrid Inorganic-Organic Nanolayered Thin Films Based on Zns-Ethylenediamine for the Photocatalytic Production of Hydrogen. L. Cerezo, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México; K. Valencia, Instituto de Ingeniería, Universidad Nacional Autónoma de México; M. Bizarro, Sandra E. Rodil, A. Hernández-Gordillo, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

Hybrid ZnS-ethylenediamine nanomaterials (ZnS(en))₂ were produced in a mixed solvent of water, butanol, and ethylenediamine by solvothermal and precipitation methods. The effect of different molar ratios ZnO/Zn²⁺ between 15 and 91 have been investigated by diverse techniques; TG-DSC analysis, X-ray Diffraction, Scanning Electron Microscopy, Infrared, and Diffuse Reflectance spectroscopy. The material was then exfoliated using a combined sonication-illumination process to obtain stacked 2D ZnS nanolayers intercalated with the organic material. After optimization, the as-prepared and exfoliated ZnS(en)₂ nanosheets were prepared as films by spin coating to evaluate the photocatalytic H₂ production reaction. The H₂ evolution reaction was performed in a homemade cell that has water containing 30 mL of ethanol-water solution (50:50 vol. %). Eight films were fixed around the internal walls of the glass reactor. The solution was magnetically stirred (at 600 rpm), irradiated with UV light provided by a 6 W lamp Pen-ray of (λ>254 nm and I₀ = 4.4 mW/cm²), and placed in the center
of the solution into the quartz tube. The system was bubbled with N₂ (to reduce the O₂ pressure), then it was sealed, and the lamp was turned on. The quantity of H₂ was measured using a Shimadzu GC-2014 gas chromatograph and N₂ as the carrier gas. The photocatalytic activity of all the as-prepared and sonicated-irradiated ZnS(en)₀.₅ samples was evaluated by 6 h and 6 cycles. The results showed an enhancement of 7 to 22 times in the H₂ production rate as a function of the synthesis and exfoliation conditions. Intrinsic hydrogen evolution rates up to 76 mmolg⁻¹h⁻¹ were achieved using the optimized exfoliated ZnS(en)₀.₅ hybrid material. This value constitutes a record in the community, which is more significant when the lamp's low power is considered. The increased photoactivity was correlated to the degree of exfoliation and the number of stacked ZnS layers in the structure.

12:00pm  TS1-1-MoM-7  CO₂ Laser Processed Nickel Catalyzed Graphene Coating for Electrocatalytic Water Splitting and Energy Storage Applications, Suparna Saha, TCG CREST (RISE), India; S. Hiwase, IISER PUNE, India; S. Ogale, IISER PUNE, TCG-CREST(RISE), India

Development of efficient, cost-effective, and environmentally friendly processes for the realization of high-quality graphene on metallic substrates is highly desirable for multiple energy applications as well as next-generation graphene-based green electronics. Several polymers including those derived from natural sources represent a rich source of carbons that can be converted into graphitic carbons by energy inputs in different forms. Lasers represent a form of energy input that is direct-write type and does not need the whole substrate to be heated at high temperatures for carbonization. Herein, we examine carbonization of natural product-derived polymer(s) into graphite (few layers graphene) carbon using CO₂ laser-assisted direct-write process. Such a process is generally termed as Laser-Induced Graphene (LIG). In particular, we demonstrate the key and interesting role played by nickel in enhancing the degree of graphitization (Ni-LIG). Indeed, the unique advantage of this nickel-catalyzed scanning laser-induced transient pyrolysis process implemented under ambient conditions is that we are able to uniformly graphitize the thermoset polymer coating that would otherwise yield hard carbons or a mixture of ordered/disordered carbon in a furnace-based pyrolysis process. It was observed that upon optimized laser processing condition, the Ni-(CH₃COO)₃·₄H₂O salt added to the polymer gets reduced to Ni (111), which in turn catalyzes the nucleation process. We note the appearance of disordered carbon chains initially, which upon interacting precisely with the nickel surface lowers the activation barrier for graphene formation by annealing the defects. Moreover, due to the very low lattice mismatch between Ni (111) and graphene, a strong interphase is formed, facilitating efficient contact and charge transfer. As the surface coating is decorated with a mixture of Ni/NiO (as confirmed by XRD and XPS), water dissociation as well as adsorption of water oxidation intermediates is promoted, leading to an impressive value of overpotential for oxygen evolution reaction (OER) at 10 mA/cm² of only 330 mV in 1M KOH. We also examined the case of urea-incorporated material to induce N-doping so as to enhance the conductivity via the incorporation of the π-conjugated system. However, the incorporated pyrrolic N defects in the carbon layer were noted to hinder the nucleation of graphitization at the Ni atom, resulting in a low I₅/I₀ ratio. This material was therefore studied for charge storage property by cyclic voltammetry and galvanostatic charge-discharge (GC) measurement. It was found that N-doped N-Ni-LIG has a higher specific capacitance compared to Ni-LIG.
Keynote Lectures
Room Town & Country A - Session KYL1-MoA

Keynote Lecture I
Moderator: Johanna Rosen, Linköping University, Sweden

1:00pm KYL1-MoA-1 Engineered Functional Coatings for Clean Energy and Sustainability Applications, Satishchandra Ogale, Research Institute for Sustainable Energy, TCG- Crest, Indian Institute of Science Education and Research, India INVITED

Functional coatings are key to all clean energy applications including energy harvesting, storage and conservation, and by implication to the emergent issues in the domain of sustainability. Coatings enable intelligent decoupling and independent manipulation of surface and bulk properties; as such, they can allow synergistic integration of various phenomena operating in energy devices on different length scales. This includes management and control of electrical, mechanical, optical, thermal and other properties of interest to realize a desired optimum performance. In this talk, I will outline this scenario by taking examples of recent research in the fields of Batteries, photo/electro-catalysis for clean fuels, hybrid perovskite solar cells, and triboelectric nanogenerators. I will also briefly discuss the scaling up issues of the employed experimental coating methods of interest to industry.
Monday Afternoon, May 20, 2024

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

Room Palm 3-4 - Session CM2-1-MoA

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

Moderators: Thomas Edwards, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, Olivier Pierron, Georgia Institute of Technology, USA

1:40pm CM2-1-MoA-1 Micromechanics During Hydrogen Charging and the Study of Hydrogen Barrier Coatings, Maria Jazmin Duarte, H. Gopalan, J. Rao, C. Scheu, G. Dehm, Max-Planck Institut für Eisenforschung GmbH, Germany

Understanding the effects of hydrogen in materials became a pressing topic with the imminent shift towards green technologies, and the use of hydrogen as energy carrier. It is expected that the use of hydrogen will increase in all industries, together with the need for safe transport and storage and consequently the development of new materials and technologies to cope with it. A critical challenge is hydrogen-induced damage, or hydrogen embrittlement, that can cause the sudden failure materials. Hydrogen barrier coatings represent, in this regard, an appealing option to prevent and/or slow down the hydrogen ingress into structural alloys that are susceptible to embrittlement.

To characterize hydrogen and its effects in materials, at the relevant small-scale dimensions where embrittlement initiates, is a substantial yet demanding task. Current studies on hydrogen effects are in their majority limited to post-mortem probes and ex-situ charging, which neglect diffusible hydrogen, its migration and desorption at the analysis time. To rise above these constraints, we designed a novel “back-side” charging approach, to perform micromechanical testing during hydrogen charging [1]. Hydrogen is generated electrochemically at the back-side and diffuses towards the testing (front-side) surface. This unique method allows differentiating between the effects of trapped and mobile hydrogen, and performing well controlled measurements with different hydrogen levels monitored over time to consider hydrogen absorption, diffusion and release.

Using this new method, we unraveled dynamic effects of hydrogen on the mechanical properties of bulk alloys [2], and recently, we successfully applied it to study of hydrogen barrier coatings [3,4]. In this talk, I will present an overview of the technique, together with the case study of an Al2O3 hydrogen barrier coating. The hydrogen diffusion on Al2O3 ~9 orders of magnitude slower with respect to the used substrate, was measured by Kelvin probe. The mechanical stability of the coating was tested by nanoindentation and nanoscratching during hydrogen loading. The accumulation of hydrogen at the substrate-coating interface reduces the critical load required for cracking and leads to local delamination. Mechanical tests were complemented by atom probe tomography, confirming the presence of hydrogen close to the substrate/coating interface, and transmission electron microscopy, revealing the underlying microstructural changes.


2:20pm CM2-1-MoA-3 The Micromechanical Behavior of Magnetron Sputtered TiN/Nb Multilayers, S. Kagerer, N. Koutnd, Institute of Materials Science and Technology, TU Wien, Austria; L. Zauner, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; T. Wójcik, Institute of Materials Science and Technology, TU Wien, Austria; G. Habler, Department of Lithospheric Research, University of Vienna, Austria; P. Polcik, S. Koloszvari, Plansee Composite Materials GmbH, Germany; O. Hunold, Oerlikon Surface Solutions AG, Liechtenstein; H. Riedt, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; P. Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria; Rainer Hahn, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Damage tolerance is a prerequisite for using protective coatings in components subject to long-term stress. Physical Vapor Deposition offers possibilities in coating architectures using combinations of ductile and hard materials, even on the nm scale. However, ductility through dislocation motion is often suppressed on the micro-scale due to geometric limitations, resulting in unusually brittle behavior. In this work, we show a linear dependence between the necessary shear stress for dislocation motion in Nb layers and the overall plastic behavior of micropillar samples.

Computational pre-screening identifies fcc-TiN/bcc-Nb as a promising system providing stable, sharp, and strong interfaces with essentially different elastic moduli. Using a TiN compound target enables a sharp interface without nitrogen cross-contamination. Layer variation and changing the TiN to Nb ratio offer insights into the small-scale plastic behavior using the micropillar compression test. These show a fluent transition from ductile deformation for thick Nb layers to a brittle behavior similar to monolithic TiN upon decreasing the Nb layer thickness.

Combining micromechanical data with TEM analysis of fractured micropillars, we correlate these observations with increased stresses necessary for dislocation motion within the confined layer slip model. Furthermore, we will show the results of unique experiments combining micromechanics with synchrotron nanodiffraction to understand the stress situation in a pillar and describe deformation mechanisms.

2:40pm CM2-1-MoA-4 Deformation Behaviour and Plasticity in FCC-BCC High Entropy Alloy Nanolaminate Structures, S. Tsiankas, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; C. Tian, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; C. Guerra, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

In recent years, metal multilayer composites have been the focus of research due to their exceptional mechanical properties. Recent experimental [1-3], theoretical, and modeling [4] studies on multilayers have indicated that the enhancement of both strength and ductility is related both to the structure and properties of the interfaces between the layers, as well as the thicknesses and properties of the individual layers [5]. In spite of the ample literature available on pure metallic nanolaminate structures, the experimental data on compositionally complex alloy multilayers is rather missing.

In this context, here we present recent experimental data on the fabrication and mechanical behavior of nanolaminate FCC-BCC high entropy alloy thin films with interlayer thicknesses 50 nm. The alternating FCC-BCC layers are separated by atomic layer deposition of 2 nm amorphous Al2O3 layer without breaking the vacuum in a new Cluster System combining both ALD and PVD in the same equipment (Swiss Cluster AG). As a model system, FCC-NiCoCrFe and BCC-NiCoCrFe-Al (with Al ~10 at. %) layers with a total thickness of 3 microns is deposited on Si (100) substrate by magnetron sputtering and subsequently tested by micro compression and nanoindentation experiments. The mechanical response of the multi-layered structures is also compared with FCC-BCC multilayer without ALD and single-layer FCC and BCC counterparts. The uniformity in composition and microstructure of interlayers is confirmed by performing S/TEM imaging along the cross-sectional samples prepared by FIB using a standard liftout procedure. The microcompression experimental results on micropillars provide clear evidence of interfaces and interlayer size effect on the mechanical response of nanolaminate at different strain rates. The post-mortem electron microscopy investigation provides insight into deformation mechanisms and deformation-induced phase transformations in the individual layers. This first study on multilayer film of two HEA’s will help fundamental studies on high entropy alloys and transformative to other complex systems.

and wear rate was lowest for PCHT specimen as hBN plays a vital role in reducing friction. The wear mechanism at room temperature was found to be abrasive wear, in contrast to oxidation wear at high temperature.

**Surface Engineering - Applied Research and Industrial Applications**

**Room Town & Country C - Session IA1-MoA**

**Advances in Application Driven Research and Hybrid Systems, Processes and Coatings**

**Moderators:** Ladislav Bardos, Uppsala University, Sweden, Vikram Bedekar, Timken Company, USA, Hana Barankova, Uppsala University, Sweden

1.40pm IA1-MoA-1 PVD Thin Film Coating Materials in Semiconductors and Impact of CHIPS Act, Shlok Sundaresh, Tosoh SMD, Inc., USA INVITED

The CHIPS and Science Act in the United States has led to significant investments in domestic semiconductor manufacturing recently. It details the importance of building a resilient domestic supply chain with funding emphasis on construction, expansion, or modernization of commercial facilities. Semiconductor manufacturing involves numerous processing steps and one of those critical steps is thin film deposition of materials on wafers to form various patterns using PVD technology. Continued pursuit of Moore’s law warrants advances in technology, and materials innovation plays a key role for achieving this. PVD sputtering target material developments are extremely critical for the performance of semiconductors as these are used as consumable sources for building them. The CHIPS Act has recognized this providing specific examples of PVD sputtering targets. The talk will thus focus on advances in manufacturing of key materials for sputtering these thin films in semiconductors along with the potential boost from the CHIPS Act towards this technology.

1.40pm IA1-MoA-3 Production and Characterization of Coating-Substrate Combinations for Ceramic Data Storage Media, Erwin Peck, TU Wien, Institute of Materials Science and Technology, Austria; B. Hajas, TU Wien, Austria; A. Kirnbauer, L. Kreuziger, TU Wien, Institute of Materials Science and Technology, Austria; C. Pfirum, Ceramic data solutions holding GmbH, Germany; G. Liedl, TU Wien, Austria; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Nowadays data storage and its sustainability is a topic of great importance, not only for cloud providers but also for other companies and even for people in their personal lives. Most of the data stored is referred to as cold data, meaning it is rarely changed and accessed (e.g. photos, research results). That cold data must be stored, in order to do that, cloud providers run server farms utilizing hard drive discs (HDD). In that way they make the data available on the users’ demand. Those server farms need a lot of energy, and the storage capacity is limited. To overcome the issue of needed energy and limited capacity, a new form of storage media is in the focus of our research. By utilizing a certain coating-substrate combination, it is possible to write data into ceramic data carriers using a femtosecond laser. By applying this method, it is possible to write a large amount (1.25 Gigabyte) of data onto a relatively small area (100 cm²) of the ceramic data carrier. Within our research we analyzed different coating-substrate combinations regarding their mechanical properties and laser ablation characteristics. The coatings investigated were synthesized by magnetron sputtering and argon nitrogen gas mixture using different composite targets e.g. Ti, Cr, TiAlCr, and AlCrNbTaTi. The coatings were deposited on different substrates including sapphire, silicon, glass, and austenitic steel. All the coatings were investigated by XRD showing a single-phase fcc-structure and hardness values ranging from 21 to 33 GPa. After investigating structure and mechanical properties, laser ablation tests were conducted to determine the laser ablation threshold and to find suitable coating-substrate combinations for the aimed application. Furthermore, after writing data into the samples, the samples were tested for their thermal stability, cross-section resistance, and corrosion resistance. These studies prove the exceptional stability and durability of such ceramic data storage media. Once written, storing the data is almost without any energy consumption and such ceramic data carriers would allow to save 99% of the currently used energy for storing such data.
Monday Afternoon, May 20, 2024

have caught extreme due to their interesting structure of alternating two- 
edge shared octahedral layers of TiC and highly porous accordion-like 
structure [1-2]. MXene shows work-function tunability, porosity variations 
and varied surface-chemistry interplay, as a function of different synthesis 
processes [3]. Sensors, Schottky diodes, energy harvesters, and storage 
deVICES are envisaged from these materials [4].

Removal of Al layers using hydrofluoric acid (HF) is one common approach 
to convert MAXene to MXene and create porous structures and active 
surface states between the inter-digitated octahedra structures. On the other 
hand, along with various other physical processes, pulsed laser deposition 
(PLD) system yields a range of thin films from stoichiometric high-quality 
thin films to defect-engineered films.

This talk will explore three different studies: i) bulk studies on the HF- 
etched-TiAlC, yielding a tuneable work-function system, as a function of 
acid concentration [3] ii) thin films of Carbon-deficient TiAlC using PLD 
showing semiconducting behaviour on n-Si substrate [4]; and iii) bulk 
chemical treatment of MXene- molybdenum oxide (MoO3) [5] 
nanocomposites to form a mutually synergistic system for gas (NH3) sensing 
at room temperature. TiAlC2 material show p-type behavior; when 
deposited on n-Si or Alumina substrate, with strained growth depending 
upon the substrate; with different termination groups and morphological 
differences. Chemically synthesized MoO3-MXenenanocomposites evolve as 
a synergistic system with improved room-temperature sensing sensitivity of 
MoO3 along with a stable, yet highly reactive -O,-OH and -F sites of MXene 
surface. These studies are further explored for wide range of device 
applications.

References
4295, 2022.

3:20pm IA1-MoA-6 Decorative Coatings in Watch Making Industry: From 
Laboratory to Industry, Joel Mattey, Positive Coating SA, Switzerland; O. 
Banakh, Haute Ecole Arc Ingenierie, Switzerland; L. Steinmann, Positive 
Coating SA, Switzerland

Discovered in the late 1960’s, the atomic layer deposition (ALD) is 
nowadays an established and widespread technology implemented in the 
industry. Despite being still predominantly applied to semiconductor 
deVICES, ALD has recently found its path into new sectors. One of them is 
the watchmaking niche market where design and reliability play a major 
role in luxury products. Due to its unique features, ALD offers attractive 
decorative coatings on complex components and brings innovation in terms 
of corrosion barrier. It is especially valid when combining the benefits of 
ALD with other technologies such as magnetron sputtering or 
electroplating. The aim of this presentation is recounting the extremely fast 
technology transfer of ALD from laboratory experiments to industrial scale 
processes. Through results and achievements, the fruitful collaboration 
between the University of Applied Sciences (HE-ARC) and Positive Coating 
SA is presented. Throughout the manufacturing sequence, the demanding 
requirements to obtain high-quality decorative coatings are discussed. 
When operating ALD technology to color tridimensional parts, simulated 
and experimental results show that fluidics regularly prevails over ALD 
process parameters. Furthermore, innovative processes using ALD as a 
substrate for obsolete technologies are addressed: namely red-gold anti- 
tarnishing, brass corrosion protection, and two-colored process without 
masking. Despite successful accomplishments, the technical and industrial 
challenges to tackle in the coming years are listed to evolve the ALD 
technology from the semiconductor to the decorative world. The 
conclusion is illustrated by specimens of luxury watches where decorative 
coatings highlight superb designs.

4:00pm IA1-MoA-8 Real-Time Particle Detection for Enhanced Coating 
Deposition Processes, Sylvain LeCoultre, C. Rieiller, Berner Fachhochschule 
ALPS, Switzerland

INVITED

Coatings and the associated vacuum deposition processes will play an 
increasingly significant role in upcoming technological trends, particularly in 
the fields of photonics, optics, and Industry 4.0. However, the demands for 
these applications are imposing increasingly stringent requirements in 
terms of defect size and particle inclusions within functional layers. This is 
primarily attributed to the ongoing reduction in the size of device 
structures. Particles ranging in size from a few hundred nanometers to a 
few microns have proven to be a major challenge during various deposition 
processes. These minuscule particles often lead to component failures, 
resulting in unacceptably high rejection rates. Therefore, the development 
of deposition technologies capable of monitoring and significantly reducing 
the incorporation of particles into coatings is essential to access and 
succeed in these emerging markets.

As part of a multi-partner research project, we are focusing on the 
development of methods for the detection and real-time monitoring of 
particles generated in physical vapor deposition (PVD) processes, with 
particular emphasis on electron beam deposition and sputtering systems. 
Our research objectives include understanding the different sources of 
particle generation, whether related to the process, mechanical 
movements or the cleanliness of the deposition reactor during a production 
campaign. It also involves determining their size distribution and tracking 
their velocity in the vacuum environment with spatial and temporal 
resolution. In addition, we aim to contribute to the development of 
applicable strategies for eliminating particle sources during the vacuum 
deposition process, thereby increasing production yields.

To achieve these goals, we are engaged in the research and development of 
an in situ particle detector solution based on the fundamental principles of 
visible light beam scattering by particles. The chosen method will be 
compared with other possible particle detection methods suitable for high 
vacuum environment. First results on particle detection during different 
phases of a deposition batch will be presented. In addition, a first insight 
into the development of a data analysis algorithm that could enable 
informed decisions to be made for the maintenance of parts to be changed 
will be discussed.

4:40pm IA1-MoA-10 Microscopic Characterization of Optical Properties 
and Film Thickness Using Imaging Spectroscopic Ellipsometry, Hanaul 
Noh, Park Systems, USA

Ellipsometry is a well-known, non-destructive optical method to measure a 
thin film’s thickness and optical properties. It has been widely used to 
characterize the complex refractive indices of materials or to control the 
quality of a film’s thickness in manufacturing processes. Demands on 
microscopic characterizations of optical properties have been greatly 
increased for new materials and structures such as 2D materials, photonic 
deVICES, to name a few. Conventional ellipsometry, however, has been 
restricted to a spatial resolution of several tens of microns due to the spot 
size limitation. Here, we introduce imaging spectroscopic ellipsometry (ISE), 
which enables 1-micron lateral resolution, and its application to novel 
materials and structures. The ISE technique can be extensively used for new 
materials research and quality control of industrial applications.

5:00pm IA1-MoA-11 Plasma PVD by Small Spiral Ta Hollow Cathode, H. 
Baránková, N. Suntornwipat, Ladislav Bardos, Uppsala University, Angstrom 
Laboratory, Sweden

Small spiral hollow cathodes represent interesting options for local plasma 
processing applications. The radio frequency powered small diameter spiral 
hollow cathodes made from 0.45 mm diameter Ta wire rolled around 0.5 
mm diameter rod have been tested in coatings by physical vapor deposition 
PVD on silicon substrates at gas pressure of 3 Torr. Both the reactive PVD of 
TaN in pure nitrogen and Ta in pure argon resulted in similar rates of 
development of methods for the detection and real-time monitoring of 
particles generated in physical vapor deposition (PVD) processes, processes 
with particular emphasis on electron beam deposition and sputtering systems. 
Our research objectives include understanding the different sources of 
particle generation, whether related to the process, mechanical 
movements or the cleanliness of the deposition reactor during a production 
campaign. It also involves determining their size distribution and tracking 
their velocity in the vacuum environment with spatial and temporal 
resolution. In addition, we aim to contribute to the development of 
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vacuum environment. First results on particle detection during different 
phases of a deposition batch will be presented. In addition, a first insight 
into the development of a data analysis algorithm that could enable 
informed decisions to be made for the maintenance of parts to be changed 
will be discussed.

5:20pm IA1-MoA-12 Improvement of Surface Adhesion of Fluoropolymer 
Using Linear Ion Beam Source, Sunghoon Jung, J. Yang, E. Byeon, D. Kim, S. 
Lee, J. Park, Korea Institute of Materials Science, Republic of Korea

Fluoropolymers, known for their excellent chemical and thermal resistances 
and low dielectric constants, play a pivotal role across diverse sectors. The 
inherent low surface energy of fluoropolymers, however, presents a notable 
challenge in terms of compatibility with other materials. Traditional
methods to integrate fluoropolymers with different substances have largely relied on sodium-based chemical etching. These methods, while effective, often compromise the surface smoothness and are not environmentally sustainable.

In this study, we propose an innovative technique for the surface enhancement of fluoropolymers utilizing a linear ion beam source. By meticulously adjusting the ion beam process parameters, we have developed fluoropolymer bases with significantly improved hydrophilic characteristics. Additionally, this advanced technology has successfully increased the adhesive strength between fluoropolymer surfaces and the copper layers in flexible copper-clad laminates. The adoption of this novel surface modification method holds immense potential, especially in fabricating components for next-generation 6G mobile communication technologies, where strong and reliable adhesion is critically important.

Protective and High-temperature Coatings
Room Palm 5-6 - Session MA2-1-MoA
Thermal and Environmental Barrier Coatings
Moderators: Sabine Faulhaber, University of California, San Diego, USA, Pantcho Stoyanov, Concordia University, Canada

1:40pm MA2-1-MoA-1 Oxygen Permeability, Degradation and Failure Analysis Formulated by Artificial Intelligence of Environmental Barrier Coatings under Adverse Environments, Kueilng Chen, National Research Council of Canada; K. Lee, NASA Glenn Research Center, USA

Environmental barrier coatings (EBCs) are typically used to protect ceramic matrix composites (CMCs) under harsh environmental attack such as water vapor-induced recession in aero-engines. Under adverse operations, the oxygen permeability of EBCs is sensitive to temperatures. The adoption of this novel surface modification method holds immense potential, especially in fabricating components for next-generation 6G mobile communication technologies, where strong and reliable adhesion is critically important.

Thermal barrier coatings (TBCs) have significant effects on the three primary heat transfer mechanisms, namely convection, conduction and radiation. Considerable efforts have been deployed over the past years to ensure that TBCs possess low thermal conductivity, however, the radiative component has been comparatively largely ignored mainly due to the complexity of the assessment techniques.

This research aims to understand and quantify the impact of high-performance TBCs on the heat management in engine combustion chamber. To accomplish this, a laboratory-scale combustion chamber rig, equipped with a kerosene burner, has been designed and built to mimic aircraft engine conditions. The burner has a tunable power level and can be operated under various flame equivalence ratios, ranging from fuel-lean to rich conditions. Multiple diagnostic tools have been integrated such as thermocouples, heat flux gauges and a multispectral IR camera. A novel approach to solve for emissivity and temperature at high temperatures (> 900°C) using IR imaging was developed, accounting for the multiple reflections inside the combustion chamber and apparent emissivity of a surface in an enclosed cavity. TBCs with different porosities were compared under 5 flame conditions, and an evaluation of the CMAS (calcium-magnesium-alumina-silicate) infiltration inside the pores and its impact on the performance of the TBCs in the combustion chamber was studied. We show and quantify how higher porosity in a TBC leads to a lower temperature on the substrate and how CMAS infiltration increases the temperature locally on the contaminated surface.

Key words:
Thermal barrier coatings (TBC), high temperature, IR imaging, heat transfer, kerosene burner, CMAS


Higher engine operating temperatures will increase the efficiency of gas turbines, saving fuel and reducing CO₂ emissions. However, it is challenging to develop TBC systems with required low thermal conductivity and high resistance to CMAS attack while maintaining or improving their resistance to high temperature impact and erosion. To speed up TBC development a high efficiency impact / erosion test method providing rapid data with small volumes of material is needed.

A novel nano-/micro-mechanical test technique has been developed to experimentally simulate the stochastic nature of the repetitive particulate impacts that occur in high temperature erosion by performing multiple impacts at different locations on the TBC surface [1]. In the randomised impact test, a specified number of individual impacts occur with defined energy and chosen statistical distribution within a set area. Analysis of instantaneous depth vs. time data from every impact shows how residual depth, coefficient of restitution and kinetic energy loss all vary throughout the test to provide evidence of changing damage mechanisms.

Single impacts, repetitive impact and randomised impact tests have been performed at room temperature on EB-PVD 7YSZ and Gadolinium Zirconate coating systems deposited on aluminised Nimonic 75 alloy coupons. Differences in erosion rate and some erosion mechanisms were well replicated in the shorter impact tests compared with erosion test data [2].

The experimental capability has recently been extended to higher temperatures. Tests were performed at 500 °C and 825 °C on the 7YSZ coating with a ~25 μm radius diamond indenter so that each impact only affected a few columns. The depth on initial impact increased with temperature locally on the contaminated surface. The kinetic behavior of erosion and its effect on life span in EBC are calculated based on the erosion rate obtained from the mechanics-based model.

A non-destructive technique based on convolution neural network (CNN) in deep learning is used to evaluate crack evolution in EBCs. The candidate crack region of interest (ROI) was identified by using Visual Geometry Group Network (VGG) as baseline network, and CNN detector was then used to refine the candidate regions which provide a comprehensive feature for better crack detection. With the information on crack evolution, a fusion lifetime prediction model was used to estimate the remaining lifetime of EBCs system. The performance of the used model on remaining life span was examined.

2:20pm MA2-1-MoA-5 Effect of Thermal Barrier Coatings on the Thermal Management of a Jet Engine Combustion Chamber, Rodrigue Beaini, Polytechnique Montréal, Canada

The aircraft engine industry depends extensively on the advancement of high-performance materials and protective coating systems to enable a continuous ascent in engine performance requirements. In this context, thermal barrier coatings (TBCs) play a key role by providing a protective layer between the hot gases generated by combustion and the underlying metallic components. This allows higher operating temperatures and pressures which results in higher engine efficiency, lower fuel consumption and reduced environmental impact.

For comparison repetitive impact tests were also performed on a bulk glass (fused silica) at 25, 250, 400, 650 and 825 °C. At higher temperature there was reduced cracking in the multiple impact tests. This was balanced by a gradual softening over the temperature range with the result that the maximum impact depths were found at intermediate temperatures.

Environmental barrier coatings (EBCs) have enabled the implementation of SiC/SiC ceramic matrix composites (CMCs) in gas turbines by protecting CMCs from H2O. Improving the reliability of CMC components requires long-life EBCs and accurate EBC-lifting. Steam oxidation-induced failure is one of the most critical EBC failure modes. NASA has developed modified Si / Yb3Si5O12 EBCs by adding dopants such as Al2O3, mullite, and/or V4O7 (Y2Al4O13) in the Yb3Si5O12 topcoat, which reduce the parabolic oxidation rates by more than ten folds in steam. Modified EBCs have shown that oxidation kinetics are highly sensitive to the chemistry of SiOx oxide scale, which in turn is influenced by the chemistry of EBC and CMC. Plasma-sprayed silicate coatings contain a large amount of amorphous phase due to the rapid quenching of molten droplets during the coating formation. Annealing is often employed to stabilize the EBC phase by crystallizing the amorphous phase prior to oxidation testing. Our study has shown that the effects of annealing on oxidation kinetics are influenced by the EBC chemistry. The current understanding of the complex relationship between selected EBC variables (EBC chemistry, CMC chemistry and annealing condition) and the EBC oxidation behavior will be discussed. Various analytical techniques such as scanning electron microscopy, x-ray diffraclorometry and transmission electron microscopy are used to help understand the relationship.

A clean and easy to characterize cross-section has been automatically prepared by the CleanMill BIB, without user intervention. Combined and always-on SEM/EDS information, automatically delivered by ChemiSEM, has highlighted cracks, oxidation, interfaces, interphases and chemical variations within the various layers. With AI-assisted IA, as long as the specimen preparation is respectful of the sample integrity, researchers can now boost their CM efficiency level.

We illustrate the synergy between CM and AI-assisted IA by treating the example of a Thermal Barrier Coating (TBC) designed as an afterburner liner of a turboramjet engine.

The effect of the B content on the structure, chemical bond character and hardness of Si–B–C–N coatings was systematically studied. The coatings fabrication process included the deposition of an Ti interlayer at a temperature of 400 °C to promote adhesion. Subsequently, Si–B–C–N coatings were prepared by high-power pulsed magnetron and rf magnetron co-sputtering from SiC and B4C targets in Ar + N2 gas mixtures. Specifically, we studied the oxidation behavior of the coatings and the evolution of the microstructure, composition, and mechanical properties upon an isothermal oxidation test performed in 15 ppm O2/Ar at 650°C. We found that an optimized Si2B3C5N15 (at.%) coatings protected the 6wt% Co-WC substrate against oxidation. Stable amorphous structure of Si–B–C–N coatings hindered inward oxidation of O.

Yet, the use of Deep-Learning (DL) as part of this process still requires setting up a meaningful ground truth, using a “human-in-the-loop” AI-assisted training steps to speed up time-to-results.

Monday Afternoon, May 20, 2024

4:20pm MA2-1-MoA-9 Characterization of SiO2 Thermally Grown Oxide Kinetics and Stress Evolution of EBCs with Al-Containing Dopants, Michael Lance, M. Ridley, B. Pint, Oak Ridge National Laboratory, USA

SiC ceramic matrix composites (CMCs) are desirable for use in combustion environments to achieve higher turbine operating temperatures, although CMCs require environmental barrier coatings (EBCs) for protection from the gas environment. EBC systems are known to primarily fail through coating delamination via growth of a thermally grown oxide (TGO) at the EBC – silicon bond coat interface especially when exposed to steam, which accelerates the TGO growth rate. The TGO undergoes a phase transformation during thermal cycling, which results in stresses that may encourage EBC spallation. Yb-silicate EBCs with mullite and yttrium aluminum garnet (YAG) dopant additions were deposited on SiC substrates with a Si intermediate bond coating and exposed to thermal cycling in flowing steam. The impact of Al dopant additions on the TGO growth rate and the impact of the SiO2 phase transformation were assessed. Photo-stimulated luminescence spectroscopy (PSLS) was used to characterize the Al-containing phases and to measure stress evolution in the EBC following exposure using the stress-induced peak shift of the R-lines of mullite and YAG. Raman microscopy was used to map the Yb-silicate phases in the EBC and the SiO2 phases in the TGO following exposure. Wavelength dispersive x-ray spectroscopy (WDS) tracked the concentration of Al in the EBC and the TGO with exposure time. This research was funded by the Advanced Turbine Program, Office of Fossil Energy and Carbon Management, U.S. Department of Energy.

Monday Afternoon, May 20, 2024

4:40pm MA2-1-MoA-10 Deposition and Characterization of Si–B–C–N Coatings by HiPIMS/RFMS Co-sputtering, L. Chang, Department of Materials Engineering, Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan; Yun-Rui Zhang, Department of Materials Engineering, Ming Chi University of Technology, Taiwan; Y. Chiang, International PhD Program in Plasma and Thin Film Technology Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan; C. Huang, Y. Zhang, B. Jiang, Department of Materials Engineering, Ming Chi University of Technology, Taiwan; W. Chen, Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan

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To be closer to reality, pharmaceutical type I glass vials that have been successfully coated with SiOxNyCz thin layer, were tested according to the severe screening conditions of the United States Pharmacopeia USP<1660> chapter. They withstood to the test by preventing the degradation of the glass matrix with an average improvement factor of about 95% compared to a bare vial.

This excellent performance can make these materials a real key for the future of the pharmaceutical industry and can be transferable to multiple applications of surface coating by adaptation of the deposition conditions.

**Protective and High-temperature Coatings**

**Room Town & Country D - Session MA3-2-MoA**

**Hard and Nanostructured Coatings II**

Moderators: Marcus Günther, Robert Bosch GmbH, Germany, Rainer Hahn, TU Wien, Institute of Materials Science and Technology, Austria, Stanislaw Haviar, University of West Bohemia, Czechia, Fan-Yi Ouyang, National Tsing Hua University, Taiwan

1:40pm MA3-2-MoA-1 In Operando Studies of Hard Coatings Using High-Energy X-Ray Diffraction, **Lina Rogström**, Linköping University, IFM, Sweden

In this work, we expose very promoting results in chemical vapour deposited silicon oxycarbonitride coatings in terms of chemical resistance in front of extremely aggressive aqueous solutions. Different precursors were used leading to various film compositions with tunable properties. Pure silica films were obtained from tetraethyloxysilicate (TEOS) precursor. However, tris(dimethylsilyl)amine (TDMSA) and a novel proprietary triisilylamidine-derivative precursor (TSAR) developed and provided by Air Liquide led to silicon oxycarbonitride films with different oxygen, nitrogen and carbon contents, depending on the deposition parameters (precursor, gas flow rates ratios and deposition temperatures).

Fils deposited on the two sides of a flat silicon monocrystalline substrate were subjected to moderately long alteration of one month in a citric acid solution with pH adjusted to 8 and under thermal conditions of 80°C. Their chemical resistance was assessed by tracking the structural evolution, the changes in the elemental composition and the calculation of the dissolved thickness if it exists. A wide range of characterization techniques were used for this purpose, namely ion beam analysis such as ERDA, RBS and NRA techniques, FTIR spectroscopy, XPS, SEM and AFM imaging techniques were also used to explore the changes occurring to surface state of our layers after exposure to the aqueous solution. Finally, nanoindentation tests have been done to verify any alteration happening to the hardness and the elasticity of the films. Very promising results were found especially for films both concentrated in N and C with a very high corrosion resistance even in such extreme chemical and thermal conditions.

5:20pm MA3-1-MoA-12 Promising SiOxNyC Coatings for Glass Protection in Aggressive Chemical Media, **Farah Inoubli**, B. Diallo, CNRS/Université D'Orléans, France; K. Topka, Air Liquide Laboratories, Japan; T. Sauvage, CNRS/Université D’Orléans, France; R. Laloo, V. Turq, CNRS-CIRIMAT, France; B. Coussat, CNRS, France; N. Pellerin, CNRS/Université D’Orléans, France

Despite of its high chemical inertia, Glass still interacts when exposed to aqueous solution. This reactivity could be problematic when it concerns particularly food and medicines containers. Thus, one of the biggest challenges that pharmaceutics and food industries are facing consist of the limitation this interaction. But how?

In this work, we expose very promising results on chemical vapour deposited silicon oxycarbonitride coatings in terms of chemical resistance in front of extremely aggressive aqueous solutions.

Different precursors were used leading to various film compositions with tunable properties. Pure silica films were obtained from tetraethyloxysilicate (TEOS) precursor. However, tris(dimethylsilyl)amine (TDMSA) and a novel proprietary triisilylamidine-derivative precursor (TSAR) developed and provided by Air Liquide led to silicon oxycarbonitride films with different oxygen, nitrogen and carbon contents, depending on the deposition parameters (precursor, gas flow rates ratios and deposition temperatures).

Fils deposited on the two sides of a flat silicon monocrystalline substrate were subjected to moderately long alteration of one month in a citric acid solution with pH adjusted to 8 and under thermal conditions of 80°C. Their chemical resistance was assessed by tracking the structural evolution, the changes in the elemental composition and the calculation of the dissolved thickness if it exists. A wide range of characterization techniques were used for this purpose, namely ion beam analysis such as ERDA, RBS and NRA techniques, FTIR spectroscopy, XPS, SEM and AFM imaging techniques were also used to explore the changes occurring to surface state of our layers after exposure to the aqueous solution. Finally, nanoindentation tests have been done to verify any alteration happening to the hardness and the elasticity of the films. Very promising results were found especially for films both concentrated in N and C with a very high corrosion resistance even in such extreme chemical and thermal conditions.
superconductors and piezoelectric crystals. The characterization of wurtzite TiAIN poses challenges due to the difficulty in synthesizing them as single-phase solid solutions. As a consequence, its thermodynamic and elastic properties are not determined, and the influence of high-temperature and crystallographic defects are unknown.

The research presented here explores the properties and behaviors of wurtzite TiAIN alloys. It covers the challenges associated with synthesizing single-phase solid solutions of wurtzite TiAIN and the unknown thermodynamic, elastic properties, and high-temperature behavior of wurtzite Ti$_x$Al$_{1-x}$N. First-principles calculations were used to predict a phase diagram, compatibility gaps and spinodal lines for both cubic and wurtzite Ti$_x$Al$_{1-x}$N and the full elasticity tensor. Metastable stoichiometric wurtzite Ti$_x$Al$_{1-x}$N films with varying Al content were grown by arc deposition using pulsed bias voltage at a low-duty cycle. High-temperature annealing induced spinodal decomposition in the wurtzite Ti$_x$Al$_{1-x}$N, resulting in nanoscale compositional modulations and age hardening of 1-2 GPa.

The high-temperature behavior of wurtzite TiAIN is affected by the presence of nitrogen vacancies. To study this in HRSTEM we grew nitrogen-deficient epitaxial wurtzite Ti$_x$Al$_{1-x}$N$_{0.5}$ films, which revealed decomposition into intermediary MAX-phases, segregating into c-TiN, w-AlN phases, and TiAl nanoparticulates after high-temperature annealing. The semi-coherent interfaces between the wurtzite phase and precipitates contribute to age hardening of approximately 4-6 GPa, persisting even after annealing at 1200°C. This study sheds light on how nitrogen vacancies impact the decomposition and mechanical properties of wurtzite TiAIN, offering valuable insights into the behavior of these materials under extreme conditions.

2:40pm MA3-2-Moa4-Enhancing the Thermal Stability of V$_{0.25}$Al$_{0.75}$N$_{0.5}$ by Oxygen Incorporation, Matej Fekete, D. Neuß, M. Hans, G. Nayak, RWTH Aachen University, Germany; Z. Czigány, Center for Energy Research, Hungary; S. Karimi Aghda, RWTH Aachen University, Germany; D. Prómetzhofer, Uppsala University, Sweden; J. Sälker, J. Schneider, RWTH Aachen University, Germany

Thermal stability and mechanical behavior are key criteria for the design of the next generation of protective coatings. Today, transition metal aluminum nitrides are benchmark coatings on tools and components because of their combined thermal, chemical, and mechanical stability. To enhance the thermal stability of metastable fcc NaCl-type V$_{0.25}$Al$_{0.75}$N$_{0.5}$ coatings, oxygen is integrated into the material system. High power pulsed magnetron sputtering at 450°C is utilized to synthesize metastable fcc V$_{0.25}$Al$_{0.75}$O$_{0.11}$N$_{0.39}$ coating and reference V$_{0.25}$Al$_{0.75}$N$_{0.5}$. Coatings are annealed in a vacuum for 30 minutes to up to 950 °C and 1300 °C for V$_{0.25}$Al$_{0.75}$N$_{0.5}$ and V$_{0.25}$Al$_{0.75}$O$_{0.11}$N$_{0.39}$, respectively.

Decomposition of V and Al within the nitride phase is observed to start at 800 and 900 °C in V$_{0.25}$Al$_{0.75}$N$_{0.5}$ and V$_{0.25}$Al$_{0.75}$O$_{0.11}$N$_{0.39}$, respectively, although a formation of a few nm scale aluminum-rich regions in as deposited V$_{0.25}$Al$_{0.75}$O$_{0.11}$N$_{0.39}$ is detected by atom probe tomography. Selected area electron diffraction data reveal the presence of wurtzite phase in the V$_{0.25}$Al$_{0.75}$N$_{0.5}$ annealed at 950 °C, while in V$_{0.25}$Al$_{0.75}$O$_{0.11}$N$_{0.39}$ annealed at 1300 °C no secondary phases are detected. The thermal stability enhancement by oxygen incorporation can be understood based on the magnitude of the relevant migration barriers as well as the formation energies for vacancies.

3:00pm MA3-2-Moa-5 Interplay of Substrate Template Effects and Bias Voltage Regarding the Microstructure of Cathodic Arc Evaporated fcc-Ti$_x$Al$_{1-x}$N Coatings, Michael Tkadletz, N. Schalk, H. Wolf, Montanuniversität Leoben, Austria; B. Sartory, J. Wosik, Materials Center Leoben Forschung GmbH, Austria; J. Keckeis, J. Tadt, Montanuniversität Leoben, Austria; M. Burghammer, European Synchrotron Radiation Facility, France; C. Czettl, CERTATI2 Austria GmbH, Austria; M. Pohler, Ceratizit Austria GmbH, Austria

Ever since the implementation of hard coatings as wear protection for cutting tools, their microstructural design has been of major interest. While the effect that deposition parameters such as the applied bias voltage or the substrate temperature have on the microstructure are frequently investigated and rather well understood, commonly less attention is paid to the used cemented carbide substrates. Yet properties like their phase composition and carbide grain size significantly influence the resulting coating microstructure. Thus, within this work, substrate template effects are studied on fcc-Ti$_x$Al$_{1-x}$N coatings grown by cathodic arc evaporation onto cemented carbide substrates with different WC grain sizes. A systematic variation of the bias voltage resulted in coarse, intermediate and fine grained coating microstructures, which revealed substrate template-based coating growth at low bias voltages and bias dominated coating growth at high bias voltages. In addition, a strong influence of the applied bias voltage on the resulting preferred orientation of the deposited coatings was observed, providing the basis to tailor their fiber texture to <100>, <110> or <111>. Elaborate X-ray diffraction and electron microscopy studies contributed to gain further understanding of the substrate template effects and the origin of that implementation of a suitable substrate layer offers the possibility to effectively prevent any influence of the used substrate on the microstructural evolution of the coating. The obtained results set the fundament to implement tailored microstructures with designed gradients of crystallite size, preferred orientation and consequently mechanical properties, which, as required, either utilize substrate template effects or avoid them.

3:20pm MA3-2-Moa-6 Decomposition of Single Crystal Hf$_x$Al$_{1-x}$N Films Grown at High Temperatures and the Effect on Mechanical Properties, Marcus Lorentzon, Linköping Univ., IFM, Thin Film Physics Div., Sweden; T. Zhu, Nagoya University, Japan; N. Takata, Nagoya University, Japan; S. Nayak, J. Palisaitis, G. Greczynski, Linköping Univ., IFM, Thin Film Physics Div., Sweden; J. Rosen, Linköping University, IFM, Sweden; J. Birch, N. Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., Sweden

TM-Al-N is an important class of ceramic coating materials that exhibit excellent functional properties. The well-studied TiAIN material system has a high hardness and elastic modulus, good thermal stability, low electrical resistivity, and can also work as diffusion barriers. A similar material, but much less studied, HfAlN offers potential for high-temperature applications thanks to the extreme temperature stability of HfN(0 at.% Al). A high flux (J = 3300 eV nm$^{-2}$ s$^{-1}$) of low energy (20 eV < E$_{kin}$ < 26 eV) ion assistance was employed with -30V substrate bias. An improved crystalline quality of HAfLN films was obtained on adding up to 30 at.% Al. Similar to the case of annealed TiAIN, characteristic spinodal decomposition (in this case surface initiated during growth), with striking check-patterned lattice of AlN-rich and HfN-rich domains is observed in lattice-resolved STEM imaging and confirmed by characteristic satellite reflections in synchrotron wide-angle x-ray scattering and in selected area electron diffraction. Thanks to the nanosized compositional modulations, the nanoindentation hardness of the films showed a substantial increase from 26 GPa to 40 GPa on adding 6 to 30 at.% Al in the HAfLN film which is lower concentrations than previously reported [2]. The fracture mechanics of HfN$_{22}$ and Hf$_{25}$Al$_{0.10}$N$_{21.5}$ films studied by micropillar compression testing showed unusual ductile behavior with uniform deformation and substantial strain hardening in the HfN film, contrary to the characteristic catastrophic brittle failure common for ceramics. When alloying with Al the pillars attain catastrophic failure on activation of a single slip system (111)<011>, although a substantially higher stress is required for the shear failure. We will uncover the microscopic origin of the non-characteristic (but beneficial) ductile behavior of HfN$_{22}$ in relation to the HfN$_{21.5}$ substrate. The nanoindentation microscopy of the film and point defect formation, in particular anti-site point defects which affect the physical properties of HfN$_{22}[3]$. We will highlight the impact of increasing Al content on the size of the check-patterned modulations in the cubic phase films and preliminary results of spinodal decomposition in high Al-content wurtzite Hf$_{25}$Al$_{0.10}$N$_{21.5}$.


4:00pm MA3-2-Moa-8 Influence of the Thickness of TiAlSiN on the Thermal Properties as Input Parameter for FEM—Simulation, K. Bobzin, C. Kalscheuer, Nina Stachowski, Surface Engineering Institute (IOT) - RWTH Aachen University, Germany; B. Breidenstein, B. Bergmann, F. Gerisch, Institute of Production Engineering and Machine Tools (IFW) - Leibniz Universität Hannover, Germany

Hard coatings like TiAIN deposited by physical vapor deposition are state of the art for wear and oxidation protection of cutting tools. The cutting performance depends on coating material and process as well as cutting edge microgeometries. Both have an influence on the thermomechanical tool loads resulting in tool wear. Therefore, for a process adapted design, the consideration of the entire system is necessary. One approach to substitute costly machining investigations and save material resources is the use of Finite Element (FE)-based chip formation simulations. However, in order to perform these simulations, information about chemical, thermal
and physical coating behavior in the temperature range relevant for machining is necessary. In the present study, nanocomposite TiAlSiN coatings with varying coating thicknesses were deposited on cemented carbide tools by HPPMS /dCmS processes. The effect of coating thickness on coating morphology, chemical composition, thermal diffusivity as well as indentation hardness and indentation modulus at $\theta = 20^\circ C$, $\theta = 200^\circ C$, $\theta = 400^\circ C$ and $\theta = 600^\circ C$ was analyzed. Additionally, the distribution of the heat, generated during turning 42CrMo4+A was simulated for the coated cutting tool as preliminary step for the chip formation simulation. A columnar morphology with constant chemical composition was determined for all coating variants. While the arithmetic mean value of the coating roughness increased with increasing coating thickness, there was no influence of coating thickness on thermal diffusivity and high temperature coating hardness measurable. Nevertheless, an influence on the tool temperature can be observed in the application behavior in turning tests as well as in the simulation. As a possible cause, the contact conditions change due to a larger cutting edge microgeometry caused by a higher coating thickness, which leads to a higher temperature. The present results show that by dimensioning the tested TiAlSiN hard coating, no influence of the selected coating thickness on properties such as thermal diffusivity and the indentation hardness of the coating has to be considered. An individual adaptation of the coating thickness within a range of 2 µm sd, 5 µm to the tool geometry is therefore easily possible for the investigated TiAlSiN coatings without further modification of the coating.

4:20pm MA3-2-MoA-9 Non-Reactive Magnetron Sputtering of Ti-Al-N Coatings, Balint Hajas, S. Berrmanschäger, T. Wojcik, TU Wien, Institute of Materials Science and Technology, Austria; D. Primetzhofer, Uppsala University, Angstrom Laboratory, Sweden; S. Kolozsvari, Plansee SE, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Hard protective coatings allow for increased lifetime of machining tools and more versatile applications. Although (Ti,Al)N coatings have a rich history in material science with various improvements for their production, little is known about their non-reactive deposition using Ti-Al-N compound targets. Reactive deposition of such (Ti,Al)N coatings is studied in-depth, showing that especially for sputtering the resulting microstructure and consequently properties (next to deposition rate) hugely depend on the N-partial pressure used. Alternatively, such nitriles can also be prepared non-reactively using nitride compound targets. Here, we use powder metallurgically prepared TiN–AlN compound targets with either 50, 66, or 80 mol% AlN to prepare (Ti,Al)N coatings with various chemical composition through non-reactive DC as well as pulsed DC magnetron sputtering.

The primary investigations focused on how the mechanical properties such as hardness and indentation modulus depend on various deposition conditions, such as sputtering power density, pulse frequency, substrate temperature, substrate-to-target distance, and magnetron condition. Detailed investigations by X-ray diffraction showed that while all (Ti,Al)N coatings obtained from the (TiN)$_{x_1}$(AlN)$_{x_2}$ target were single-phase faceted cubic (fcc) structured those obtained from the (TiN)$_{y_1}$(AlN)$_{y_2}$ target were single-phase hexagonal close packed (hcp) wurtzite-type structured. The hcp-phase fraction within the (Ti,Al)N coatings prepared with the (TiN)$_{x_1}$(AlN)$_{x_2}$ target strongly depends on the deposition condition. The maximum hardness of the fcc-(Ti,Al)N coatings was ~38.2 GPa, and that of the hcp-(Ti,Al)N coatings was 29.3 GPa. When compared with the reactive deposition of fcc-(Ti,Al)N using similar deposition conditions, the non-reactive route allows for a doubled deposition rate, thus contributing to reducing energy consumption for their preparation.

4:40pm MA3-2-MoA-10 nc-Sic/a-C Coating for Industrial Applications, Mojmir Jilek, O. Zindulka, SHM sro, Czechia; Z. Studeny, University of Defence, Czech Republic

Silicon carbide is one of the hardest materials. In the form of thin layers, it is prepared primarily using CVD technology. Presented PVD deposition technology (rotary sputtering of segmented targets with high power) allows deposition of SiC based coatings with hardness higher than 60GPa more than 10µm thick. This coating shows nanocrystalline composite structure of nc-SiC/a-C.

In cutting test, our coating achieved 60% lifetime compared to thick diamond layer. In contrast to diamond layer, the SiC coating deposition is simpler and coated tools can also be easily reground, or chemically decorated.

5:00pm MA3-2-MoA-11 Synthesis and Investigation of Crystalline (Ta,Al)B$_2$ and AlB$_2$, Thin Films, Chun Hu, S. Lin, Institute of Materials Science and Technology, TU Wien, Austria; P. Pöllmann, S. Mrad, RWTH Aachen University, Germany; T. Wojcik, Institute of Materials Science and Technology, TU Wien, Austria; J. Schneider, RWTH Aachen University, Germany; N. Koutná, P. Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria

Transition metal diboride thin films are promising functional materials with outstanding mechanical properties and thermal stability. However, development of magnetron-sputtered TiB$_2$ thin films is challenging, since their composition typically deviates from 1:2 metal-to-boron stoichiometry. We developed (Ta$_{1-x}$Al$_x$)B$_2$ (x=0–0.48, y=1.23–2.29) thin films and use Ta-Al-B as a model system to study the correlation of microstructure, boron stoichiometry, and mechanical properties implementing experimental and computational materials science. The proposed reasons for off-stoichiometry include angular distribution of the sputtered species, their scattering in the gas phase, re-sputtering and potential evaporation from the grown films for the complex evolution of film compositions, as well as energetic preference for vacancy formation and competing phases as factors for governing the phase constitution. The changes in stoichiometry correlate with the evolution of microstructure, hardness, and elastic modulus. Increasing y from 1.23 to 1.46 leads to the highest hardness (38.8 GPa) among (Ta$_{1-x}$Al$_x$)B$_2$, studied here due to promoted formation of the AlB$_2$-prototype phase. (Ta$_{1-x}$Al$_x$)B$_2$ with y=1.87-2.29, corresponding to x up to 0.48, reveal gradually decreasing hardness (down to 31.3 GPa) due to the increased AlB$_2$-fraction. Complementing the studies for Ta$_{1-x}$Al$_x$B$_2$ solid solutions, we also synthesized crystalline AlB$_2$, (x = 1.99, 1.97, 2.27) thin films and studied mechanical properties, thermal stability, and oxidation resistance. This is the first report about AlB$_2$ thin films with an AlB$_2$-prototype crystal structure, which is difficult to crystallize due to the close-to-zero formation energy. The AlB$_{27}$ thin film shows an exceptional oxidation resistance with an onset temperature of ~1000 °C.

5:20pm MA3-2-MoA-12 Tribocorrosion and Biocompatibility Analysis of Carbide-derived Carbon (CDC) Surface Modification for Hip Implants, Yani Surf, H. Kanniyappan, M. Karunanidhi, M. Daly, M. McNallan, M. Mathew, University of Illinois at Chicago, USA

Total hip replacement (THR) suffers from inferior tribocorrosion damage, which may lead to the premature failure of hip implants. Carbide-derived carbon (CDC) is a carbon material derived from carbide precursors. Previously, we have proved that CDC can effectively protect Ti6Al4V from tribocorrosive damages under open-circuit potential (OCP). Nonetheless, some fundamental properties and biological analysis of CDC are still lacking. Therefore, this study aims to characterize CDC’s thickness and biological responses before and after tribocorrosion tests to evaluate CDC as a biomaterial.

CDC was synthesized on the Ti6Al4V disk [11 mm dia x 7 mm] by electrolysis method and confirmed by Raman spectroscopy. Prior to the experiments, the control group Ti6Al4V disks were polished with a mirror finish (Ra<50 nm). The tribocorrosion testing was conducted on a customized reciprocal sliding (±2 mm) tribocorrosion system at 1 Hz for 3600 cycles, which was connected to a Gamry potentiostat. Bovine calf serum (BCS) with 30 g/L glucose and 3 g/L sodium succinate was used as the electrolyte to simulate human body fluid. Three electrodes were used where the working electrode is the sample, the counter electrode is a graphite rod, and the reference electrode is a standard calomel electrode (SCE). The electrochemical protocol was followed with three stages, which are (i) initial stabilization with OCP, (ii) tribocorrosion stage with OCP and potentiostatic (PS), and (iii) final stabilization with OCP. To measure thickness, a diamond saw sectioned the disk, and the ion-milled section was examined under SEM with EDS. MG-63 human osteoblast-like cells were employed to test the cytocompatibility of CDC, and the cell viability was quantified using the Alamar blue assay. Also, the bioactivity of CDC was studied with 4,6-diamidino-2-phenylindole (DAPI) staining assay live/dead assay.
Monday Afternoon, May 20, 2024

As a result, the produced CDC shows an excellent tribocorrosion performance, presenting around 30-fold lower potential variation than Ti6AI4V. Also, the CDC was detected by Raman spectroscopy and found under SEM at the wear scar even after the tribocorrosion test. Interestingly, a carburized layer of approximately 5 μm was observed; however, a distinct layer of CDC was not showing under SEM. Regarding the biocompatibility analysis, no significant difference was found in CDCs cell proliferation compared to the control group Ti6AI4V, as living cells were shown on the sample. According to the amount and the cell shapes, no noticeable difference was found between CDC and the Ti6AI4V, verifying CDC's biocompatibility on the Ti6AI4V substrate.

**Functional Thin Films and Surfaces**

*Room Town & Country A - Session MB1-MoA*

**Thin Films and Surfaces for Optical Applications**

**Moderators:** Silvia Schwyn-Thoney, Evatec AG, Switzerland; Juan Antonio Zapien, City University of Hong Kong

1:40pm **MB1-MoA-1 Improvements to Multilayer Dielectric Coatings to Enable Internal Confinement Fusion at the National Ignition Facility (NIF), Colin Harchcock, Lawrence Livermore Laboratory, USA**

**INVITED**

Since the advent of the laser, it has been theorized that high power lasers could be used as drivers for inertial confinement fusion (ICF), which has the possibility of revolutionizing our energy generation and dependance. As such, the US Department of Energy (DOE) has invested in this technology since the early 1970s, culminating in the building of the National Ignition Facility (NIF) from 1990-2009. However, it is quickly understood that the damage to the multilayer dielectric (MLD) interference coatings in the laser system may be key fluence and power limiting components. As such there was a huge, interdisciplinary effort to understand laser matter interactions leading to damage and the associated laser-damage prone precursors and mitigations. In this talk, we will discuss the basic layout of the NIF laser system and the associated coatings. Notable were the issues with the coating of high quality, meter-sized optics with good uniformity and high damage performance — this necessitated the use of electron beam evaporation for many of the high fluence, large aperture mirrors. For each of these MLD coating types, we will discuss the typical issues, typical damage-prone precursors and the associated mitigations. For many of the mirrors, nodular-type defects have been shown to increase the local electric field, absorption and greatly decrease the damage resistance of the coating. Furthermore, we will discuss other defects, such as stoichiometric issues, crystallinity, and nanobubbles.

2:20pm **MB1-MoA-3 Ultra-Low Thickness Thin Film Multilayer Devices for Application in Water Window Regime of Soft X-Ray, Piyali Sarkar Roy, A. Biswas, D. Bhattacharyya, Bhabha Atomic Research Centre, India**

In this paper we present the important results on Co/Ti, Cr/Ti and Cr/Sc multilayers (ML) which theoretically show good potentials as soft X-ray mirrors, nodular type defects have been shown to increase the local electric field, absorption and greatly decrease the damage resistance of the coating. Furthermore, we will discuss other defects, such as stoichiometric issues, crystallinity, and nanobubbles.
As a result, we present a study on the electrical properties of thin ITO coatings at cryogenic temperatures below 12 K in correlation with their optical properties. Additionally, we demonstrate the initial findings on developing silicon-based light detectors that incorporate ITO films and utilize the Neganov-Luke effect.


2:30pm MB1-Moa-6 Strongly Thermochromic VO₂-Based Smart Coatings for Room-Temperature Applications Prepared on Glass, Michael Kaufman, J. Vlček, S. Hostounek, University of West Bohemia, Czech Republic. Thermochromic Vanadium dioxide (VO₂) exhibits a reversible phase transition from a low-temperature monoclinic VO₂ (M1) semiconducting phase to a high-temperature tetragonal VO₂ (R) metallic phase at a transition temperature of approximately 68°C for the bulk material. The automatic response to temperature and the abrupt decrease of infrared transmittance without attenuation of luminous transmittance in the metallic state make VO₂-based coatings a promising candidate for thermochromic smart windows reducing the energy consumption of buildings.

To meet the requirements for large-scale implementation on building glass, VO₂-based coatings should satisfy the following strict criteria simultaneously: a deposition temperature close to 300 °C, a transition temperature close to 25 °C, an integral luminous transmittance T500 > 60%, a modulation of the solar energy transmittance ΔT > 10%, long-term environmental stability, and a more appealing color than yellowish or brownish colors in transmission.

The paper deals with a scalable sputter deposition technique for the preparation of strongly thermochromic YSZ/W and Sr co-doped VO₂/SiO₂ coatings on standard soda-lime glass at a relatively low substrate surface temperature (320°C) and without any substrate bias voltage. The W and Sr co-doped VO₂ layers were deposited using a controlled high-power impulse magnetron sputtering of a W-V target combined with a simultaneous pulsed DC magnetron sputtering of a Sr target in argon-oxygen gas mixtures. The bottom antireflection Y-stabilized SrO: (YSZ) layers were deposited using a controlled reactive high-power impulse magnetron sputtering of a Zr-Y target, while the top antireflection SiO₂ layers were deposited using a reactive mid-frequency bipolar dual magnetron sputtering of two Sr targets.

The fundamental principles of this technique, and the design, structure and optical properties of the thermochromic coatings are presented. The coatings exhibit a transition temperature of 22-25 °C with an integral luminous transmittance T500 up to 64% (at almost the same luminous transmittance above the transition temperature) and ΔT > 11%. Such a combination of properties, together with the relatively low deposition temperature (320 °C), has not yet been published by other teams for thermochromic VO₂-based coatings prepared by a scalable deposition technique compatible with the existing magnetron sputter systems in glass production lines and in large-scale roll-to-roll deposition devices.

4:00pm MB1-Moa-8 Progress in Infrared Transparencies under Opto Electro Thermo and Mechanical Environments, Sam Zhang, Harbin Institute of Technology, China. Invited

In recent years, there has been a growing interest and research focus on infrared optical thin films as essential components in infrared optical systems. In practical applications, extreme environmental factors such as aerodynamic heating and mechanical stresses, electromagnetic interferences, laser interferences, sand erosions, and rain erosions all lead to issues including cracking, wrinkling, and delaminations of infrared thin films. Extreme application environment imposes stringent requirements on functional films, necessitating high surface hardness, stability, and adhesion. Additionally, for multispertial optical transmissions, infrared optical thin films are expected to exhibit high transmittance in the visible and far-infrared wavelength bands while possessing tunability and optical anti-interference properties in specific weight ranges. Electromagnetic shielding requires superior electrical performance, while resisting laser interference demands rapid phase change capabilities. This paper focuses on current research progresses in infrared optical thin films under extreme conditions such as opto, electro, thermos and mechanical environments.
The present work evaluates the tribological performance of self-lubricating iron and nickel-based alloys during sliding contact against aluminum. The microstructure and phase composition of the deposited self-lubricating alloys are characterized using X-ray diffraction, scanning electron microscopy. Afterwards, their friction and wear performance against aluminum is evaluated under dry contact conditions and with additional supply of lubricant at room and elevated temperatures. The experiments are performed using a load scanner tribometer in a single pass configuration in order to mimic the conditions found in forming processes. The results show that the self-lubricating coatings are able to provide better frictional control when compared to the tool steel independently of the amount of lubricant applied. Further, the use of self-lubricating claddings results in a reduction of galling, particularly at elevated temperatures. This
overall tribological performance makes the presented self-lubricating alloys excellent candidates for numerous applications in the metal forming industry.

3:00pm MC1-2-MoA-5 Tribological Study of Magnetron Sputtered W-S(C) Thin Films Sliding Against Aluminium at High Temperatures, Todor Vuchkov, S. Jahan Sunny, A. Cavaleiro, University of Coimbra, Portugal

Forming of Aluminium is often performed at elevated temperatures due to its poor formability and springback at room temperature. Forming of aluminium at elevated temperatures causes significant tribological issues like adhesive wear and galling, i.e. there can be significant material transfer from the workpiece to the tool/die. Due to the harsh conditions (temperatures up to 500°C), liquid lubricants cannot be utilized and solid lubricants can be an alternative. Self-lubricating thin films deposited by magnetron sputtering are good candidates for alleviating this issue, especially the ones containing transition metal dichalcogenides since they provide good lubrication in environments that lack humidity. In this study we deposited three types of films containing transition metal dichalcogenides (TMDS), of which one consisted only of WS, and two films were alloyed with carbon (~27 and 35 at. % of carbon). We utilized various techniques for characterizing the physico-chemical properties of the deposited films like scanning electron microscopy, X-ray diffraction at elevated temperature and thermo-gravimetric analysis. The mechanical properties were assessed using scratch testing and nanoindentation.

Tribological testing was performed against aluminium (1000 series) balls at room temperature, 200° and 400°C. The unalloyed WS coating had more porous columnar morphology while the carbon-alloyed ones showed increase compactness with reduced intercolumnar porosity. The thermal analysis indicated that the maximum operating temperature should be ~400-430 °C, for the pure WS coating, and a higher value of ~480-490°C for the carbon alloyed films. The thin films had good adherence to the tool steel substrates with an Lc2 critical load of 20-30 N and no gross delamination up to 70 N of load. The tribological results indicate that the unalloyed WS coating is the best solution for friction reduction against aluminium at the examined testing temperatures (up to 400°C). The carbon alloyed coatings also provided friction reduction but friction instabilities were observed and the film with the highest carbon content suffered excessive galling at 400°C. In terms of wear, the unalloyed WS coating generally suffered more wear compared to the other coatings. The results of the study present a high potential of the TMD-based sputtered coatings for applications involving sliding against aluminium at elevated temperatures.

3:20pm MC1-2-MoA-6 Improved Anti-Friction of Diamond-Like Carbon Incorporating Titanium, Jae-II Kim, Y. Jong, J. Kim, Korea Institute of Materials Science (KIMS), Republic of Korea; N. Umehara, Nagoya University, Japan

Diamond-like carbon (DLC) is commonly introduced as a solid lubricant and anti-wear coating. On the other hand, the tribological performance of DLC is highly dependent on the intercontact with the mating material, which may result in high friction. The lubricity of DLCs is believed to be due to the carbonaceous transition layer formed on the mating materials. Industrially, steel- or copper-based alloys have been used as counterparts against DLCs to date, however, it is hard to achieve low friction in tribopairs with them due to the difficulty in forming a carbonaceous transfer layer.

We attempted to solve this problem by doping highly reactive titanium into DLC. Among many transition metals, titanium in particular has a large number of d-orbital vacancies, which can easily interact with the 2p-orbital of carbon. Therefore, we introduced the idea that this chemical property can promote the formation of a carbonaceous transfer layer, which we aimed to form a low-friction C/C contact interface to enhance the lubricity of the DLC/steel tribopair.

Ti-doped DLC was fabricated by co-depositing DLC with a filter cathode vacuum arc method and Ti with an unbalanced magnetron sputter. The tribological performance as a function of Ti concentration was investigated, and the tribofilms formed on the counterparts were chemically characterized. In conclusion, we report that the Ti-doped DLC exhibited enhanced long-term low-friction characteristics and superlubricity in various environments.
To reach these milestones, a deeper understanding of DLC coatings is required, namely regarding the intricate relationship of friction and wear rates within diverse tribosystems, where parameters such as relative humidity and the material of the counterbody show decisive influence. In this work, DLC coatings were deposited using a modified commercially available PA-CVD system on AISI 4140 steel. Two kind of coatings were produced, a-C:H and a-C:H:Si, at temperatures of 450 °C and 20 °C. Process gas consisted of a mixture of argon, acetylene, and HMDSO as silicon precursor. Characterization was carried out by means of X-ray photoelectron spectroscopy, as well as GDOES and EDX. Tribological behavior was evaluated by means of Pin-on-Disk, using the coated sample as the disk, a 12 N normal load, a speed of 0.4 m/s and a total sliding distance of 2000 m. Counterparts were 6 mm balls, of which three different materials were used: AISI 52100 bearing steel, Al2O3, and Si3N4. Test chamber was conditioned using forced air recirculation and beakers containing either water or regenerated silica gel to create a humid or a dry environment, respectively. Friction coefficient was registered during the entire test. The wear track was evaluated with optical and confocal microscopy, as well as SEM/EDX and Raman spectroscopy. Hardness and elastic modulus increased with deposition temperature, and the values were doubled with silicon doping. However, a lower friction coefficient and wear volume loss were found in Si-free samples. In general, the coatings showed varied responses to the different environments and counterparts: a-C:H showed oxidation with higher humidity, whereas a-C:H:Si exhibited high wear in the drier ambient, producing several peaks in the friction coefficient during the test. The steel counterpart exhibited a lubricious oxide layer that helped reduce the friction coefficient, thus performing better in the humid environment. The Si3N4 counterpart showed the highest adhesion when sliding against a-C:H:Si, although a rather low friction coefficient and wear was shown when testing the Si-free samples.

5:00pm MC1-2-MoA-11 Evaluation of the Sliding Wear Performance of Binary CrN and Nanocomposite CrSiCN Coatings in Arctic Environments, N. D’Attilio, Forest Thompson, N. Madden, South Dakota School of Mines and Technology, USA; E. Asenath-Smith, US Army Corps of Engineers Cold Regions Research and Engineering Laboratory, USA; G. Crawford, South Dakota School of Mines and Technology, USA

The efficiency, service lifetime, and durability of engineering components operating in the severe cold and dry environments found in Earth’s polar regions can potentially be improved using protective coatings based on transition metal nitrides. However, the tribochemical wear behavior of these ceramic materials is particularly sensitive to operating conditions. Thus, there is a need to understand the influence of arctic environments on the sliding wear performance of these coatings. In this work, binary CrN, columnar CrSiCN, and glassy CrSiCN coatings were produced using filament-assisted reactive magnetron sputter deposition. The coatings were characterized using energy dispersive X-ray spectroscopy, X-ray diffraction, transmission electron microscopy, and mechanical properties. The mechanical properties of the coatings were tested using nanoindentation and the wettability of the coatings was determined using tilting-base contact angle goniometry. A ball-on-flat tribometer equipped with an active cooling stage and dry air source was used to assess the tribological performance of the coatings under various combinations of coating surface temperatures and environmental dwellpoints. Ultimately, the microstructure and amorphous phase content was found to play a major role in the performance of CrN-based coatings in these environments. The wear resistance of all coating types was found to suffer under a combination of low surface temperature (-20 °C) and low dewpoint (-33 °C), while their frictional behavior under frosting conditions (-20 °C surface temperature, -10 °C dewpoint) was primarily controlled by the presence of ice at the contact zone.

5:20pm MC1-2-MoA-12 Designing Hydrogen-Free Thick Diamond Like Multilayer Carbon Coatings for Load Bearing Applications, Muhammad Usman, City University of Hong Kong

Diamond like carbon (DLC) coatings are in focus from a last few decades due to its exceptional mechanical and tribological properties. High hardness, low coefficient of friction and wear rate are some of the intrinsic characteristics. Due to this unique combination, it is widely used in microelectromechanical systems (MEMS), automotive sector, tools and dies, laser barcodes scanners etc. However, industrial bearings, load bearing implants and machine elements are high load applications. Single layer DLC can be divided into two (1) hard (2) soft. Both (hard, soft) types have their own limitations: hard DLC possesses high compressive residual stresses and experiences buckling induce adhesion failure under high load whereas soft DLC lacks wear resistance and better mechanical properties [1]. Researchers shifted from single layer to multilayer architecture in DLC to achieve high hardness and toughness simultaneously as these are inversely correlated [2-4]. This was made possible by stacking alternate hard and soft layers which not only reduce compressive residual stresses in the coating but also increase toughness compared to hard monolayer [3]. Thus, load bearing capacity of the coating increases. The current research aims to evaluate the impact of overall thickness of multilayer DLC (found to be excellent in our previous research) on atomic bonding, mechanical properties, residual stresses, scratch adhesion and wear resistance particularly at high contact stress which are missing previously. Therefore, new multilayer DLC coatings are designed with alternate hard and soft layers using closed field unbalanced magnetron sputtering system. Discrete sharp interfaces are produced by selecting two different bias voltages. Hard to soft layer ratio (1:1) and layer thickness (50nm) are kept constant for all specimens: 0.5µm, 1µm, 2µm, 3µm, 4µm thick coatings (Fig. 1) are deposited onto steel substrate having Cr/CrC, interlayer. Scanning electron microscope (SEM), Raman spectroscopy, nanoindenter, scratch adhesion tester and tribometer are employed for characterization of specimens. Raman analysis depicts decreasing ls/lw ratio and increasing full width at half maximum (FWHM) trend by increase in overall coating thickness. Hardness and residual stress are in inverse and direct relation to thickness respectively. Interestingly, scratch adhesion resistance is found to be within same range for all specimens. Moreover, this multilayer DLC design exhibited excellent wear resistance under high loading conditions. Wear rate values are within one order of magnitude for all samples.

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Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-2-MoA

Coatings for Batteries and Hydrogen Applications II

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, Chen-Hao Wang, National Taiwan University of Science and Technology, Taiwan

1:40pm TS1-2-MoA-1 Effect of Atomic Layer Deposited Films on Three-Dimensional Electrodes for Lithium-Ion Batteries, P. Lin, National Chung Hsing University, Taiwan; Chih-Liang Wang, National Tsing Hua University, Taiwan

The great capability of atomic layer deposition (ALD) in precisely controlling the film quality, such as thickness, composition and conformality has been paid much attention. Herein, we presented a study of coating nanocomposite metal oxides via ALD on three-dimensional electrodes for lithium-ion batteries. The three-dimensional electrodes were prepared by the hydrothermal synthesis of TiO2 nanorods on carbon cloths. The nanocomposite metal oxides of TiO2 and ZnO were deposited on TiO2 nanorods by ALD. The effect of metal oxides on electrochemical performance was systematically investigated by using different ALD cycles of TiO2 and ZnO. The results indicated that the reversible capacity and rate performance of three-dimensional electrodes can be improved after ALD nanocomposite metal oxides. The improved performance can be attributed to the function of ALD TiO2, to not only alleviate the volume change and the growth of solid electrolyte interphase but also improve electronic conductivity. More details related to battery performances and film properties, influenced by the ALD cycle of individual metal oxide, will be reported in the presentation.

2:00pm TS1-2-MoA-2 Mechanism Study of MoO2@TiO2 as the Anode of Lithium Ion Battery by Various In Situ Techniques, Zhen Chong, National Cheng Kung University (NCKU), Taiwan; Y. Shen, Hierarchical Green-Energy Materials Research Center (Hi-GEM), Taiwan; J. Huang, National Cheng Kung University (NCKU), Taiwan

To pursue a safe and stable energy storage system, lithium ion batteries (LIBs) with titanium dioxide (TiO2) as the anode, having no dendrite formation during the charge/discharge cycles, have been promoted. TiO2 having low specific capacity (330mAh/g theoretically, 272mAh/g at 0.2C in this work), would need to be modified by adding molybdenum (Mo) to enhance the capacity as the impedance will decrease and the lithium ion diffusion rate will increase to meet the requirements. Thus, we successfully synthesized MoO2@TiO2, having a shell-core structure and augmented the capacity performance (995mAh/g at 0.2C in first cycle). To explain the
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reactions occurred in the cell, various in situ techniques are used. The in situ X-ray diffraction analysis is suitable for the observation of intercalation/deintercalation of lithium ion in the electrodes during the charge/discharge process; while the in situ Raman spectroscopy is reliable for the study of the reactions in the electrolyte, especially the formation of solid electrolyte interphase (SEI) layer; the in situ thermal analysis is also used to understand the side reaction occurred during the cycles. These techniques provided thorough details of the MoO$_2$/TiO$_2$ as the anode material of LIB and made it more preferable to be commercialized.

2.20pm TS1-2-MoA-3 Effects of Additives on Electrochemical Performance of Sodium Ion Batteries, Ting Ching Lin, J. Huang, National Cheng Kung University (NCKU), Taiwan; C. Chang, National University of Taiwan, Taiwan

In recent years, the surge in electric vehicle popularity and the push for renewable energy development by various governments globally have enhanced energy security, mitigated the risk of fuel leaks, and lessened the dependence on imported fuels. This has been achieved by ensuring a steady supply of electricity and diversifying fuel sources. As the demand for lithium continues to rise with the increased adoption of lithium-ion batteries, attention is turning towards sodium ion batteries due to the limited availability of lithium resources. Sodium ion batteries are gaining traction, particularly in the electrical and electronic sectors. Their operational principle closely mirrors that of lithium-ion batteries, encompassing positive and negative electrodes, isolation membranes, and electrolytes. Notably, sodium ion batteries offer cost advantages over lithium batteries, with more readily available precursor materials for the negative electrode and a lower carbonization temperature during graphite negative electrode production. Despite these merits, sodium ion batteries currently encounter challenges, such as lower energy density and storage capacity compared to lithium batteries. The cycle life of existing sodium ion batteries also falls short of that seen in commercial lithium batteries. The primary hurdles stem from the lower energy density and suboptimal cycling performance, which heavily rely on the formation of solid electrolyte interface (SEI) films on the electrode surface.

To address these challenges, the research proposes a novel approach: the combination of different kinds of new ion additives to form a composite additive. The aim is to create a stable and dense SEI that exhibits high electronic insulation, and ion conductivity. This approach seeks to overcome the limitations of sodium ion batteries, particularly their low energy density and poor cycling performance, by fostering the development of an enhanced SEI.

In this research, we used electrochemical impedance spectroscopy (EIS) to measure interface resistance, and used X-ray photoelectron spectroscopy (XPS), Scanning Electron Microscope (SEM), Fourier-transform infrared spectroscopy (FTIR) to observe the electrode surface and analyze the SEI film. The results indicate that the addition of the NaDOP ionic additive effectively improves the retention of battery capacity and establishes a durable SEI film.

Keywords: sodium ion batteries, new ion additives

2.40pm TS1-2-MoA-4 Effect of SiO$_2$/rGO via Phosphorus Doping as Anode Materials for Lithium-Ion Batteries, Wen-Feng Lin, J. Huang, S. Brahma, National Cheng Kung University (NCKU), Taiwan; Y. Shen, Hierarchical Green-Energy Materials Research Center (Hi-GEM), Taiwan

Lithium-ion batteries have been widely applied in our daily lives and there is an ongoing demand for LIB with higher energy density, lower self-discharge, longer cycling life and better safety. Titanium dioxide (TiO$_2$) has emerged as a highly promising anode material for lithium-ion batteries due to its remarkable cycling stability, impressive rate performance, cost-effectiveness, and environmental friendliness. Nevertheless, the main obstacles associated with this material include its limited electronic/ionic conductivity and lower theoretical capacity. In order to overcome this issue, our research has been modifying high-capacity material (e.g., SnO$_2$ into TiO$_2$, with an eye to promoting its theoretical capacity. Modifying SnO$_2$ into TiO$_2$ reduces the impedance and increases the Li-ion diffusion rate. The SnO$_2$/TiO$_2$ composite is synthesized by the chemical bath with Sn$(BF_4)_2$, HBF$_4$, Na$_2$SnO$_3$ and TiO$_2$ (rutile and anatase mixed phase) followed by annealing at different temperature. From the TEM and XRD results, the SnO$_2$/TiO$_2$ composite had been successfully synthesized. It can be inferred from the figure that the structure of the composite might be the shell of the SnO$_2$ & TiO$_2$ solid solution while the core remains TiO$_2$ structure. However, the table below shows the serious fading problem of SnO$_2$/TiO$_2$ composite with different annealing temperature during the first and second cycle. Active lithium loss (ALL) in the initial lithiation process causes irreversible capacity of LiIB due to the formation of unstable solid electrolyte interface (SEI) layer on the electrode surface. To resolve the problem, pre-lithiation has been widely accepted as one of the most promising strategies to compensate for active lithium loss. Our group have been dedicated to trying various pre-lithiation techniques, such as electrochemical and thermal evaporation of lithium. Electrochemical pre-lithiation aims to generate stable SEI layers by applying constant voltage while lithium evaporation deposition involves depositing various thickness of lithium to achieve different levels of pre-lithiation. The ultimate goal would be giving out advantages and challenges of each one then finding out the optimal approach to improve cycling performance of tin-based anodes in lithium-ion batteries.

3.00pm TS1-2-MoA-5 The Research of Different Pre-Lithiation Methods to Enhance Coulombic Efficiency of SnO$_2$ Modified TiO$_2$ as Anode Material in Lithium-Ion Battery, Cheng-Hsun Ho, J. Huang, National Cheng Kung University (NCKU), Taiwan; Y. Shen, Hierarchical Green-Energy Materials Research Center (Hi-GEM), Taiwan

Lithium-ion batteries have been widely applied in our daily lives and there is an ongoing demand for LIB with higher energy density, lower self-discharge, longer cycling life and better safety. Titanium dioxide (TiO$_2$) has emerged as a highly promising anode material for lithium-ion batteries due to its remarkable cycling stability, impressive rate performance, cost-effectiveness, and environmental friendliness. Nevertheless, the main obstacles associated with this material include its limited electronic/ionic conductivity and lower theoretical capacity. In order to overcome this issue, our research has been modifying high-capacity material (e.g., SnO$_2$ into TiO$_2$, with an eye to promoting its theoretical capacity. Modifying SnO$_2$ into TiO$_2$ reduces the impedance and increases the Li-ion diffusion rate. The SnO$_2$/TiO$_2$ composite is synthesized by the chemical bath with Sn$(BF_4)_2$, HBF$_4$, Na$_2$SnO$_3$ and TiO$_2$ (rutile and anatase mixed phase) followed by annealing at different temperature. From the TEM and XRD results, the SnO$_2$/TiO$_2$ composite had been successfully synthesized. It can be inferred from the figure that the structure of the composite might be the shell of the SnO$_2$ & TiO$_2$ solid solution while the core remains TiO$_2$ structure. However, the table below shows the serious fading problem of SnO$_2$/TiO$_2$ composite with different annealing temperature during the first and second cycle. Active lithium loss (ALL) in the initial lithiation process causes irreversible capacity of LiIB due to the formation of unstable solid electrolyte interface (SEI) layer on the electrode surface. To resolve the problem, pre-lithiation has been widely accepted as one of the most promising strategies to compensate for active lithium loss. Our group have been dedicated to trying various pre-lithiation techniques, such as electrochemical and thermal evaporation of lithium. Electrochemical pre-lithiation aims to generate stable SEI layers by applying constant voltage while lithium evaporation deposition involves depositing various thickness of lithium to achieve different levels of pre-lithiation. The ultimate goal would be giving out advantages and challenges of each one then finding out the optimal approach to improve cycling performance of tin-based anodes in lithium-ion batteries.

3.20pm TS1-2-MoA-6 Study on the Characteristics of Garnet-Type Solid Electrolytes in Lithium Metal Solid-State Batteries with Multilayer Interfaces, Hung-Ju Chen, J. Hung, S. Lin, National Cheng Kung University (NCKU), Taiwan

Lithium batteries (LIB), which is a rechargeable battery, mainly used in related electronics industries, such as transportation vehicles, medium to large uninterrupted power systems (UPS), solar systems, energy storage systems, electric hand tools, aerospace equipment, power battery market and aviation battery. The LIB life would decrease with increasing in the number of charge and discharge cycles. Besides, the risk of LIB electrolyte is a liquid organic solvent, which is easy to burn and explode in case of fire. Recently, solid-state electrolytes have attracted attentions and show the many advantages including high safety, high energy density, and greater temperature tolerance. Among different types of solid-state electrolytes, garnet-type LLZTO (Li$_{0.5}$La$_{0.5}$Zr$_{0.5}$Ta$_{0.5}$O$_{3}$) electrolyte has high ionic conductivity (10$^{-4}$S/cm) and chemical stability towards lithium metal. However, lithium dendrites will be generated during the charge and discharge process of solid electrolyte batteries. The dendrites could lead to short circuit and failure of battery. Moreover, poor contact in the interface between solid electrolyte and lithium metal could cause the increased impedance and decreased conductivity. The aim in this study is to use different types and proportions of metal fluorides to modify the interface; meanwhile, the interface forms an electronically insulating and lithium-
friendly lithium fluoride layer to promote the chemical diffusion of lithium in lithium metal alloys and reduce interface impedance. After the project, we expect that a new generation of lithium metal solid-state batteries will be developed.

4:00pm TS1-2-MoA-8 Characterization Study of Sustainable Lithium Ion Battery with Cathode of Recycled LiNi_{x}Mn_{y}Co_{1-x-y}O_{2} (NMC). Yi-Chieh Tseng, National Cheng Kung University (NCKU), Taiwan; Y. Shen, Hierarchical Green-Energy Materials Research Center, Taiwan; J. Huang, National Cheng Kung University (NCKU), Taiwan.

Nowadays, to meet the requirements of applying on portable electronic devices and electronic vehicles, energy storage system need to have high energy density and high power density. LiNi_{x}Mn_{y}Co_{1-x-y}O_{2} (NMC) as the cathode for lithium-ion batteries (LIBs) could fulfill the demands. However, NMC is considered not friendly to the environment and harmful to man. To reduce the mining of poisonous, we had recycled the 622 and 811 NMC powder from the used battery of the electrical racing cars. By ultrasonic washing the electrodes in sodium chloride (NaCl) solution, the powder containing lithium (Li), nickel (Ni), magnesium (Mn), cobalt (Co), iron (Fe), aluminum (Al) and copper (Cu) is obtained. To remove the undesirable elements (Fe, Al and Cu), we washed the powder with various acids and used the Cyanex 272 to extract the target elements. From the X-ray diffraction (XRD) pattern, the recycled 622 and 811 NMC powder showed the characteristic peak of Ni, Mn and Co, proving the effectiveness of the extraction method. It was then assembled into coin cell (CR2032), still showing stable and relatively high capacity performance. In situ techniques are also used to examine the stability of the battery by recycled material, to be commercialized in the future. As the sustainability is the key requirement to be commercialized, the recycled battery with NMC as the cathode would have strong competitiveness.

4:20pm TS1-2-MoA-9 Investigation of Y-doped Li_{7}La_{3}Zr_{2}O_{12} (Y-LLZO) Coatings by Colloidal Coating Process for the Electrolyte of all Solid-state Battery. Yen-Yu Chen, G. Yao, National Pingtung University of Science and Technology, Taiwan; X. Yan, Chinese Culture University, Taiwan.

Lithium ion batteries (LIBs) were widely applied on computer, communications, and consumer electronics for decades, as well as on the electric vehicles in recent years. Due to the risks of liquid electrolytes for current LIBs, solid state electrolytes for LIBs were investigated. In this study, Y-doped Li_{7}La_{3}Zr_{2}O_{12} (Y-LLZO) materials were prepared by a solid-state reaction method. After well-dispersed, Y-LLZO coatings were deposited on the LiCoO_{2}/Y-LLZO composite anode from the Y-LLZO suspensions by a spin-coating method. The crystal phase analysis by the X-ray diffraction (XRD) method shows, the cubic perovskite phase of Y-LLZO can be obtained after calcined at 900°C for 12 h. The grain size of the Y-LLZO powders observed by the scanning Electron Microscopy are most within several μm. The crystal phase of the Y-LLZO samples after sintered at 950°C for 1 h is still mainly perovskite phase but become the tetragonal structure. A few of minor La_{2}Zr_{2}O_{7} phase can be found in the sample, that may due to the generation of the volatile lithium species during sintering. The Y-LLZO sample with Al_{2}O_{3} sintering aid shows higher density and larger grain size after sintering. The thickness of the Y-LLZO coatings are around several μm. The detail electrical properties will be shown in the following report.

Keywords: All solid-state lithium ion battery, LLZO, coatings, colloidal process, solid electrolyte
Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM2-2-TuM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes II: Fracture and Fatigue
Moderator: Matteo Ghidelli, CNRS, France

8:00am CM2-2-TuM-1 Minimizing FIB Artifacts in Microcantilever Fracture: A Case Study on the Role of Grain Boundaries in Microfracture, Subin Lee, Y. Zhang, Karlsruhe Institute of Technology (KIT), Germany; S. Brinckmann, Forschungszentrum Jülich GmbH, Germany; M. Bartosik, Montanuniversität Leoben, Austria; C. Kirchlechner, Karlsruhe Institute of Technology (KIT), Germany

In recent years, the application of Focused Ion Beam (FIB) for small-scale fracture testing has gained significant prominence. While simple cantilever-based geometries are commonly used for micro-fracture studies, concerns persist regarding FIB-induced artifacts, specifically those caused by a Ga ion beam, affecting the accurate measurement of fracture toughness at the micron scale. These concerns include issues such as residual stresses resulting from ion implantation, chemical interactions of gallium ions leading to segregation at the notch front, and the limited size of the notch root radius.

In this presentation, we demonstrate bridge-notch micro cantilever fracture which can minimize FIB artifacts by using atomically sharp natural cracks. Departing from the conventional through-thickness notch, we employ a well-defined bridge-notch for a single cantilever fracture test [1]. Through in situ SEM fracture tests, direct observations reveal that extremely thin bridges fail first, generating sharp natural cracks which is free of FIB artifacts. Consequently, this enables a more precise measurement of fracture toughness with reduced scatter. This phenomenon is observed across four different nitride hard coating systems.

Utilizing the bridge notch approach, which enhances statistical analysis, we study the impact of grain boundaries in microfracture. Testing columnar-grained nitride coatings with two loading directions parallel and perpendicular to the film's growth direction, we find that longer crack path results in higher fracture toughness. Furthermore, using a multi-layered coating with an epitaxially grown top layer, a nano-grained structure in the upper coating region, it is revealed that the epitaxially grown part without grain boundaries exhibits a 30% higher fracture toughness compared to the nano-grained coating. This documents that the fracture toughness of hard coatings is controlled by grain boundary fracture.


9:00am CM2-2-TuM-4 Influence of Annealing-Induced Substrate Element Diffusion on the Microstructure and Mechanical Properties of Ti/TiCN Coatings Synthesized by Chemical Vapor Deposition, Fabian Konstantinuk, M. Schiester, Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria; M. Tkačletz, Department of Materials Science, Montanuniversität Leoben, Austria; C. Czettl, CERATIZIT Austria GmbH, Austria; N. Schalk, Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

Ti/TiCN deposited by chemical vapor deposition (CVD) is widely used as hard coating system for cemented carbide cutting tools, typically under an Al2O3 top layer. During the deposition of the Al2O3 top layer, the underlying Ti and TiCN layers are exposed to high temperatures. Therefore, the present study focuses on the influence of this Al2O3 deposition step, which is mimicked by a vacuum-annealing treatment, on the microstructure and mechanical properties of the Ti/TiCN coating. By applying advanced characterization techniques such as scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), atom probe tomography (APT), and micro-mechanical bending tests on both, as-deposited and annealed coatings, changes in the microstructure and mechanical properties were studied. It was found that W and Co diffusion takes place along the Ti and TiCN grain boundaries from the substrate into the coating. While the hardness, Young’s modulus, and fracture toughness remained unaffected by the annealing treatment, a significant decrease of the fracture stress with increasing annealing time was observed.

9:20am CM2-2-TuM-5 Mechanical Properties of Thin Films Deposited by HIPIMS onto Flexible Substrates, Tereza Kosutova, Uppsala University, Department of Electrical Engineering, Sweden; M. Tavares da Costa, Karlstad University, Sweden; K. Gamstedt, Uppsala University, Department of Materials Science and Engineering, Sweden; D. Drozdenko, Charles University, Czechia; T. Kubart, Uppsala University, Department of Electrical Engineering, Sweden

Our study focuses on the strength and ductility of thin films deposited by magnetron sputtering on flexible substrates. Although thin films are widely used in surface engineering, their application on foils brings new requirements on the mechanical properties of the coating material as well as the substrate-coating interface. Here, we aim on the determination of mechanical properties of thin films deposited by dc and high power impulse magnetron sputtering (HIPIMS). The main goal is to identify deposition conditions that ensure good adhesion and ductility of the layers and therefore facilitate applications of coated metal foils.

In-situ testing in an SEM is used to quantify the film cracking during tensile loading and thus analyse the distribution of fracture strain and interfacial shear strength of the coating material. This technique is complemented by the strain field analysis of the substrate foils determined by digital image correlation to identify defects that could induce stress concentration and premature failure. Thin films of copper, titanium and amorphous carbon are evaluated as examples with different intrinsic ductility. Furthermore, the effect of interlayers was investigated. The behaviour of the films deposited on two different foils of aluminium and PET is compared.

To identify the impact of different deposition parameters, we analysed a series of samples deposited using different values of the duty cycle and the substrate bias. The results are correlated to the morphology, microstructure and chemical composition analysed mainly by SEM, XRD and EDX techniques. Whereas the copper exhibits high ductility and a good adhesion can be achieved with an ion assistance, the fracture behaviour of the titanium is dependent on the growth conditions.

9:40am CM2-2-TuM-6 Fatigue-Induced Abnormal Grain Growth in Metallic Thin Films, Q. Li, Georgia Institute of Technology, USA; A. Barrios, Colorado School of Mines, USA; Y. Yang, Georgia Institute of Technology, USA; M. Jain, Sandia National Laboratories, USA; Y. Liu, Georgia Institute of Technology, USA; B. Boyce, Sandia National Laboratories, USA; T. Zhu, Olivier Pierron, Georgia Institute of Technology, USA

This presentation describes a microelectromechanical system (MEMS) based setup to investigate grain growth in ultrafine grained and nanocrystalline metallic thin films under high/very high cycle loading conditions (i.e., up to 10^6 cycles). The advantage of the technique is that it can test different materials (fcc, bcc, different textures) under identical loading conditions. The governing hypothesis is that abnormal grain growth occurs under this loading regime, and that the family of growing grains is mainly dictated by elastic anisotropy. Our preliminary results on Au and Al thin films are compared to our previous work on ultrafine grained Ni. Abnormal
Diamond-like carbon (DLC) coatings are frequently used to improve wear performance of technical components in tribological systems. Appropriate fatigue properties of the coating system are fundamental to ensure the functionality. The mechanical failure of the coating can lead to spallation and delamination processes already through low external stresses and hence to total component failure. Therefore, precise measurements are mandatory. Established analysis like the Rockwell test according to DIN 4856 as well as scratch tests are performed with a single overload above the critical strength of the DLC coating disregarding real operating conditions and failure mechanisms e.g. fatigue through cyclic loads. In our study, we performed cyclic nanoindentation fatigue measurements of DLC coatings to consider application-related stresses. The coating systems were deposited by PVD and PACVD techniques varying e.g. the thicknesses of the functional and support layer systems. Cyclic nanoindentation measurements with spherical diamond indenters were performed to evaluate the fatigue behaviour. We have shown that promising results can be obtained from this type of measurements. Suitable test parameters were defined to investigate a wide range of different coating systems within a few hours by adjusting static force and force amplitude. Effects of different coating designs, layer thicknesses and mechanical properties (e.g. indentation hardness, indentation modulus, residual stress and yield strength) of the DLC layer could be evaluated. The critical stress for various DLC layer thickness was evaluated with a FEM simulation and compared to the results obtained from the fatigue measurements. With this, essential adjustments of the mechanical properties of the DLC layer were found to increase the fatigue limit. Furthermore, the effect of an additional pre-treatment by annealing under elevated temperatures from 250 °C up to 450 °C was investigated. The results of the nanoscale fatigue test provide information on previously unknown effects that could not be detected with nanoindentation hardness tests. For various DLC systems the thermal degradation under application related stresses could be shown. Our new measurement technique reveals that previous measurements e.g. adhesion measurement results from typical single overload or hardness measurements tests are not conclusive enough to consider application-related load spectra and that cyclic loads are necessary to guarantee the requested operation condition testing environment. Hence the developed fatigue test allows us to adapt the coating systems to the requirements of the real components.

10:00am CMZ2-TuM-7 Nanoscale Fatigue Measurements on Diamond-Like Carbon Coatings, Joshua Vetter, M. Günther, P. Hofmann, S. Grosse, Robert Bosch GmbH, Germany; S. Schmauder, University of Stuttgart, Germany

Diamond-like carbon (DLC) coatings are frequently used to improve wear performance of technical components in tribological systems. Appropriate fatigue properties of the coating system are fundamental to ensure the functionality. The mechanical failure of the coating can lead to spallation and delamination processes already through low external stresses and hence to total component failure. Therefore, precise measurements are mandatory. Established analysis like the Rockwell test according to DIN 4856 as well as scratch tests are performed with a single overload above the critical strength of the DLC coating disregarding real operating conditions and failure mechanisms e.g. fatigue through cyclic loads. In our study, we performed cyclic nanoindentation fatigue measurements of DLC coatings to consider application-related stresses. The coating systems were deposited by PVD and PACVD techniques varying e.g. the thicknesses of the functional and support layer systems. Cyclic nanoindentation measurements with spherical diamond indenters were performed to evaluate the fatigue behaviour. We have shown that promising results can be obtained from this type of measurements. Suitable test parameters were defined to investigate a wide range of different coating systems within a few hours by adjusting static force and force amplitude. Effects of different coating designs, layer thicknesses and mechanical properties (e.g. indentation hardness, indentation modulus, residual stress and yield strength) of the DLC layer could be evaluated. The critical stress for various DLC layer thickness was evaluated with a FEM simulation and compared to the results obtained from the fatigue measurements. With this, essential adjustments of the mechanical properties of the DLC layer were found to increase the fatigue limit. Furthermore, the effect of an additional pre-treatment by annealing under elevated temperatures from 250 °C up to 450 °C was investigated. The results of the nanoscale fatigue test provide information on previously unknown effects that could not be detected with nanoindentation hardness tests. For various DLC systems the thermal degradation under application related stresses could be shown. Our new measurement technique reveals that previous measurements e.g. adhesion measurement results from typical single overload or hardness measurements tests are not conclusive enough to consider application-related load spectra and that cyclic loads are necessary to guarantee the requested operation condition testing environment. Hence the developed fatigue test allows us to adapt the coating systems to the requirements of the real components.

10:20am CMZ2-TuM-8 Bending Fatigue Testing of 3D-printed PETG and ABS to Investigate Feasibility for Tidal Turbine Blades, H. Myers, Oxford University, UK; Y. Chen, Steve Bull, Newcastle University, UK

Three-point fatigue bending tests (1Hz) of 3D-printed PETG and PETG specimens conducted in air or seawater are reported in the current study. These are used to produce S-N curves for ABS and PETG. The results indicate no significant effect of seawater on fatigue life by comparing the lifetimes of samples tested in seawater with the S-N curves produced. The S-N curves for the two materials are similar, indicating a common feature controlling fatigue life which is hypothesised to be defects introduced in 3D printing. Preliminary examination with 3D optical microscopy corroborates this as a plausible explanation. Finally, approximate calculations are used to demonstrate that these materials may feasibly be used for tidal turbine blades, but any design must especially consider blade strength and stiffness, possibly at the expense of hydrodynamic efficiency.
to operate within sensor temperature ranges and discern the composition and concentration of mixed gases. The n-type semiconductor nature of ZnGa2O4 enables the detection of NO2 and H2S molecules. This semiconductor exhibits rapid and robust sensing responses along with high signal intensity towards NO2 and H2S, thereby anticipating an enhancement in sensor operational efficiency, particularly in terms of elevated temperature utilization. Hence, this study employs ab initio calculations based on the density functional theory to determine the surface energy of ZnGa204[111]. The analysis reveals that the ZnGa204[111] surface comprises Ga, Zn, and O elements. Findings indicate that the surface energy for Zn-Ga-O-, O-, and Ga-terminated ZnGa204[111] range between 0.516 to 0.2335 eV/Å2, 0.0516 to 0.7789 eV/Å2, and 0.0464 to 0.5918 eV/Å2, respectively. The Ga-terminated ZnGa204 has the lowest surface energy of 0.0464 eV/Å2 in a Ga-rich environment, showing the Ga-terminated ZnGa204[111] is the most favorable surface. The work function change of Zn-Ga-O-, O-, and Ga-terminated ZnGa204[111] are 3.70 eV, 0.48 eV, and 6.35 eV, respectively. This highlights that the Ga surface atoms demonstrate a maximum work function change, consistent with previously experimental observations.

Surface Engineering - Applied Research and Industrial Applications

Room Town & Country C - Session IA2-1-TuM

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications I

Moderators: Jan-Ole Achenbach, KCS Europe GmbH, Germany, Masaki Okude, Mitsubishi Materials Corporation, Japan

8:00am IA2-1-TuM-1 Influence of Plasma Carburizing on Corrosion Behavior and Interfacial Contact Resistance of Austenitic Stainless Steels, Phillip Marvin Reinders, R. Kaestner, G. Bräuer, Technische Universität Braunschweig, Germany

Austenitic steels are known for their high corrosion resistance but at the same time have low wear resistance and high interfacial contact resistance (ICR), which limits their application e. g. as bipolar plates in Proton Exchange Membrane Fuel Cells (PEMFC). Plasma diffusion treatment, specially the well-known plasma nitriding, improves the hardness and interfacial contact resistance but mostly worse the corrosion behavior in PEMFC environment.

Aim of this study is to evaluate the less known plasma carburizing as a suitable process for functionalization austenitic stainless steels. For this purpose, a number of processes were executed under specific variation of temperature ranging from 360 °C to 450 °C and duration of 10 to 16 h. The samples were analyzed using x-ray diffractometer, x-ray photoelectron spectroscopy, SEM, Vickers microindentation, potentiodynamic polarization and ICR measurements.

It could be shown that the corrosion current density (1.78 µA·cm⁻²) of the treated samples are an order of magnitude lower than those of the reference (17.38 µA·cm⁻²). The ICR was also reduced from > 1000 mΩ·cm⁻² down to 31 mΩ·cm⁻². After corrosion, even lower values around 15 mΩ·cm⁻² were achieved. The targets according to DOE (< 1 µA·cm⁻² and < 10 mΩ·cm⁻²) were almost achieved. A comparison to the plasma nitrided samples was also performed and shows the high potential of plasma carburizing.

Keywords: plasma carburizing, s-phase, austenitic stainless steel, corrosion behavior, interfacial contact resistance, bipolar plate

8:20am IA2-1-TuM-2 Laser-Induced Diffusion of an Aluminum Clad in an Aerospace Aluminum Alloy: Microstructure and Corrosion Behavior, Milton Lima, E. Morais, S. Silva, R. Siqueira, Institute for Advanced Studies, Brazil

The AA2024-T3 AlClad alloy is an aluminum alloy widely used in the aerospace industry. The AlClad designation refers to the application of pure aluminum coating on the alloy surface to improve corrosion protection. Although this alloy has satisfactory mechanical behavior and corrosion resistance for use in aerospace applications, the aluminum coating often wears or peels during service, exposing the substrate to the corrosive environment. The objective of this work was to improve the adhesion of the coating to the alloy substrate through fiber laser glazing, where different current values of the pumping diode were used. This treatment aimed to improve the anchorage between the aluminum layer and the alloy substrate, making the structures more reliable and secure. The laser used was a continuous wave ytterbium-doped fiber laser with a...
wavelength of 1.07 µm, beam quality (M2) equal to 9, minimum beam diameter of 0.1 mm and displacement speed of 50 mm/s. Argon gas was also used to protect the specimen and the lens with a flow rate of 7 l/min. The analyses were performed using methods such as profilometry, pin-on-plate slip wear, nano-indentation, light optical microscopy, scanning electron microscopy, energy dispersive spectroscopy and electrochemical corrosion tests. Based on the results obtained, it was found that the objective of the study was achieved for all glazed specimens when the pumping current exceeded 50%. There was an increase in the metallurgical bonding between coating and substrate and a decreasing surface roughness with increasing diode pump current. In conditions where the laser pump current was between 50% and 70% the corrosion current densities values are similar to the material, without laser glazing, which indicates that the corrosion resistance was not affected in these cases. In this way, specimens with better coating adhesion, surfaces with lower average roughness and greater hardness were obtained. Consequently, less wear was observed while keeping corrosion resistance similar to that provided by the pure aluminum layer.

8:40am IA2-1-TuM-3 Tribological and Corrosion Behaviour of Crn and AlCrn Coatings over Nitried Medium Alloy Steel, J. Maskavizan, E. Dalbon, National University of Technology (UTN), Argentina; Sonia Brühl, National University of Technology (UTN), Argentina

Different Cr based coatings were deposited over medium alloy AISI 4140 steel in industrial facilities (Oerlikon Balzers Argentina), to improve wear and corrosion resistance in aggressive environments, like the plastic forming industry, and other applications in the aluminum industry. As AISI 4140 is a soft steel, tests were carried out in two conditions: i) quenched and tempered (Q&T), ii) Q&T plus ion nitriding.

Friction and adhesive wear test were in a carried out in a rotational pin on disk machine using an alumina ball 6 mm in diameter as counterpart. The coatings were characterized by SEM and XRD. The corrosion test consisted in anodic polarization in a chloride solution. Finally, the film adhesion was tested by Rockwell C indentation and Scratch test at constant loads.

Both coatings resulted about 2.7-3 microns width. They presented good adhesion tested with Rockwell C indentation and Scratch test at constant loads. In the corrosion test, only the CrN film showed a quasi-passive zone in NaCl solution, meanwhile the AlCrN presented active dissolution. The observation of the wear tracks and the film microstructure, so as the surface after corrosion, allowed to explain the difference between nitrided and non nitrided substrates primarily, having this last combination a low load bearing capacity. Between both films, some slightly differences between mechanical properties explain the best behavior of CrN.

9:00am IA2-1-TuM-4 Influence of the Cathodic Bias Parameters on Corrosion Resistance in the Micro-Arc Oxidation Coating of AZ31B Magnesium Alloy, Shih-Yen Huang, Y. Lee, Y. Chu, National Taiwan University, Taiwan

Micro-arc oxidation (MAO) is a surface treatment applied to valve material to form a multifunctional ceramic coating based on the principle of anodizing. By regulating electrical parameters and adjusting electrolyte composition, the MAO coating has the capability to meet diverse specifications across numerous domains. Among the various MAO process equipment, the bipolar pulse power supply stands out for its flexible process parameters and fast coating growth rate, which is attributed to the introduction of cathodic bias. The incorporation of cathodic bias has been proven to benefit the properties of the MAO coating by reducing the discharging energy and promoting the crystalline transition within the oxide phase of aluminum. However, the impact of cathodic bias in the MAO process is seldom discussed in magnesium alloy applications.

In this research, AZ31B magnesium alloy was used as the substrate to produce MAO coating, with the objective of clarifying the mechanism of cathodic biason the growth mechanism of MAO. Under controlled anodic bias parameters and cathodic duty ratio, the best corrosion resistance, as observed in the electrochemical impedance spectroscopy (EIS) result, was achieved with an impedance value of 2.55x10⁶ Ω·cm² when the total charge quantity input through cathodic bias equaled that through anodic bias. Under the same condition, the corrosion resistance decreases regardless of whether the cathodic charge quantity is higher or lower than the anodic charge quantity, and a significant decrease in impedance value by two orders of magnitude was found when the ratio of cathodic charge quantity to anodic charge quantity exceeded 1.33. Moreover, under controlled cathodic charge quantity, MAO coatings were found to exhibit an impedance value of 10⁶ Ω·cm² while the ratio of cathodic current density to anodic current density remained below 1. However, there was a notable decline in impedance value when the ratio exceeded 1.33. These results suggest that the influence of both the total charge quantity and the instantaneous input current density of the cathodic bias on the corrosion resistance of MAO coatings might be attributed to the limiting current density in the cathodic bias period.

9:20am IA2-1-TuM-5 Nanolubricants: Pioneering Sustainable Solutions for the Lubrication Industry, Anirudha Sumant, Argonne National Laboratory, USA

Over the past decade, the forefront of tribological studies has been illuminated by the exceptional properties of graphene, along with other 2D materials and their synergies with various nanomaterials. These cutting-edge nanolubricants have demonstrated unparalleled wear and friction performance across diverse systems. Their remarkable ability to achieve near-zero levels of friction and wear (known as superlubricity), extends even to macroscopic scales in different environments and under moderate to high contact pressures. This positions them as a promising alternative to traditional oil-based lubricants. Despite their impressive performance, the sustained and long-term reliability of these solid nanolubricants under more intricate tribological conditions remains a subject of ongoing investigation. Establishing their credibility as a potential replacement for oil-based lubricants necessitates a deeper understanding of their behavior in complex scenarios.

At Argonne National Laboratory, we have made significant strides in developing various nanolubricants. Our research showcases the attainment of superlubricity on rough steel contacts, even under high contact pressures (~1GPa), in both linear and sliding-rolling contacts as well as at high temperatures in a ambient environment. Furthermore, these nanolubricants exhibit stability over extended periods, enduring 70 kilometers of linear sliding without failure.

Our investigation delves into the role of tribochemistry at the micro/nanoscale and its profound impact on tribological performance at the macroscale. We present compelling examples resulting from collaborations with industry partners, particularly within the automotive sector, focusing on applications such as metal stamping. This progress not only sets the stage for future breakthroughs but also marks a significant stride toward realizing oil-free superlubricity in real-world applications. By doing so, these research efforts make a substantial contribution to the broader mission of decarbonization and offer sustainable solutions for the evolving lubrication industry.
Tuesday Morning, May 21, 2024

Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-1-TuM

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

Moderators: Gustavo Garcia-Martin, REP-Energy Solutions, Spain, Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK, Eli Ross, Pratt & Whitney, USA

8:20am MA1-1-TuM-2 Tunable Aluminate Coatings for Surface Finish and Improved Oxidation and Hot Corrosion Behaviour of Additive Manufactured Ni-Based Superalloys, Fernando Pedraza, D. PIEL, T. KEPA, La Rochelle University, France

INVITED

The widespread use of additive manufactured (AM) components has become a hot topic over the past 10 years. Many of the mechanical properties are surface-dependent because of the derived roughness due to e.g. semi-molten powders. The reactivity of the AM materials also increases because of the greater active surface. In addition, AM materials contain many microstructural defects including e.g. dislocations, twins, various grain sizes, etc. which make the materials more susceptible to attack in particular under high temperature conditions where the harsh gas and molten reagents can go through. While different alternatives including e.g. chemical and electrochemical polishing, laser remelting, etc. have been proposed to lower the roughness and densify the surface, the AM materials still degrade fast.

The alternative that will be presented in this paper is based on the use of aluminium-based coatings made by slurry. As opposed to electrolytic or gas phase processes where the coating follows the surface roughness, the slurry process partly melts the surface, blends the uppermost layers of the AM alloy with the coating material and results in a diffused gradient layer that can be tailored to tune the chemical composition and microstructure. The samples will be given for different additive manufactured nickel-based alloy systems including the popular equiaxed or single crystalline nickel-based superalloys.

Simple nickel aluminate coatings will be shown to dramatically improve the oxidation resistance of IN-718 at temperatures as high as 800°C and of Alloy 699 at 1000°C through the development of a thin and adherent Al2O3 scale. The application of Al/Si slurry coatings improves dramatically the hot corrosion resistance under Na2SO4 against conventional vapour phase and simple Al slurries due to the layered segregation of SiW. The incorporation of microreservoirs made of MCAlN in the aluminium diffusion coating matrix can in contrast improve both the oxidation and the hot corrosion resistance.

9:00am MA1-1-TuM-4 Application of Machine Learning Algorithms to Characterize Aluminate Diffusion Coatings and to Predict their Ageing Behavior, Vladislav Kolarik, M. Juez Lorenzo, Fraunhofer Institute for Chemical Technology ICT, Germany; P. Praks, IT4Innovations National Supercomputing Center, VSB - Technical University of Ostrava, Czechia; R. Praksova, IT4Innovations National Supercomputing Center, VSB - Technical University of Ostrava, Czechia

Aluminate diffusion coatings are an efficient and economic technique to protect steels against corrosion at high temperatures in harsh environments. They can be deposited as aluminum slurry through various deposition methods, such as spraying or brushing, followed by a heat treatment to form the diffusion coating. Machine learning algorithms offer a significant potential for optimizing and customizing the coatings for a specific application with desired coating characteristics and for predicting the ageing behavior during operation. The experimental effort can be minimized reducing the costs significantly and accelerating the development. Symbolic Regression was chosen to investigate the potential of machine learning to determine the slurry deposition parameters that lead to the targeted coating characteristics and to predict the ageing behavior.

Output parameters characterizing the diffusion coating were defined as well as input parameters on which they depend. Experimental data from former projects were used to train the algorithm applying a train/cross-validation split of 50/50. To assess the robustness of the coating system the thickness of the deposited slurry was calculated top-down from the experimental data after different ageing times and plotted versus the values adjusted during the slurry deposition process. The result reveals the deviation to the adjusted values and separates the sample sets, where the deposition process was under control from those with high fluctuation of the slurry thickness deviation. Output parameter characterizing the ageing progress, such as coating thickness, number of layers and their thicknesses,
pores concentrations and FeAl precipitations in the FeAl layer were calculated as a function of time inferring predictions. The results show that machine learning is highly useful for complex systems influenced by numerous parameters, whose interrelation and meaningfulness is difficult to be described by classical physical modelling.

9:20am MA1-1-Tum-5 Pack-Aluminizing Mechanisms in Stainless Steel Additively Manufactured, E. B. Varela, PGMEC-Universidade Federal do Paraná, Brazil; H. Abreu-Castillo, PIPE - Universidade Federal do Paraná, Brazil; G. Prass, J. Pacheco, Instituto SENAI de Inovação em processamento a laser., Brazil; Ana Sofia C. M. D’Oliveira, Universidade Federal do Paraná, Brazil

Sustainable development of high temperature parts typically requires surface treatment to enhance performance, including metallic parts processed by additive manufacturing (AM). Challenges of diffusion processes in these surfaces depend on the microstructure of the AM phase being protected and are being addressed in this investigation. This research contributes to the discussion of the impact of additive microstructure on the diffusion mechanisms and characteristics of aluminide coatings. Pack-aluminizing was applied to AM AISI316L stainless steel processed by PTA-DDE, L-DDE and L-PBF. Pack-aluminizing was carried out at 850°C for 1h and with a pack-mixture composition of 10%AI3+3HCl+87%Al2O3. Results show that, regardless of the substrate condition, aluminized coatings are composed of an external FeAl, intermetallic layer and an interdiffusion region exhibiting two sub-layers, an intermediate layer of the intermetallic FeAl and an internal layer of a-FeAl close to the substrate. The first evidences of the impact of additive multilayer structures is the non-uniform interface interaction with the substrate associated with the interlayers regions. Changes in the microstructure in these regions are a consequence of solidification mechanisms of each deposited layer creating local fluctuations in the atomic diffusion rate. The substrate microstructure also impacts the thicknesses of each layer, external and interdiffusion regions of the aluminized coatings. With the thicker external layer exhibited by the roller substrate (21.5±1.3 µm) and the thicker interdiffusion layer for the Stainless steel processed by PTA-DDE (3.6±0.4 µm): It is interesting to point out that inspite of the differences in microstructure L-DDE and L-PBF AM materials exhibit very similar features that differ from PTA-DDE. Results revealed that arc evaporated TiAlN as a promising protective coating material mitigating high-corrosion effects on superalloys. TiAlN coatings with varying metal ratios were arc evaporated onto a NiCoCr-based superalloy and subjected to hot-corrosion testing in a specially designed hot corrosion rig. Utilizing a Na2SO4-MgSO4 salt mixture, both coated and uncoated samples were thermally treated in an SOX-rich atmospheres for a duration of up to 30 h. The primary objective was to enhance the understanding of the corrosion mechanisms of TiAlN coatings under low-temperature hot corrosion (LTHC, at 700°C), as well as high-temperature hot corrosion (HTHC, at 850°C) conditions. The scale formation was analyzed through x-ray diffraction (XRD), nancindentation, and elastic recoil detection analysis (ERDA) calibrated x-ray fluorescence (XRF) to achieve precise chemical quantification. Subsequently, a subset of selected compositions based on structural and mechanical criteria is analyzed concerning their oxidation resistance. In-situ XRD monitors the formation of oxide scales in synthetic air environments up to 1200°C. In addition, conventional oxidation experiments in a box furnace contribute to a comprehensive understanding of the oxidation behavior of these TMCs. The formed scales are thoroughly described by transmission electron microscopy unraveling details on the diffusion kinetics of the oxide formers. This research not only explores the fundamental mechanisms that determine the scale formation of TMCs, but also provides valuable insights into the growth mechanism of ternary face-centered cubic (fcc) TM-Al/Si-C solid solutions synthesized by PVD techniques.

Tuesday, May 21, 2024

10:00am MA1-1-Tum-7 Structural Evolution and Oxidation Resistance of Al/Si Alloyed Transition Metal Carbide Thin Films, Sophie Richter, Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; E. Ntemou, D. Primetzhofer, Department of Physics and Astronomy, Uppsala University, Sweden; T. Wójcik, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; O. Hunold, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; S. Kołoszvári, P. Polcik, Plansee Composite Materials GmbH, Germany; J. Ramm, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; H. Riedl, Institute of Materials Science and Technology, TU Wien, Austria

Transition metal carbides (TMCs) are known for their mechanical properties, high-temperature stability and melting points exceeding 3000 °C. However, their exceptional high-temperature properties are offset by their sensitivity to oxidation. This study focuses on an alloying strategy incorporating Al and Si as strong oxide-forming elements to extend their oxidation resistance in demanding environments. Using a combinatorial physical vapor deposition (PVD) approach, group IV to VI transition metal carbides were systematically investigated by co-sputtering Al and Si next to TiAlN. This comprehensive study is a benchmark for a wide range of structural and chemical compositions, which are thoroughly characterized by x-ray diffraction (XRD), nancindentation, and elastic recoil detection analysis (ERDA) calibrated x-ray fluorescence (XRF) to achieve precise chemical quantification. Subsequently, a subset of selected compositions based on structural and mechanical criteria is analyzed concerning their oxidation resistance. In-situ XRD monitors the formation of oxide scales in synthetic air environments up to 1200°C. In addition, conventional oxidation experiments in a box furnace contribute to a comprehensive understanding of the oxidation behavior of these TMCs. The formed scales are thoroughly described by transmission electron microscopy unraveling details on the diffusion kinetics of the oxide formers. This research not only explores the fundamental mechanisms that determine the scale formation of TMCs, but also provides valuable insights into the growth mechanism of ternary face-centered cubic (fcc) TM-Al/Si-C solid solutions synthesized by PVD techniques.
Protective and High-temperature Coatings
Room Town & Country D - Session MA3-3-TuM

Hard and Nanostructured Coatings III
Moderators: Marcus Günther, Robert Bosch GmbH, Germany, Rainer Hahn, TU Wien, Institute of Materials Science and Technology, Austria, Stanislav Havír, University of West Bohemia, Czechia, Fan-Yi Ouyang, National Tsing Hua University, Taiwan

8:00am MA3-3-Tum-1 Physical Properties of Pure Tantulum Nitrides Thin Films, Angeline Poulon-Quintin, Univ. Bordeaux, CNRS, ICMCB, France; A. Achille, ICMCB, CNRS, France; D. Michau, CNRS, ICMCB, France; M. Cavarroc, SAFRAN, France

Transition metal nitrides coatings are widely studied because of their good optical, mechanical, thermal... properties. Depending on the microstructure, coatings present different properties. For tantulum nitride (TaN), stable (hexagonal) and metastable (cubic) phases can be deposited as coatings. In this study, their physical and adherence properties on 316L stainless steel and AlN substrates depending on the microstructure and the thin film PVD technique used, are compared. Both Reactive High Power Impulse Magnetron Sputtering (R-HIPMS) and Reactive RadioFrequency Magnetron Sputtering (RF-MS) were selected. Characterisations of structures and films microstructures were realised by Grazing Incidence X-Ray diffraction and Electron Microscopies (SEM and TEM). Scratch tests and nanohardness measurements were used to compare adherence and mechanical properties. Electrical properties were explored with a four-point probe.

The correlation between microstructure, process and physical properties is discussed. The aim of this study is to show the interest for specific applications of the hexagonal TaN thanks to the quantification of its physical properties and/or tuning its microstructures.

8:20am MA3-3-Tum-2 Magnetron Sputtered CrTa, CrTa Coatings, Jan-Ove Söhngen, V. Ott, S. Ulrich, M. Stueber, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Refactory alloy thin films can exhibit unique properties which make them suitable candidates in high temperature applications. The model system chosen for our study is Cr-Ta. CrTa coatings with various Ta contents were synthesized by magnetron sputtering utilizing acombinatorial experiment in thin film deposition. We used a segmented circular target consisting of two half plates of pure Cr and Ta for the deposition at 250 W DC target power, 0.4 Pa Argon pressure, 0 V substrate bias and ≈ 150°C substrate temperature. Polished steel substrate samples of 10x10x1 mm³ were placed in a horizontal line opposite to the target. Thus, we obtained different Cr-Ta coatings with various Ta content in a single deposition experiment.

The amount of Cr and Ta determined by electron micro analyses was used to classify the XRD (X-Ray diffraction) results:

4. All coatings are crystalline.
5. The XRD reflections of the coatings with Ta content between 15.3 at.% and 39.7 at.% exhibit similar shape and suggest these coatings are polycrystalline and grow in a single-phase bcc (body centered cubic) solid solution structure.
6. In contrast to the coatings with a lower amount of Ta, the XRD reflections of coatings with 68.5 at.% Ta content show a broad (110)-signal, indicating a much smaller crystal size and the (110) reflection of the coating with 80 at.% Ta exhibits a sharp reflection near the position of the (110)-reflection of the bcc structure and a broader shoulder, suggesting an overlap of different reflections.

This indicates a transition in the microstructure of the coatings with increasing Ta content. No intermetallic phase TaCr was found in any of these coatings. Pure crystalline Ta coatings were not bcc structured. Transmission electron microscopy analyses will resolve the microstructure further.

Mechanical properties of the coatings were studied by micro-indentation. The hardness and Young’s modulus of the Cr-Ta coatings in dependence of their Ta content and as well of the pure Cr and Ta coatings will be discussed. Due to solid solution strengthening, the Vickers hardness of the Cr-Ta coatings exhibits a local maximum in relation with the Ta content.

8:40am MA3-3-Tum-3 Overview and Trends in Application Driven Developments of Wear Resistant Coatings, Denis Kurapov, Oerlikon Surface Solutions AG Pféiffer, Zweigniederlassung Balzers, Liechtenstein

INVITED

The long history of the wear protective coating deposited by physical vapour deposition (PVD) technology starts more than 40 year ago from the coatings applied on cutting and forming tools. During the last years the requirements on the wear resistance in tooling industry getting more and more demanding giving strong impulses for development of new surface solutions and deposition technologies.

With significantly increased level of requirements on the performance of the wear protective coatings the development of new solutions goes more and more into direction of tailored solutions. Development of such solutions based on understanding of the wear mechanisms and correlation between coating properties and its performance. Deposition technologies need to be developed in the way to enable deposition of the coatings with desired properties.

In this paper we present an overview of the latest developments of surface solutions and PVD technologies. The main focus put on history and recent advances in development of wear protective coatings as well as on progress in arc evaporation and magnetron sputtering deposition technologies.

9:20am MA3-3-Tum-4 Enhancing the Thermal Stability and Cutting Performance of fcc-AlCrN by Oxygen Incorporation, A. Michau, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; Tomasz Wojcik, P. Kutrowatz, Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; D. Kurapov, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; H. Riedl, Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria

Protective coatings applied in advanced machining processes typically encounter extreme thermo-mechanical loads easily exceeding temperatures above 1000 °C. In this context, the thermal stability and, hence, the decomposition behaviour of the applied coatings is still the key-parameter for enhanced durability. Recent studies on oxygen incorporation in (Ti,Al)O(N) highlighted the potential of defect-engineered meta-stable structures, as for the formation of wurtzite AlN domains, the non-metal mobility is decisive in the shared oxygen/nitrogen sublattice. Here, relatively small amounts of oxygen are efficient to double the required energy to form w-AlN out of (Ti,Al)O(N) compared to (Ti,Al)N.

Based on these results, we thoroughly investigated the decomposition behaviour of oxygen-doped AlN in hexagonal AlN coatings grown by arc evaporation. During the reactive growth, the oxygen was incorporated by
varying the flow rates between 15 to 70 scmp compared to 940 to 990 scmp nitrogen (p$_{dep}$ around 4 Pa). All coatings were grown using an Oerlikon Balzers INNOVANTA kila equipped with AlCr$_7$/30 targets. These variations lead to purely fcc structured $\mathrm{AICr}_9\mathrm{Cr}_6\mathrm{N}_8(\mathrm{Cr},\mathrm{N})$ coatings obtaining as-deposited hardness values of 40 ± 2 GPa. The decomposition behaviour was investigated in tailormade vacuum annealing treatments (T$_{an}$ = 700 to 1200 °C) as well as cutting tests, clearly indicating enhanced stability for the oxygendContaining coatings. The detailed phase decomposition process was investigated by transmission electron microscopy (TEM) using selected area electron diffraction, energy-dispersive x-ray spectroscopy, and high resolution TEM. The incorporation of oxygen delays the fcc to w-AIN transition from at least 800 to 1000 °C, which correlates with the results observed in the cutting tests. In more detail, crater and flank wear formation and progress are clearly delayed during wet and dry milling operations. In summary, this study highlights the potential of defect engineering via oxygen incorporation, enhancing the thermal stability of metastable fcc-structured AlCrN based coatings. In contrast to metal alloying approaches, the non-metal sublattice adaption is a simple but highly effective way to tune the properties of well-established nitrides.

9:40am MA3-3-TuM-6 Enhancing Toughness in Nanocomposite AlCrSiN Thin Films by Crack Deflection at Sublayers: Correlating Microstructure and Micromechanical Properties, Kevin Kutlesa, M. Meindlhummer, Montanuniversität Leoben, Austria; A. Lassing, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; R. Daniel, Montanuniversität Leoben, Austria; A. Medjahed, C. Hugenschmidt, R. TuM, C. Saringer, L. Mathes, C. Czettl, M. Pohler, Technical University of Munich, Germany; M. Tkadletz, Montanuniversität Leoben, Austria

Wear-resistant transition metal nitride (TMN) thin films are recognized for their exceptional hardness, high Young’s modulus, superior thermal stability and oxidation resistance. However, their application is often limited by their brittleness leading to a low fracture toughness. This contribution presents a design approach encompassing (i) a nanocomposite AlCrSiN microstructure, (ii) a multilayer architecture reinforced with (iii) precisely controlled precipitation within targeted sublayers. The objective is to enhance the toughness of TMN thin films while preserving high hardness and other functional properties.

Cathodic arc evaporation was used to deposit two reference monothinic thin films, namely $\mathrm{AlCrSi}_4\mathrm{N}_9$ and $\mathrm{AlCr}_3\mathrm{Si}_3\mathrm{N}_4$, along with a multilayer thin film consisting of alternating sublayers of these two materials. A carefully adjusted vacuum heat-treatment at 1050°C for 5 min was applied to tailor the microstructure through precipitation. Qualitative analysis of the heat-treatment’s impact on thin film microstructure was conducted using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Additionally, insights into the assembly and elemental distribution in the nanocomposite microstructure were obtained through energy-dispersive X-ray spectroscopy in TEM. Cross-sectional synchrotron X-ray nanodiffraction (CSnanoXRD) at the ID13 beamline of ESRF in Grenoble facilitated the correlation of cross-sectional variations in phases, texture, microstructure, and residual stresses with the architecture and thermal history of the thin films. The nanoscale characterization revealed a nanostructured microstructure composed of cubic Cr(Al)N and wurzite Al(Cr)N nanocrystals with sizes of ~5 nm. In the material with lower Si content, the heat-treatment induced the precipitation of cubic Cr(Al)N, while in the higher Si content material precipitation was effectively suppressed. Consequently, in the heat-treated multilayer, a cross-sectional alternation of sublayers with significant precipitation and sublayers devoid of any precipitation was observed. Mechanical properties were assessed through in-situ bending tests on freestanding microcantilevers prepared by focussed ion beam milling. The Young’s modulus, fracture stress and fracture toughness were determined by loading up to fracture unnotched and notched cantilevers, respectively. A stepwise crack-propagation was observed in the heat-treated multilayer, revealing an unprecedented extrinsic toughening mechanism that significantly improved the fracture response.

10:00am MA3-3-TuM-7 Mechanical Properties and Tribological Performance of AlCrMoN TiSiN Nanostuctured Multilayer Coatings, Ming-Xun Yang, Y. Chang, National Formosa University, Taiwan

A TiSiN coating with a nanocomposite structure where TiN grains are surrounded by a SiN matrix possesses excellent mechanical properties and make it a promising selection for wear protection of cutting tools in machining applications. However, TiSiN coatings suffer from high residual stresses and thus limit the tribological performance and hinder high temperature applications of monolithic TiSiN coatings. Recently, Mo-containing AlCrMoN coatings have received widespread attention because of improved tribological performance and toughness. In this study, the mechanical and tribological properties of AlCrMoN/TiSiN coatings with different modulation geometries, namely modulation period and modulation ratio were elaborated. During the coating process of AlCrMoN/TiSiN, CrMoN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. An impact fatigue test using a cyclic loading device and a pin-on-disc wear tests at room temperature and 590 °C were conducted to evaluate the correlation between tribological properties and coating structures of the deposited coatings. X-ray diffraction (XRD) was used to characterize the microstructure, phase identification and residual stress. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM). A Rockwell indentation tester and a scratch tester were used to evaluate the adhesion strength between the coating and the substrate. The coating hardness and the elastic modulus were measured by nanoindentation. The addition of AlCrMoN into TiSiN to form a multilayer architecture provides an alternative for a hard-and-lubricious coating. The design of gradient and multilayered AlCrMoN/TiSiN coatings is anticipated to be advantageous in applications to enhance the mechanical properties and wear performance of mechanical parts and cutting tools.
Tuesday Morning, May 21, 2024

9:00am PP1-1-TuM-4 TaB thin film synthesis from an industrial-sized DC Vacuum arc source, Igor Zhirkov, A. Petruhins, A. Shamsigar, Materials Design Division, IFM, Linköping University, Sweden; S. Kolozsvári, P. Poliček, PLANSEE Composite Materials GmbH, Germany; J. Rosen, Materials Design Division, IFM, Linköping University, Sweden
Thin films of transition metal borides are gaining increasing attention due to their physical and chemical characteristics. Most publications in this area focus on TiB₂ synthesized through various sputtering techniques, targeting applications as protective hard layers. Tantalum diboride (TaB₂), another structure with interesting properties, especially for high temperatures, is much less explored. The elastic modulus of TaB₂ is ~2 times lower than that of TiB₂, but displays similar high hardness, combining high strength with high resistance to elastic and plastic deformation. Deposition of TaB₂ coatings with the industrially relevant physical vapor deposition (PVD) process DC vacuum arc is virtually absent in the literature. Still, DC arc deposition allows synthesis of coatings with a deposition rate unreachable for any other PVD technique. This motivates development and investigation of arc processes for TaB₂ synthesis. In the present work, we investigate DC arc plasma generation and deposition of TaB₂, and compare to previously investigated TiB₂. We use an industrial scale arc plasma source, Hauzer CARC+, which utilizes plane cathodes of 100 mm in diameter. Process stability and cathode dependent features of arcing is evaluated, and plasma analysis with respect to charge-state resolved ion energy is performed, showing a high ionization degree, and ion energies extending well above 100 eV. It is well known that plasma generation from compound cathodes gives a mass-dependent angular distribution for the elements of the compound, which is confirmed for the here investigated borides. This, in turn, is one of the factors contributing to a resulting film composition diverging from the cathode composition. The plasma characterization and macroparticle generation is correlated to deposited thin films; their composition, structure and properties. Altogether, the results show that DC vacuum arc is an industrially relevant technique for deposition of metal diborides.

9:20am PP1-1-TuM-5 Plasma enhanced magnetron sputtering and its applications in industry, Jianliang Lin, Southwest Research Institute, USA

Plasma enhanced magnetron sputtering (PEMS) technology is an advanced version of the conventional magnetron sputtering technique. The PEMS technique draws electrons off of hot filaments installed in a sputtering system when electrons have gained enough energy to exceed the work function of the filaments. The electrons collide with neutral atoms and generate a large number of ions through impact ionization. As a result, a global hot filament assisted plasma is formed in the entire chamber which is independent of the magnetron discharge plasma. The hot filaments also provide additional thermal energy without using external heating elements. Plasma diagnostics showed that the majority of the ions in the PEMS plasma exhibited low energies of less than 5 eV. However, a significant increase in the ion flux can be achieved by increasing the hot filament discharge current. The extra ion fluxes provide enhanced ion bombardment on the substrates, which is beneficial for improving the structure and properties of coatings. The PEMS plasma can be utilized to perform different surface engineering tasks, e.g. plasma cleaning/etching, plasma nitriding, and coating depositions. It can be easily combined with other magnetron sputtering techniques, e.g. DC, RF, pulsed DC, and high power impulse magnetron sputtering (HiPIMS) to enhance ion fluxes and thermal energies. In this presentation, the principle and characteristics of the PEMS technology will be introduced. Technical examples of PEMS coatings for different industry applications will be reviewed, for example, solid particle erosion resistant coatings for aerospace and OIl&Gas, duplex coatings for die casting dies, low friction nanocomposite coatings for combustion engine piston rings, protective coatings for high temperature sCo2 environment, etc.

Tuesday Morning, May 21, 2024
35
8:00 AM

8:40am PP1-1-TuM-3 Design of an innovative cathodic arc source with high deposition rate and low macroparticles generation, Raül Bonet, Eurecat Technological Center of Catalonia, Spain; L. Carreras, Tramamientos Térmicos Carreras S.A., Spain; J. Orrit, J. Bonet, Eurecat Technological Center of Catalonia, Spain

Within the group of PVD techniques, the cathodic arc evaporation technique stands out for its performance, which is characterized by a nearly 100% ionized, high energy plasma. Its versatility, lower economic cost compared to other deposition techniques and easy industrial scaling has led to a massive industrial implementation for the preparation of coatings and thin layers of different nature. One of the disadvantages of the cathodic arc technique is the generation of macroparticles because of the electric arc discharge on the cathode surface. This fact can be an important technological limitation for those cases where a good surface finish, low friction coefficient or good wear and corrosion resistance is required. Traditionally, this problem has been solved by applying magnetic filters that separate the macroparticles from the plasma ions. However, this solution involves a considerable reduction in the deposition rate, which makes its industrial implementation difficult. On the other hand, in order to reduce the coating process costs, cathodic arc sources that allow a high deposition rate are required.

In this work, an innovative cathodic arc source has been designed to achieve a deposition rate of up to 20 microns/hour, with a reduction of 80 % of macroparticles. In order to increase the deposition rate, a high-current pulsed source (100-500 A, 10-20000 Hz) has been used to generate the arc discharge between the anode and cathode. On the other hand, to reduce the generation of macroparticles, an optimized magnetic field configuration around the cathode has been obtained by means of Finite Elements Method (FEM) simulation, which allows to induce a fast and homogeneous movement of the electric arc on the cathode surface. Standard transition metal nitride (CrN, AlTiN) hard coatings obtained using this source exhibit excellent surface finish and improved mechanical properties in terms of adhesion and hardness.
Considering these aspects, high-performance coating technologies, such as HiPIMS, are becoming more and more interesting for the market. Thanks to HiPIMS dense, hard, adhesive, and droplet-free layers can be deposited in highest quality with high energy efficiency at high deposition rates. Furthermore, well-chosen HiPIMS pulse parameters combined with an appropriate bias synchronization can avoid high residual stress of coatings for sharp edged cutting tools.

In our presentation we show that optimization of HiPIMS pulse parameters leads to a significant increase in metal ionization, accompanied by improved coating properties of an AlTiSiN layer. The improved coating properties include above all a denser microstructure and a smoother surface, which allows to skip time consuming and energy-intensive post-treatment steps. Brilliant shine and best optical appearance are related with low friction and perfect chip removal during use. This combination of layer properties is a guarantee for a perfect surface finish of the workpiece.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-3-TuM
Coatings for Batteries and Hydrogen Applications III
Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, Chen-Hao Wang, National Taiwan University of Science and Technology, Taiwan
8:00am TS1-3-TuM-1 Oxygen Vacancy in Atomic Metal Oxide Clusters Demonstrate Outstanding Electrochemical Activity, Tsan-Yao Chen, National Tsing Hua University, Taiwan; K. Wong, National Central University, Taiwan
INVITED
Hierarchical structured heterogeneous catalyst comprising atomic metal oxide clusters with high contents of oxygen vacancy (O⁻) and the carbon or Co oxide supported metal / oxide nanoparticle (NPs) is developed for electrocatalytic application. Such a catalyst processes a collaboration between O²⁻ and the neighboring atoms in the electrochemical reaction. With this characteristic, the reaction kinetics of all steps are simultaneously operated consequent leading to a quantum leap on the current density and stability of the redox reaction. Apart from using noble metals, atomic scaled Co oxide clusters (CoOₓ₋₁) were employed. Those clusters are decorated in surface defect regions of Co oxide supported pd nanoparticles (CoOₓ-Pd) by using self-aligned nanocrystal growth followed by ultra-high-speed quench reaction with strong reduction agent. The decorated Coₓ₋₁ localize electrons from the neighboring atoms and thus boost the activity of CoOₓ-Pd in ORR. With a proper reaction time and loading control, the CoOₓ-Pd enhance its mass activity by 340 times as compared to that of commercial Pt catalysts in an alkaline electrolyte of 1.0M KOH.

8:40am TS1-3-TuM-3 Enabling Lightweight PEMFCs Based on PVD-Coated Aluminium Bipolar Plates for Aviation Applications, Parnia Navabpour, G. Sarzono, S. Field, Teer Coatings Limited, UK; K. Zhang, University of Birmingham, UK; H. Sun, Teer Coatings Limited, UK
The aviation sector is a significant player in the global energy crisis and toward climate change. It currently accounts for 12% of transport-related CO₂ emissions and 2-3% of all anthropogenic emissions. To tackle this, targets have been set by various governments and organisations on aviation CO₂ emissions and fuel efficiency. One tenable way to achieve these targets is through the use of hydrogen fuel cells for propulsion and/or auxiliary power units (APUs) in aircraft. The specific power of the fuel cell stack is a critical key performance indicator in the aviation industry, with bipolar plates being one of the most important components in a fuel cell stack, in terms of volume, weight and cost. Conventional PEMFCs utilise bipolar plates which are made from graphite or stainless steel. Hundreds of cells are needed within a multi-kW stack, hence a relatively small weight saving per plate will result in a large weight saving in the stack. The use of aluminium bipolar plates will enable the delivery of power densities double those of stainless steel bipolar plates. Challenges remain, however, with the corrosion of aluminium bipolar plates. This work focuses on the development of highly conducting and corrosion resistant coatings, aimed for PEMFC aluminium bipolar plates. The coatings were deposited using closed-field unbalanced magnetron sputtering technology and were evaluated for their adhesion and mechanical properties, as well as interfacial contact resistance and corrosion performance. Aluminium bipolar plates were coated and used in single cell fuel cells and tested under accelerated stress test conditions. The coated aluminium bipolar plates were compared with graphite plates and show the potential for using coated aluminium bipolar plates within PEMFCs.

Tuesday Morning, May 21, 2024

Day 1: Nano-structured Heterogeneous Catalysts
Tuesday Morning, May 21, 2024
Session TS1-3-TuM
8:00am TS1-3-TuM-1 Oxygen Vacancy in Atomic Metal Oxide Clusters Demonstrate Outstanding Electrochemical Activity, Tsan-Yao Chen, National Tsing Hua University, Taiwan; K. Wong, National Central University, Taiwan
INVITED
Hierarchical structured heterogeneous catalyst comprising atomic metal oxide clusters with high contents of oxygen vacancy (O⁻) and the carbon or Co oxide supported metal / oxide nanoparticle (NPs) is developed for electrocatalytic application. Such a catalyst processes a collaboration between O²⁻ and the neighboring atoms in the electrochemical reaction. With this characteristic, the reaction kinetics of all steps are simultaneously operated consequent leading to a quantum leap on the current density and stability of the redox reaction. Apart from using noble metals, atomic scaled Co oxide clusters (CoOₓ₋₁) were employed. Those clusters are decorated in surface defect regions of Co oxide supported pd nanoparticles (CoOₓ-Pd) by using self-aligned nanocrystal growth followed by ultra-high-speed quench reaction with strong reduction agent. The decorated Coₓ₋₁ localize electrons from the neighboring atoms and thus boost the activity of CoOₓ-Pd in ORR. With a proper reaction time and loading control, the CoOₓ-Pd enhance its mass activity by 340 times as compared to that of commercial Pt catalysts in an alkaline electrolyte of 1.0M KOH.

8:40am TS1-3-TuM-3 Enabling Lightweight PEMFCs Based on PVD-Coated Aluminium Bipolar Plates for Aviation Applications, Parnia Navabpour, G. Sarzono, S. Field, Teer Coatings Limited, UK; K. Zhang, University of Birmingham, UK; H. Sun, Teer Coatings Limited, UK
The aviation sector is a significant player in the global energy crisis and toward climate change. It currently accounts for 12% of transport-related CO₂ emissions and 2-3% of all anthropogenic emissions. To tackle this, targets have been set by various governments and organisations on aviation CO₂ emissions and fuel efficiency. One tenable way to achieve these targets is through the use of hydrogen fuel cells for propulsion and/or auxiliary power units (APUs) in aircraft. The specific power of the fuel cell stack is a critical key performance indicator in the aviation industry, with bipolar plates being one of the most important components in a fuel cell stack, in terms of volume, weight and cost. Conventional PEMFCs utilise bipolar plates which are made from graphite or stainless steel. Hundreds of cells are needed within a multi-kW stack, hence a relatively small weight saving per plate will result in a large weight saving in the stack. The use of aluminium bipolar plates will enable the delivery of power densities double those of stainless steel bipolar plates. Challenges remain, however, with the corrosion of aluminium bipolar plates. This work focuses on the development of highly conducting and corrosion resistant coatings, aimed for PEMFC aluminium bipolar plates. The coatings were deposited using closed-field unbalanced magnetron sputtering technology and were evaluated for their adhesion and mechanical properties, as well as interfacial contact resistance and corrosion performance. Aluminium bipolar plates were coated and used in single cell fuel cells and tested under accelerated stress test conditions. The coated aluminium bipolar plates were compared with graphite plates and show the potential for using coated aluminium bipolar plates within PEMFCs.
Vanadium redox flow batteries (VRFBs) have emerged as compelling candidates for large-scale energy storage systems. In this research, we present an innovative approach to surface modification of graphite felt (GF) electrodes utilizing the high power impulse magnetron sputtering (HiPIMS) system. The focus of this study involves the deposition of VNbMoTaWO and tungsten (W) onto GF within both argon (Ar) and oxygen environments, aimed at optimizing the VRFB electrode. A pivotal aspect of our investigation lies in the systematic variation of tungsten concentration, allowing for a comprehensive exploration of its nuanced effects on VRFB performance. Through severe electrochemical analyses and comprehensive battery tests, we meticulously unravel the intricate interplay between tungsten composition and VRFB efficiency. This research not only enhances our fundamental understanding of surface modification of GF electrodes in VRFBs but also holds significant promise for the practical application of these energy storage systems. The achieved improvements in performance and stability, facilitated by the elucidation of tungsten’s impact, signify a crucial step forward in advancing the viability and reliability of VRFBs in the landscape of large-scale energy storage.

Metal hydrides (MHx) provide a promising solution for a future hydrogen-based energy economy due to their high hydrogen storage density and safety advantages compared to compressed or liquefied hydrogen. However, so far, current hydrogen storage materials lack the requirements in one or more of capacity, absorption/desorption temperature and pressure, fast kinetics and cost. Thin films were proposed to ease the absorption/desorption cycles by maximizing the surface-to-volume ratio. Moreover, thin films can be used as a model to develop new material compositions. In this paper, we study the relationships between microstructure and composition of Ti2Zr1-x thin films, in order to reduce the absorption/desorption temperature increase their rate and to increase storage capacity. To achieve this goal, a series of Ti2Zr1-x thin films were deposited, on copper and silicon substrates, using pulsed-DC double-magnetron co-sputtering apparatus. The microstructure was controlled by changing the substrate bias voltage, while the composition was controlled by adjusting the power ratio to the Zr and Ti targets. The thin film’s hydrogenation was conducted as follows: The samples were held at 350°C under vacuum (< 5x10^-3 Pa) for 1 hr for surface activation, then the chamber was filled with pure hydrogen to 9.6±0.5x10^-4 Pa. The samples were held under H2 for 6 hours at 350°C before the chamber was evacuated and cooled down. Temperature-Programmed Desorption (TPD), Glow Discharge Spectroscopy (GDS), XRD and electron microscopy were used to study the microstructure of the films, hydrogen storage capacity, desorption temperature, and the durability for multiple absorption/desorption cycles. When deposited on copper substrate, puros TiH thin films showed a desorption temperature of 320-360°C, which was lower by ~150°C compared to dense TiH thin films. However, the puros TiH thin film had 25% less hydrogen stored. Moreover, the effect of the microstructure was not found in thin films deposited on Si substrates. The composition of Ti2Zr1-x thin films had also an effect on the desorption temperature and thin films with compositions of Ti62Zr38Hx and Ti50Zr50Hx showed hydrogen desorption onset temperatures lowered than TiH. These preliminary results show the ability of both microstructure and composition to control the properties of hydrogen storage materials.
The inventions of integrated circuits (1958) and the prediction of Moore’s Law (1965) will celebrate its 66th and 59th anniversary in 2024, respectively. The foundation of semiconductor industry and its amazing achievement has dramatically changed the way we lived.

With the advents of Artificial Intelligence (AI), Machine Learning and AR/VR (Artificial Reality, Virtual Reality) applications enabled by advanced semiconductor technology, there are high hopes we will see significant breakthrough in many areas such as vaccine research, auto-pilot, astrophysics and super computing, etc.

Taiwan plays a critical role as a hub of semiconductor R&D and manufacturing for the past several decades. In this presentation, the latest innovation of thin film materials and plasma-related process to drive the success of advanced technology nodes will be described. Furthermore, the future challenges and opportunities beyond 3nm nodes in order to keep Moore’s Law alive will also be presented.
Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM1-2-TuA
Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II
Moderators: Naureen Ghafoor, Linköping University, Sweden, Michael Tkadletz, Montanuniversität Leoben, Austria
1:40pm CM1-2-Tua-1 Structural Evolution of Nanoparticles Under Realistic Conditions Observed with Bragg Coherent X-Ray Imaging. Marie-Ingрид Richard, CEA Grenoble, France INVITED
The advent of the new 4th generation x-ray light sources represents an unprecedented opportunity to conduct in situ and operando studies on the structure of nanoparticles in reactive liquid or gas environments. In this talk, I will illustrate how Bragg coherent x-ray imaging [1] allows to image in three dimensions (3D) and at the nanoscale the strain and defect dynamics inside nanoparticles as well as their refacticing during catalytic reactions [2–4]. As an example, we successfully mapped the lattice displacement and strain of a Pt nanoparticle in electrochemical environment (see Figure 1). Our results reveal that the strain is heterogeneously distributed between highly- and weakly-coordinated surface atoms, and propagates from the surface to the bulk of the Pt nanoparticle as [bis]ulphates anions adsorb on the surface [5].
We will also discuss the possibility to measure particles as small as 20 nm [6] and to enable high-resolution and high-energy imaging with Bragg coherent x-ray diffraction at 4th generation x-ray light sources [7]. Finally, I will highlight the potential of machine learning to predict characteristic structural features in nanocrystals just from their 3D Bragg coherent diffraction patterns [7].
We acknowledge funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 818823).
In-situ and in-vacuo investigations of the thin films play a great role in the understanding of the thin-films growth processes, especially at the first stages. At the same time, a small amount of the material at these stages requires high precision and sensitive investigation techniques. Some synchrotron and neutron techniques are the most relevant for this task. However, in most cases, these investigation techniques have strict requirements for a sample and its environment.
In this work, we are presenting a possible solution to this problem - compact pulsed laser deposition (PLD) tools. The PLD method has a wide range of deposited materials and outstanding flexibility. The “sputtering instrument” of PLD - pulsed laser - is placed out of the vacuum chamber. That allows us to make the chamber as compact as possible.
The first realization example is an in-line PLD setup (fig. 1 supplementary) built for the MARIA neutron reflectometer (FZ Jülich, FRM-II), operating in a magnet gap in the presence of a high magnetic field. The height of the chamber is only 80 mm. At the same time, it has a sample temperature of up to 600K at the deposition position and down to 10K at the investigation position. A portable load-lock chamber allows reaching vacuum level up to 10^-6 mbar.
Recently, we have designed and tested a new portable cubic PLD chamber at P23 beamline “in situ X-Ray diffraction and imaging” PETRA III synchrotron (fig. 2 supplementary), which was used for in situ study of BaTiO3 thin films growth dependences. This experiment was focused on the critical thickness of the film depending on the strain induced by different substrate material. The substrates MgO(100), LaAlO3(100), SrTiO3(100) were used to apply compressive and tensile strains. Findings show possible effects of film thickness, growth temperature, and cooling rate.
The liquid-jet ultrabright X-ray source Excillum might be used for arrangement a laboratory-scale synchrotron-like machine. The usage of specially developed Montel optics allows to arrange a mm-scale spot on the sample with intensity comparable with 2nd generation Synchrotrons (10^14 ph/s*mm²). Specially developed compact lab-scale PLD machine can be easily attached to any analytical stage for vacuum transfer of samples and in-vacuo investigations of growth steps and interfaces formation by XPS (ARPS), XRR, XRD, XRF etc. techniques (fig.3 supplementary).
3:00pm CM1-2-Tua-5 Grain Boundary Segregation/Complexions in MT-CVD Ti(C,N) Thin Hard Coatings Analyzed by Nano-SIMS and Atom Probe Tomography, Idriss El Azhari, J. Barrirero, Saarland University, Germany; N. Valle, Luxembourg Institute of Science and Technology (LIST), Luxembourg; J. Garcia, Sandvik Coromant, Sweden; C. Pauly, F. Soldera, Saarland University, Germany; L. Llanes, Universitat Politècnica de Catalunya, Spain; F. Mücklich, Saarland University, Germany
Ti(C,N) is one of the most utilized thin hard coatings in metal-cutting industry in the last twenty years. In prior works, the authors carried out multi-scale testing and characterization experiments in which industrial cutting inserts coated with Ti(C,N) wear resistant hard coatings are contrasted to Zr(C,N) coated counterparts. The purpose was to comprehend the influence of the coating’s microstructural features on the deformation behavior of each coating and the corresponding impact on the entire coated cutting tool system. The investigation showcased that the more compatible coefficient of thermal expansion of Zr(C,N) with the substrate, the better cohesive strength at the grain boundaries and the plastic deformation were found to assign to the Zr(C,N) coated hardmetal improved structural integrity and fracture toughness in comparison to Ti(C,N) [1,2].
In this work, the focus is shifted toward Ti(C,N) to understand the correlation between deposition temperature and its impact on the microstructural features and segregation/complexions at the grain boundaries. For this purpose Ti(C,N) was deposited on a WC-Co substrate at two different temperatures (885°C and 930°C) using a moderate temperature CVD process (MT-CVD). Electron Backscatter Diffraction (EBSD) is used to examine microstructures. High-resolution secondary ion mass spectrometry imaging (nano-SIMS) and atom probe tomography (APT) were combined to investigate compositional variations inside single crystals and segregation at the grain boundaries. It is shown that segregation of chlorine at the grain boundaries is affecting not only the grain size of the columnar crystals, but texture and crystal shapes are indeed affected and modified as the chlorine concentration is decreasing with increasing temperature deposition. Methods to tailor the microstructure of these compounds are discussed and suggested.
Bibliography
Surface Engineering - Applied Research and Industrial Applications

Room Town & Country C - Session IA2-2-TuA

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications II

Moderators: Satish Dixit, Plasma Technology Inc., USA; SangYul Lee, Korea Aerospace University, Republic of Korea

1:40pm IA2-2-TuA-1 Transformative Manufacturing of Adaptive Wire Feedstocks with Atomic Layer Deposition of Nb2O5 onto Uranium, Mai Her, R. Bloom, I. Usay, T. Gorey, Los Alamos National Laboratory, USA

This study investigates the efficacy of Atomic Layer Deposition (ALD) in mitigating atmospheric corrosion of Depleted Uranium (DU). Three distinct samples, denoted as Sample A, B, and C, were obtained from the same DU wire. Prior to experimentation, all samples underwent nitric acid etching to eliminate native oxides. Sample B was subjected to ALD using a home-built reactor under conditions of 1 x 10^-6 Torr and 200°C, with a 5 nm film of Nb2O5. The ALD process employed H2O and Nb(NBu4)(NEt3) as precursor materials. Samples A and C, conversely, were not subjected to ALD treatment; instead, they were thermally treated at 65°C for 24 hours. Subsequently, Sample A was exposed to the atmosphere, while Sample C was maintained under vacuum. Sample B was also heated to 65°C and exposed to atmospheric conditions for the same duration. Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis revealed minimal to negligible U2O3 formation on Sample B, showcasing the exceptional effectiveness of the 5 nm thick Nb2O5 film in preventing atmospheric corrosion of DU. This investigation underscores the potential of ALD as a viable method for improving DU materials from atmospheric degradation with ultra-thin films.

2:00pm IA2-2-TuA-2 Impact of Novel Thermal Spray Material Solutions for Future Aerospace Applications and the Impact on Sustainability for the Environment and Business, Matthew Gold, Rolls-Royce North America

This presentation discusses the sustainability of materials and processes as applied to surface solutions in gas turbine engines. With the Aerospace industry under increasing pressure to improve the environmental performance of gas turbines, there is a growing need to reduce emissions and improve efficiency. This paper will outline the challenges associated with conventional materials and processes as well as the future materials that are being considered.

With an increase in turbine temperatures, industry is moving towards more advanced materials systems for survivability. Over the last decade, industry has increased its use of rare earth oxides in thermal barrier coatings to help overcome the challenge of survivability in this harsh environment. This advance in materials comes with an impact on sustainability for the environment and business.

This presentation discusses these advanced materials for future applications and the challenges that will be encountered for sustainability. This will include raw materials, abundance, availability, and the need to understand the impact of process efficiency on their usage.

2:40pm IA2-2-TuA-4 Evaluation of Thick Erosion-Resistant TiCrN Coating Deposited on Engine Impellers, Q. Wang, The University of British Columbia; Aurora Scientific Corp, Canada; L. Hsu, Aurora Scientific Corp, Canada; Da-Yung Wong, The University of British Columbia, Canada; Aurora Scientific Corp, Canada; Surftech Corp, Taiwan; Metal-nitride hard coatings deposited through physical-vapor-deposition (PVD) techniques are increasingly being utilized in aircraft engines to protect compressor components against erosion caused by sand particles. Among these coatings, TiCrN, a ternary nitride coating with nano-layered configuration, exhibits promising results for application on turbine engine impellers to enhance erosion resistance. However, the deposition of TiCrN on impeller blades poses a unique challenge due to the sharp leading and trailing edges with curved airfoils, causing a shadowing effect during coating deposition. This can lead to non-uniform coating at sharp edges, resulting in spallation caused by high residual stress. To address this challenge, we employed various strategies, including a specially designed fixture providing two-axial rotation to the impeller, the incorporation of masking fingers to mitigate high coating deposition rates at sharp edges, modification of the ion cleaning process to enhance coating adhesion, and adjustments to chamber conditions such as increased working pressure using a mixture of N2 and Ar gases while reducing the substrate bias voltage to reduce coating residual stress. The TiCrN coating applied to a stainless-steel impeller and flat coupons by using cathodic arc deposition, underwent comprehensive characterization and testing. The coated impeller exhibited excellent surface coverage without spallation or cracking. The TiCrN-coated blades displayed consistent chemical compositions, and the surface roughness values (Ra) were maintained below 0.7 μm. The average hardness value of the coating was 2204 HV. The coating had excellent coating/substrate adhesion strength with critical loads higher than 40 N. Compared to the uncoated 1Cr11Ni2W2MoV substrate alloy, the TiCrN-coated blades demonstrated more than two times improvement in erosion resistance at 30°, 60° and 90° impingement angles. Furthermore, the TiCrN-coated samples exhibited no signs of corrosion damage after exposure to salt fog for 60 hours. In conclusion, the TiCrN coating applied to the stainless-steel substrate demonstrated exceptional performance in terms of erosion resistance, highlighting its potential for use in protecting turbine engine impellers in aircraft engines.
Liquid-infused Porous Surfaces approach (SLIPS) being one of the most innovative and intriguing possible solutions to inhibit ice accretion or weaken the ice adhesion strength without any power supply [2]. This study presents the design of anti-wetting hybrid SLIPS coatings for cold environments that comprise an inorganic, porous ceramic scaffold with grafted fluoroalkyl silane molecules infused with a lubricant polymer. The reduction of ice adhesion was determined with the Double Lap Shear Test, while the dynamic behavior of droplets was evaluated via goniometric contact angle hysteresis calculation, at both room and sub-zero temperatures [3, 4].

For the modeling of the different icing phenomena that happen on the proposed air intake, dedicated testing methodologies have been developed: i) direct impingement of supercooled droplets through an icing wind tunnel located in a cold climate chamber, and ii) running wet icing in which there is a water flow coming from an upstream heated area.

The coatings, validated through laboratory experiments and tests in icing wind tunnels, will undergo further testing in real-world icing conditions using a flight test aircraft as part of NATO’s AVT-332 activity “In-Flight Demonstration (CDT) of Icophobic Coating and Ice Detection Sensor Technologies”.


Tuesday Afternoon, May 21, 2024

5:00pm IA2-2-TuA-11 Development of Environmentally Friendly Solid Carburizing for Improving Fatigue Properties of AISI 4118 Steel, Tomofumi Aoki, D. Kasai, Graduate School of Science and Technology, Keio University, Japan; M. Hayama, Keio University, Japan; S. Takesue, Kyoto Institute of Technology, Japan; M. Tsukahara, Y. Misaka, Neturen Co., Ltd., Japan; J. Komotori, Keio University, Japan

Gas carburizing is used extensively in the industry to improve the fatigue properties and the wear resistance of steel. However, the process is time-consuming and emits large amounts of gases, such as CO2. Thus, we focused on atmospheric-controlled induction heating fine-particle peening (AIH-FPP) to resolve these challenges.

AIH-FPP combines induction heating and fine-particle peening. Shot media was projected onto a specimen heated with an IH coil. In AIH-FPP, when carbon is used as the projection media and steel is used as the base material, carbon can diffuse into the steel, and carburizing can be achieved rapidly. We named this process environmentally friendly solid carburizing, as it controls CO2 emission and lessens the environmental burden. Accordingly, the aim of this study is to improve the fatigue properties of steel in a reduced time using this process. The material used in this study was SCM 420H (AISI 4118 or equivalent) and the steel was machined into hourglass-shaped specimens. The air in the chamber was replaced with N2 gas. The specimens were heated to 1273K for 30 s and then held at the temperature for 60 s. While heating and maintaining the temperature, steel particles coated with carbon were projected. The specimens were then cooled with N2 gas. Afterward, these wererouchened. We also prepared conventional gas carburized specimens.

An electron probe micro analyzer (EPMA) was employed to analyze the distribution of carbon concentration. The microhardness of each specimen was examined on their longitudinal section using a micro Vickers hardness tester. The fatigue test was conducted under axial loading with the stress ratio of -1 at room temperature, and test frequency of 10 Hz.

Environmentally friendly solid carburizing process diffused carbon up to 300 μm from the specimen surface and increased the carbon content on the specimen surface to approximately 0.5 mass%. No significant decrease in hardness was observed in the vicinity of the specimen surface. This result suggests that grain-boundary oxidation did not occur. This is because of the extremely low O2 present in the treatment chamber, indicating that no CO was produced during the treatment. In addition, we consider that C-H2 is not produced during the treatment due to the displacement of the air with N2 gas in the chamber. These results strongly suggest that the carbon diffused in this process by a mechanism different from the conventional gas carburization.

The fatigue life at the stress amplitude of 700 MPa was approximately 10 times longer than that of a conventional gas carburized specimen. This is because of the higher hardness on the specimen surface.

Protected and High-temperature Coatings
Room Palm 1-2 - Session MA1-2-TuA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II
Moderators: Gustavo Garcia-Martín, REP-Energy Solutions, Spain, Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK, Eli Ross, Pratt & Whitney, USA

1:40pm MA1-2-TuA-1 Fabrication, Characterisation and Fretting Wear Testing of Magnetron Sputtered Cr and CrN Coated Zr Alloy Cladding for Enhanced Accident Tolerance in Light Water Reactors, T. Rachid Netto, Manchester Metropolitan University, Brazil; A. Evans, Peter Kelly, Manchester Metropolitan University, UK; D. Goddard, J. Cooper, National Nuclear Laboratory, UK

Research into accident-tolerant fuels (ATFs) for light water reactors (LWRs) has focused on improving the safety of zirconium alloy fuel rod claddings and one of the more developed approaches is the use of chromium coatings deposited onto the claddings. In addition to performing in oxidising conditions, normal operation also causes fretting wear on the fuel rod surface, which requires tribological improvements.

The aim of this work, therefore, is to produce Cr and CrN coatings using the magnetron sputtering technique for Zr alloy nuclear fuel rod cladding
material to enhance oxidation and mechanical resistance. This research is examining how the integrity and microstructure of the coating is affected by deposition conditions and coating thickness. The coatings were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), optical profilometry and contact angle goniometry. A linear reciprocating wear tester was used to mimic fretting. Our results demonstrate that fretting resistance can be related to the different densities and thickness of coating produced and, in turn, related to the deposition parameters.

2:00pm MA1-2-Tua-2 Fuel-cladding Thermochemical Interaction Study of Cr2O3 Coating Deposited by DLI-MOCVD on Zircaloy-2 Substrate, Kenza Zougagh, Université Paris-Saclay, CEA, Service de Recherche en Matériaux et procédés Avancés, France; R. Chanson, A. Quaini, F. Rouillard, S. Gossé, Université Paris-Saclay, CEA, Service de recherche en Corrosion et Comportement des Matériaux, France

In a nuclear reactor, the fuel cladding is the subject of particular attention since it constitutes the first safety barrier. Its mechanical integrity must therefore be guaranteed in a wide range of conditions from nominal operation to hypothetical incidental conditions.

The idea of improving the behavior of the zirconium-based claddings with the addition of external coatings in the frame of ATF (Accident Tolerant Fuels) is now widespread. However, internal thin films coatings can also be an effective solution to increase the resilience of fuel claddings under undesirable situations. There are many fewer developments proposing the addition of these internal coatings, probably due to the difficulties encountered in developing proper homogenous layers along the full-length.

In this work, chromium oxide is studied as a candidate material for an internal layer of the nuclear fuel cladding for the mitigation of pellet-cladding thermochemical interaction. This coating is deposited by the DLI-MOCVD process on a Zircaloy-2 substrate. This process has been already demonstrated relevant for coating the internal surface of nuclear fuel claddings [1]. This study highlights the influence of the process parameters on the coating properties. After satisfactory film deposition, physicochemical and microstructural properties of the coating are characterized. The performance of the chromia layer against Zircaloy – UO2 interaction is investigated at high temperature between 400 and 800°C using diffusion couple testing with natural UO2 pellets. Moreover, the interaction between the chromia layer and Zircaloy is studied at temperatures up to 1200°C. All experimental results are compared to thermodynamic predictions using the Calphad method.


2:20pm MA1-2-Tua-3 Evaluation of Wear and Corrosion Resistance in Acidic and Chloride Solutions of Pvd-Crn Coatings on Untreated and Plasma Nitrided Aisi 4140 Steel, A. Maskavizan, E. Dalibon, National University of Technology (UTN), Faculty of Conception del Uruguay, Argentina; S. Farina, CNEA and CONICET, Buenos Aires, Argentina; J. Quintana, CNEA (CAC), Buenos Aires, Argentina; Sonia P. Brüh, National University of Technology (UTN), Faculty of Conception del Uruguay, Argentina

CrN coatings deposited by Physical Vapor Deposition (PVD) are widely used due to their high hardness and high wear resistance, low friction coefficient and superior corrosion resistance. The latter makes this coating appropriate for protecting forming tools, moulds and components used in chemical processing.

In this work, single layer CrN coatings were deposited on plasma nitrided and non treated AISI 4140 steel. The influence of nitriding on the wear resistance, coefficient of friction and corrosion resistance in acidic solutions and chloride solutions was studied. The thickness of the coatings was measured using optical microscopy, and surface hardness was assessed with a Vickers microindenter. Adhesion was determined using Rockwell indentation applying 150 kg and Scratch test at different constant loads. Sliding wear resistance was studied with Pin-on-Disk tests under different normal loads and sliding distances, the coefficient of friction was registered during the tests and volume loss was calculated. Corrosion tests were carried out using a 3.5 % NaCl solution and a 0.5 M H2SO4 solution as electrolytes. Nitrided steel without any coating was used also as comparison. Coating thickness was approximately (2.6 ± 0.4) μm and surface hardness reached a value of (1960 ± 160) Hv0.1, being this a composed hardness because of the low film thickness. Adhesion was good for both substrates, non nitrided and nitrided steel, in both cases, it could be classified as HFI according to VDI 3198 standard. In the case of the Scratch test, in the only coated samples, without nitriding as pre treatment the film cracking was observed at 50 N in the track, whereas in the duplex sample the coating had a better load bearing capacity and reached 70 N without damage. No delamination was detected around the scratch track in all cases. Wear volume loss was undetectable in the pin-on-disk test for the coated systems, whereas it was approximately 30 × 10^-3 mm^3 for the nitrided and 150 × 10^-3 mm^3 for the untreated steel. In the corrosion tests, the coating showed a passive behaviour as tested in NaCl solution and the corrosion current density was significantly lower for coated samples in the H2SO4 solution, proving that the CrN coating is suitable for protecting the steel substrate in both chloride and acidic media.

2:40pm MA1-2-Tua-4 Deposition using CHC-PVD Method and High Temperature Oxidation of TiAlCrYSi Coatings on Tial, Radoslaw Swadzba, Lukaszewicz Research Network – Upper Silesian Institute of Technology, Poland; B. Mendala, I. Swadzba, Silesian University of Technology, Poland; U. Schultz, N. Laska, R. Bauer, German Aerospace Center (DLR), Germany

This work concerns the application of Closed Hollow Cathode - Physical Vapor Deposition (CHC-PVD) method for the deposition of TiAlCrYSi on a 48-2 TiAl alloy. During the deposition process the samples were placed within the hollow cathode with diameter of 80 mm and length of 160 mm and the process gas mixture TiAlCrYSi-15 at 5×10^-5 mbar. Thermochemical Interaction Study of Claddings [2]. This study highlights the influence of the process parameters on the coating properties. After satisfactory film deposition, physicochemical and microstructural properties of the coating are characterized.

The performance of the chromia layer against Zircaloy – UO2 interaction is investigated at high temperature between 400 and 800°C using diffusion couple testing with natural UO2 pellets. Moreover, the interaction between the chromia layer and Zircaloy is studied at temperatures up to 1200°C. All experimental results are compared to thermodynamic predictions using the Calphad method.


3:00pm MA1-2-Tua-5 Empowering PVD for Corrosion Protection: TiMgGdN Coatings with Game-Changing Corrosion Performance, Holger Hoche, T. Ulrich, M. Oechsner, TU Darmstadt, Germany; P. Polick, Plansee Composite Materials, Germany

Today, PVD technology is not the 1st choice for surface functionalization under corrosive conditions. Sate of the art for applications in corrosive environments is corrosion protection base layers by electroplating followed by a PVD top layer. This effects sustainability and economic factors in a negative way.

The authors successfully developed coatings by alloying the well known TiN with MgGd. TiMgGdN. The coatings were deposited by DC magnetron sputtering in an industrial DC magnetron PVD unit by using powder metallurgical TiMgGdN-targets. The targets were custom built by Plansee Composite Materials. With an only 5 μm coating thickness of the monolithic TiMgGdN, corrosive mild steel substrates can be protected for at least 1000 h in the salt spray test against corrosion [1]. After experimentally improving the mechanical, microstructural and corrosive properties of these coatings, the corrosion protection mechanism of alloying MgGd into the TiN matrix will be explained. Therefore, TiN and TiMgN coatings were compared with TiMgGdN coatings regarding their microstructural, chemical, physical and corrosion properties. Corrosion properties were investigated by different corrosion tests and the coatings were analyzed before and after the corrosion test using nanoindentation and chemical analysis to gather knowledge regarding the coating stability during corrosive stresses.
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It will be shown that the excellent corrosion performance is mainly influenced by Mg and MgGd, respectively. Different corrosion protection mechanisms were identified. Depending on the chemial composition of the coating, the corrosion performance, stability and microstructure of the coatings can be controlled. Here, especially Gd contributes to the corrosion performance and coating stability.


4:00pm MA1-2-Tua-8 Investigations of Water Vapor Enhanced Oxidation on TiAl-Based Alloys: Evaluation of Protective Coating Systems, Ronja Anton, N. Lasko, German Aerospace Center (DLR), Germany

Currently, intermetallic y-TiAl alloys are being used as material for turbine blades in the low-pressure turbine to replace the heavier Ni-based superalloys due to their low cost per kg and high specific enthalpy. The limitation to service temperatures below 800 °C is due to strength and creep resistance at elevated temperatures, as well as a reduced oxidation resistance. The latter can be surpassed with the aid of remarkably effective oxidation-protective coatings. These coatings result in the formation of a dense, thermally grown oxide (TGO) scale, Al2O3. However, new turbine engine concepts, such as the Water Enriched Turbomach (WET) engine concept or the use of hydrogen-based fuels in jet engines, introduce higher amounts of water vapor. Now, not only the y-TiAl alloys need to be evaluated under more severe conditions, but also the highly studied protective coatings need to be tested in this harsher environment. The mechanism by which water vapor content and temperature may be affecting uncoated and coated y-TiAl alloys needs to be understood.

For a further enhancement of the protection, a coating system with a ceramic top coat should be considered. Protective coating systems on SiC/SiC CMCs forming SiO2 as a TGO layer, mostly contain Yb- or Y-silicates as a top coat due to their low oxygen diffusion and matching coefficient of thermal expansion (CTE). A protective coating system for y-TiAl alloys with Al2O3-forming bond coats could be completed by Yb-aluminates, which also show low oxygen diffusion and CTE comparable to the alloys.

In the present work, y-TiAl alloys were tested isothermally under water vapor enhanced oxidation up to 30 wt.% water in a tube furnace. The growth of a thick Al2O3/TiO2 mixed oxide scale was analyzed on uncoated y-TiAl alloys. Different coating concepts such as Ti-Al-Cr, Al-Si and Ti-Al-C deposited by DC magnetron sputtering could already improve the resistance of y-TiAl alloys in dry oxidation conditions. In water vapor enhanced oxidation processes, the growth of the protective Al2O3 oxide scale is increased. In order to assess the need for an ceramic top coat, the oxide growth as a function of temperature and different water contents was evaluated. Therefore, different analyses like SEM, EDX, XRD and thermogravimetric analyses were performed. Finally, first concepts of Yb-aluminates as a protective ceramic top layer by using the previously established layers as bond coating are introduced in terms of reactive sputter deposition, phase stability and improvement of the coating system.

4:20pm MA1-2-Tua-9 Effect of Duty Cycle and N2 Flow Rate on Structure and Oxidation Behavior of VN Coatings Deposited by High Power Impulse Magnetron Sputtering, Ruo-Syuan Chen, J. Huang, National Tsing Hua University, Taiwan

Unlike traditional nitride metal protective coatings, VN coatings possess not only superior mechanical properties and corrosion resistance but also self-lubrication characteristics. The formation of Magnéli oxide phases at high temperature can enhance wear resistance [1]. Previous literature indicated that the duty cycle and N2 flow rate have significant influence on the quality and properties of VN thin films [2-4]. Although there have been numerous studies on the oxidation behavior of VN coatings, the influence of nitrogen flow rate and duty cycle on their structure and oxidation behavior remains unclear. Therefore, this study aims to investigate the oxidation behavior of VN coatings deposited at different duty cycles and N2 flow rates. VN coatings with a thickness of 1 mm were deposited on Si substrate by high power impulse magnetron sputtering (HIPMS). The duty cycles were controlled to be 3% and 10%. The N2 flow rates were set at 2 and 4 sccm. After deposition, the N/V ratios of the coatings were determined using X-ray photoelectron spectroscopy and the microstructure was observed by scanning electron microscopy (SEM). X-ray diffraction was used to characterize the crystal structure and the preferred orientation of the coatings. The residual stress of the specimens was measured by laser curvature measurement and average X-ray strain combined with nanoindentation methods [5,6]. The oxidation behavior of the coatings was investigated using thermo-gravimetric analysis at temperature ranging from 400 to 700°C in dry air atmosphere. From the experimental results, the oxidation behavior of the VN coatings was discussed.


Tribology and Mechanics of Coatings and Surfaces

Room Town & Country B - Session MC2-1-TuA

Mechanical Properties and Adhesion I

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, Alice Lassnig, Austrian Academy of Sciences, Austria, Bo-Shiuann Li, National Sun-Yat Sen University, Taiwan

1:40pm MC2-1-TuA-1 Boosting Mechanical Properties of Metallic Thin Films Through Advanced Nanoeengineered Design Strategies, B. Francesco, LSPM-CNRS, France; A. Brognaer, Max-Planck-Institut für Eisenforschung, Germany; P. Djemia, D. Faurie, LSPM-CNRS, France; A. Li Bassi, Politecnico di Milano, Italy; G. Dehm, Max-Planck-Institut für Eisenforschung, Germany; Matteo Ghidelli, Laboratoire des Sciences des Procédés et des Matériaux (LSPM), CNRS, France

The current trend toward miniaturization in devices components in key technologies such as micro-/nanoelectronics, energy production, sensors and wear protection requires the development of high-performance nanostructured films with superior mechanical properties. Especially, mutually excluding structural properties such as high yield strength and ductility need to be combined, but also high adhesion with the substrate and large fatigue resistance. In order to trigger microstructure-induced material properties, control of the micro-scale structure, atomic composition, average grain size, and layer/film thickness must be optimized based on nanoeengineering design concepts.

Here, I will present recent results for several class of advanced thin film materials including nanostructured metallic glasses (ZrCuO, ZrCuAlO...)[1-3] high entropy alloys (CoCuCrFeNi, Al/CuCoFeCrNi) and nanolaminates (fully amorphous, amorphous/crystalline)[4], showing how the control of microstructure affect the and micro-scale mechanical behavior and enable ultimate mechanical properties.

Among the main results, I will show the potential of Pulsed Laser Deposition (PLD)[1, 2] as a novel technique to synthesize nanostructured cluster-assembled ZrCu, ZrCuAlO, and CoCuFeNi films, reaching ultimate yield strength (>4 GPa) and ductility (>15 %) for ZrCuAlO films. I will show how the control of the sublayer thickness (from 100 down to 5 nm) in fully amorphous nanolaminates influences the deformation behavior suppressing the shear bands formation, while tuning the mechanical properties with mutual combination of large ductility (> 10%) and yields strength (>2.5 GPa). Finally, I will show how alternating CrCoNi (crystalline)/TiZrNbHf (amorphous) nanolayers in an high compressive yield strength (3.6 GPa) and large homogeneous deformation (~15%)[4].

Overall, our results pave the way to the development of nanostructured thin films with boosted mechanical properties and wide application range.

Refs.
Understanding and controlling residual stress in sputtered metal-nitride films is important because of the impact it can have on their properties. Numerous studies have quantified the stress for different systems and processing conditions and modeling has attempted to explain the stress in the terms of the underlying kinetic processes. Although ternary nitride alloys are used in many applications, there is much less understanding of stress in these systems relative to the binary alloys. In this work, we present results of stress in Ti2N, TiN, and ZrN at different growth rates and pressures. Comparison of the ternary alloy with the two constituent binary alloys sheds light on how the addition of a second metal element modifies the stress. The results are interpreted in terms of mechanisms that have been proposed for explaining the stress generation in sputter-deposited films. These include tensile stress due to island coalescence and compressive stress due to insertion of excess atoms into the grain boundary and the effect of energetic particle bombardment.

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to equi-biaxial tensile loading [4] with in-situ X-ray diffraction and electrical resistivity measurements at Synchrotron SOLEIL. The evolution of Al film stress, width of the Al diffraction peak and electrical resistivity could be determined as a function of L thickness and applied strain. The Al and oxide layer thickness and microstructure as well as crack density and spacing after testing were investigated using scanning and transmission electron microscopy. Our results reveal a positive influence of the preceding ALD step on the mechanical properties of the Al thin films. All films with artificial ALD interlayers show reduced roughness and grain width in their PVD sputtered Al layers, resulting in a higher 0.2% yield stress, while overall maintaining ductile electro-mechanical behavior. This is possibly due to modifications of the PI substrate surface through ALD. Significant embrittlement was observed only in the Al film with 25 nm interlayer thickness. Most notably, comparison of a 5 nm artificial and natural interlayer shows a similar resistivity but a two-fold increase in yield strength in the artificial case. Adhesion between metal film and polymer substrate was evaluated with the tensile induced delamination method, indicating better adhesion (lower buckle density) with artificial AlO x interlayers.


Tuesday Afternoon, May 21, 2024

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP1-2-TuA
PVD Coating Technologies II
Moderators: Christian Kalscheuer, RWTH Aachen University, Germany, Vladimir Pankov, National Research Council of Canada

1:40pm PP1-2-TuA-1 Use of van der Waals Layers and Ultrahigh Vacuum Environment to Control Composition and Crystallinity in Sputter-Deposited Thin Films, Suneel Kodambaka, Virginia Tech, USA; K. Tanaka, A. Decker, S. H. Oh, J. F. Scott, T. Blake, M. Liao, University of California at Los Angeles, USA; C. Ciobanu, Colorado School of Mines, US; M. Goorsky, University of California at Los Angeles, USA

Compositional control in sputter-deposited thin films is typically achieved via changing the deposition parameters, such as partial pressure of the reactive gases, substrate temperature, deposition fluxes, and the target composition. Common approaches to improve crystallinity, to increase grain size and the grain orientation in thin solid films typically involve the use of single-crystalline substrates, high substrate temperatures combined with low deposition fluxes, and energetic ion beams.

In this talk, I will present approaches involving the use of ultra-low (e.g., 0.002%) partial pressures of the reactive gases and van der Waals (vdW) layers as buffer layers to grow thin films of desired composition and enhanced crystallinity. Using Ta-C and Mo-S as model materials systems, we demonstrate compositional tunability and improved crystallinity. We also showed that Ta-C thin films grown on Ta-C(0001) covered with hexagonal boron nitride (hBN), a vdW-bonded material, are more highly oriented than those films grown directly on bare Ta-C(0001) under identical deposition conditions. That is, heteroepitaxial growth across a vdW layer seemingly yields better crystalline quality than homoepitaxy. We observe similar highly-oriented growth of face-centered cubic Pd, body centered cubic Mo, and hexagonal MoS 2 thin films on hBN-covered substrates. Our results provide new insights into the factors underlying the growth of highly-oriented thin films.

2:20pm PP1-2-TuA-3 Methods for Rapid Modeling of PVD Processes to Establish a Digital Twin of a Coater, Stephanie Lucas, Laboratoire d’Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, Belgium; G. Atanosoff, AccuStrata, USA; P. Moskovkin, J. Muller, Laboratoire d’Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, Belgium; E. Huyse, Innovative Coating Solutions - ICS, Belgium

Thin film materials are key components in a variety of applications including automotive and mechanical engineering, optics, nanotechnology, medical applications, photovoltaics and displays. Their performance and reliability depend to a high degree on the precision, reproducibility and intrinsic performance of the coatings involved. Besides empirically derived knowledge, fundamental insights of the mechanisms underlying the synthesis process and intrinsic material properties can be easier acquired through a coupled process and material modelling approach. Therefore, with increasing size, throughput, functional integration of coated products as well as market specific regulatory requirements, a simulation-driven development of deposition processes and advanced thin film materials becomes a necessary tool.

The Virtual Coater™ project aims to realize an easy-to-operate and computer-low-resources computational material-modelling platform that serves as a transition environment to accelerate the development of thin
film materials and the related deposition processes. Making use of existing and validated simulation tools, it provides a multi-physics approach for the prediction of deposition process features as well as intrinsic film properties. Process features from a 3D description of industrial coater includes the prediction of film uniformity and deposition rate, whereas intrinsic film properties are linked to the composition, microstructure and morphology (e.g. density, surface roughness and defects), optical, mechanical and electrical properties. Besides detailed models of process dynamics and film material models, this simulation framework is capable of real-time capable process simulation.

These developments together will lead to a much efficient approach and tool to support the co-design of coating materials and substrate systems, optimization of PVD processes, and reduced overall new coating system development cycle time by 50-100%, and material savings and waste reductions for developing the new coating systems by at least by 4-5 folds, comparing to traditional experimental trials and error approaches.

We will present the latest developments in the field (ours and from others), and we will demonstrate how a modeling platform built on optimized fast multi-scale algorithms can depict a “digital twin” of an industrial magnetron sputtering system, and how it can be used to tune the deposition process to achieve desirable coating properties. Extension toward coating properties optimization with Genetic Algorithms will also be presented together with 2D and 3D examples.

Tm: Virtual Coater and NASCAM are trademarks of the University of Namur, Be.

2:40pm  PP1-2-TuA-4 Generating Spokes in Direct Current Magnetron Sputtering Discharges by an Azimuthal Strong-to-Weak Magnetic Field Strength Transition, Martin Rudolph, W. Dijamiko, Leibniz Institut of Surface Engineering (IOM), Germany; O. Rottende, H. E. Schuegengel, Evatec AG, Switzerland; D. Kalonov, Leibniz Institut of Surface Engineering (IOM), Germany; J. Patscheider, Evatec AG, Switzerland; A. Anders, Leibniz Institut of Surface Engineering (IOM), Germany

Spokes in magnetron discharges are zones of enhanced excitation and ionization that can be suspected to influence the ion ejection from the plasma toward a substrate and by that influence a deposited thin film morphology. Here, we show that spokes can be generated at a desired location by introducing a step in the magnetic field strength along the racetrack. For the experiments we use a magnetron with a 300 mm Al target operated in direct current mode. Two magnetic field strength transitions are obtained when splitting the racetrack into a section with a weak parallel magnetic field strength above the racetrack of ≈ 40 mT, and a strong magnetic field strength section with ≈ 90 mT. Using a gated intensified charge-coupled device (ICCD) camera, we observe the generation of spokes where drifting electrons transit from the strong to the weak magnetic field. The generated spokes move against the electron Hall drift into the strong magnetic field section, thereby creating a region of high spoke activity. The observation can be explained by an accelerating electron drift velocity as the magnetic field strength weakens. At the transition from the weak to the strong magnetic field, we observe a region of enhanced light emission that we attribute to the accumulation of electrons due to a lower drift velocity in a strong magnetic field. The observed effect is similar to a cross-corner effect known from rectangular magnetrons and we confirm here that this effect is primarily due to the change in the magnetic field strength and not caused by the geometry of the racetrack.

3:00pm  PP1-2-TuA-5 The Surface Temperature of a 2° Water-Cooled Ti Target Measured During DC Magnetron Sputtering, Stephen Muhl, J. Cruz, A. Gorzon, Universidad Nacional Autonoma de Mexico

The lateral temperature of a 2° diameter water-cooled titanium target was measured using an electrical floating fine, 0.005° wire, type K chromel-alumel thermocouple. The temperature measurements were performed as a function of the DC plasma power (power densities of 1.0, 2.2 and 4.1 W/cm2) and Ar gas pressures of 10 to 60 sccm. Typically, the temperature difference between the centre of the target and inside the racetrack was more than 200 °C, the racetrack temperature increased almost linearly with the applied power to a maximum value of ~840 °C.

The target temperature was also investigated as a function of the N2 gas concentration in the Ar gas mixture (1 to 20%), and these measurements are compared with the elemental composition of the deposits produced.

4:00pm  PP1-2-TuA-8 Black Metal Thin Films Deposited on Cooled Substrates by Sputtering, Midori Kawamura, H. Iino, H. Mori, Y. Otomo, T. Kiba, Y. Abe, Kitami Institute of Technology, Japan; M. Ueda, Hokkaido University, Japan; M. Micusik, Slovak Academy of Sciences, Slovakia; M. Hruska, M. Novotny, P. Fitl, University of Chemistry and Technology, Czechia

Black metal thin films with a porous structure being broadband light attractor are attractive for various applications such as photothermic conversion and photodetection. Recently, they are expected to be applied to gas sensors, due to their large surface area. In addition to vacuum evaporation, sputtering has also been reported as a method for preparation of black metal thin films [1]. It has been well known that porous films can be obtained at low substrate temperature and high Ar gas pressure based on the structure zone model by Thornton. We have attempted to prepare black Al, Ag and Au thin films by sputtering on the substrate cooled with liquid nitrogen to suppress surface diffusion of atoms. The sputtering power and Ar gas pressure were also changed to obtain the films with porous structure. An RF magnetron sputtering system, in which the substrate can be cooled by liquid nitrogen, was mainly used for the deposition. The films were deposited on glass and Si substrates at room temperature, 80°C, and 170°C with Ar gas pressure of 6.5 - 33.3 Pa and sputtering power of 100 - 150 W at background pressure below 3.3 x 10⁻³ Pa. The deposited films were characterized by four point probe, SEM, AFM, XRD, XPS, and spectrophotometer. The Al films obtained at low temperature were black in color. However, metallic luster was observed from the backside of glass substrate. It means that a porous layer was formed after a thin dense layer was formed on the substrate. It was also found that black films formed by deposition at high Ar gas pressures and high RF powers. The light absorption of the films obtained was as high as 80% for the black Al films. The samples had a columnar structure and (100) crystal orientation. In conclusion, our results show that black metal films can be obtained by sputtering at low temperatures, high gas pressures and high RF powers. As shown in the figure, conditions which we explored for Al deposition are beyond the SZM. We are currently engaged in experiments with new deposition conditions, such as sputtering in Kr gas and DC power discharge, and results of these experiments will be presented as well.

Acknowledgement This work was supported by JST SICORP Grant Number JPMJSC2108, Japan, the Ministry of Education, Youth and Sports of the Czech Republic project No. 8F21008, and project No. JP22420 from the International Visegrad Fund.


2:40pm  PP1-2-TuA-9 Intelligent Lubricating Coatings Based on the Oblique Angle Deposition Technology, J. Liang, K. Li, K. Le, Shusheng Xu, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

This research introduces an innovative approach to construct intelligent lubricating coatings by filling lubricants into the oblique angle deposited hard porous film. Oblique angle deposition as an attractive technique in physical vapor deposition is utilized to synthesize nanostructured thin films with controlled modification of morphology, such as porosity and column inclination. Under the influence of the shadowing effect, the oblique angle deposited TiN-based films often display porous morphology. Thus, the process begins with the oblique angle deposited porous TiN-based films. The hard porous films cannot only conduct as a load-bearing layer to improve the wear resistance, but also serves as storage space for the lubricant. In this research, carbon filled porous TiN coatings have been constructed, which exhibits lower friction than TiN film while yet having similar mechanical properties to the latter. Furthermore, humidity-adaptive “chameleon” coating was designed by filling the MoS2 on oblique angle deposited porous TiCN film. Under low humidity condition, the filled MoS2 lubricant release to the contact surface to form a low friction triofilm. While this MoS2-based tribofilm would fail and be removed by the friction force under high humidity condition, but the carbon phase in TiCN films would immediately release to contact surface to form a new low friction triofilm. Therefore, the constructed MoS2 filled TiCN coatings can respond to changing humidity conditions by self-adjustment of contacted surface properties to maintain good tribological performance in fluctuating humidity conditions. In conclusion, the research indicates that oblique angle deposition of hard porous film to store the lubricants offers a novel strategy to design the intelligent lubricating coatings. By reasonable design of the structure and composition of porous film and filled lubricants, various intelligent coatings are expected to be constructed, marking a

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Topical Symposium on Sustainable Surface Engineering Room Palm 5-6 - Session TS2-TuA
Sustainable Processing and Materials Selection for Surface Solutions
Moderators: Jörg Vetter, J.Vetter-S3-consulting, Germany, Fan-Bean Wu, National United University, Taiwan

1:40pm TS2-TuA-1 Microplasma-Enabled Upcycling for Nanomaterials Synthesis and Applications, Wei-Hung Chiang, National Taiwan University of Science and Technology, Taiwan

Microplasmas are a special class of electrical discharges formed in geometries where at least one dimension is less than 1 mm. As a result of their unique scaling, microplasmas operate stably at atmospheric pressure and contain large concentrations of energetic electrons (1-10 eV). These properties are attractive for a range of nanomaterials synthesis and nanostructure engineering such as metal nanostructures and semiconductor nanomaterials [1]. Recently, we found that the energetic species including radicals, ions and electrons generated in the microplasmas were capable of initiating electrochemical-assisted reactions for the nucleation and growth of graphene quantum dots (GQDs), silicon quantum dots (SiQDs), and metal nanoclusters (MCs). Moreover, we discover a simple and controlled synthesis of metal/metal, metal/quiet heterostructures using our unique microplasma engineering. In this presentation, I will discuss these topics in detail, highlighting the advantages of microplasma-based system for the synthesis of well-defined nanomaterials for emerging applications including detections of SARS-CoV-2 proteins [2], cancer and neurotransmitter biomarkers [3, 4], drug delivery [5] and environmental applications such as clean water production [6] and CO2 adsorption [7]. These experiments will aid in the rational design and fabrication of nanomaterials for nanotechnology-enhanced biosensors and may also have significant impact in emerging applications for next generation biomedical applications.

References

2:20pm TS2-TuA-3 Enhancing Hydrogen Production in 2D Materials via Surface Modifications: An Atomistic Study, N. Khossossi, S. Sagar, Poulium Dey, TU Delft, Netherlands

Hydrogen (H2) is one of the most potential candidates of sustainable energy produced in an eco-friendly manner. However, there are several challenges to be met before realization of H2 as an energy source. Known bottlenecks are slow kinetics and high overpotential associated with Hydrogen Evolution Reaction (HER), inefficient storage and H2 induced mechanical degradation of structural materials e.g., steels. To establish a viable ‘H2-based economy’, such bottlenecks could be addressed by designing materials with enhanced properties. To this end, the development of strategies for surface modification e.g., single-atom catalysts (SACs) supported on two-dimensional (2D) materials, are highly desirable. In this study, we perform Machine Learning (ML) assisted high-throughput screening of SACs supported on a 2D Ga-based system to expedite the prediction of HER overpotential. Firstly, Density Functional Theory (DFT) calculations are performed to investigate the catalytic properties of the system for HER. Our results reveal that, akin to many other 2D materials, the pristine Ga-based system is inert for HER due to its weak affinity towards hydrogen. However, the defective Ga-based system with surface sulfur-vacancy, exhibits highly desirable HER catalytic activity. Subsequently, we demonstrate the ML-accelerated prediction of HER overpotential for all transition metals on the system. By leveraging DFT calculations performed on 14 distinct SACs, we put forward a ML based model that maps the HER overpotentials to the atomic properties of the corresponding SACs. The trained ML model exhibits exceptional prediction accuracy and significantly reduces the prediction time compared to DFT calculations. Moreover, we identify an intrinsic descriptor that elucidates the relationship between the atomic properties of SACs and the overpotential. Our study thus provides valuable insights and a robust methodology for screening SACs on 2D materials, facilitating the design of high-performance catalysts for HER.

References


The hydrogen market is growing rapidly. The industry is developing for technical solutions for hydrogen generation and hydrogen-based electricity generation for mobile and stationary applications, and universities and institutes are investigating solutions for the long term. Today’s challenge is to bridge the gap between current low to medium technology maturity.
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level and market demand: how to be able to produce hydrogen on large scale and how to scale fuel cell production to high volumes? IHI Hauzer and IHI Ionbond are working on this challenge for many years, developing low cost coatings to supply to the market either by machine solutions and coating services. Key components of electrolyzers and fuel cell stacks like bipolar plates, PTL sheets and CCM’s need high quality coatings to enable good catalyst performance, good electrical conductivity and good corrosion properties. For bipolar plates and PTL sheets, Hauzer and Ionbond have developed coatings based on PVD and DOT technology. In the presentation, both technologies will be addressed, including the current status of market introduction and our expected further roll-out within the next years. For PVD, the current main challenges related to machine and process solutions for high speed inline coating will also be addressed. For DOT technology the current main challenges are related to upsampling production capacity in the near future and optimizing precious metal use further. We will further address the requests from the market especially the electrolyzer business and give an outlook about possible solutions to serve these demands.

4:00pm T52-TuA-8 Iron Aluminide-Based Coatings as Sustainable Alternative for High Temperature Wear Protection, Harald Rojacz, K. Pichelbauer, M. Rodriguez Ripoll, AC2T Research GmbH, Austria; G. Piringer, University of Applied Sciences Burgenland, Austria; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Strengthened iron aluminides show excellent mechanical properties up to 600°C. Therefore, coatings based on the intermetallic phase Fe3Al are promising candidates to replace Co-, Cr- and Ni-rich coatings; critical raw materials with a high ecological impact. Different strengthening mechanisms can be used in order to increase the hardness of such coatings. Silicon can be used to for solid solution strengthening, whereas carbon as well as the combination Ti and B can be used to precipitate hardphases, intended to result in increased wear resistance. In this study, the influence of different amounts of alloying on the processing and moreover the wear resistance was evaluated. A thorough analysis of the materials and the present phases was conducted, using scanning electron microscopy, electron backscatter diffraction, hot hardness testing, nanoindentation as well as high temperature abrasion testing. Results show that the hardness can be significantly increased from ~260 HV10 to ~ 350 HV10 via solid solution strengthening with silicon or TiB2 precipitations. Over 405 HV10 can be achieved by precipitating perovskite-type carbides Fe3AlC0.6. Hot hardness results show a good stability of the coatings >500°C. The wear results show a significant reduction of abrasive wear at high temperatures when strengthened, leading to lower wear rates at elevated temperatures due the increased formation of mechanically mixed layer. The obtained wear rates were used to estimate a lifetime utilised for ecological impact calculations from cradle to gate to compare the developed coatings with other wear protection coatings. Here, a reduction of the ecological impact of ~80% compared to cobalt based coatings can be assessed, showing the high potential of iron aluminide-based claddings as high temperature wear protection.
Metal sheet transformation processes still represent a fundamental sector of activity for the mechanical industry and for PVD coatings as well, as the latest have a primary role in reduction of production costs, thanks to the increase of the life of the molds and the reduction of friction during the molding phase.

Lafer has always invested in research for innovative surface treatments including coatings, aimed to improve the state of the art, in order to increase wear resistance of the moulds. This research focuses on the mold throughout its entire life cycle, starting from its machining process and ending to its application on the field. For this reason, the goal is twofold: namely to develop a coating for cutting tools used during mold construction while creating a high-performance coating for ferrous metal sheet deformation.

The starting point considered the cutting tool: once the geometry and the material to be machined were defined (1.2379 steel hardened to 62 HRC), the influence of cutting edges preparation, coating and post-finishing techniques were investigated with the aim of minimizing tool wear.

Various coatings formulations on the market, specific for this application, were tested (AlTiN, AlCrN, AlTiSiN) and subsequently an AlTiSiN-based coating was developed using HiPIMS technology: the study allowed the improvement of the thickness uniformity, increasing the coating adhesion while optimizing its hardness and elastic modulus. All the tested solutions were compared in terms of the wear of the cutting edges, finding that the HiPIMS AlTiSiN coating reached the best performances.

The second part of the project concerned the mold: a demanding geometry for ferritic metal sheet molding was identified and the cutting tools for the machining of the mold were prepared with the method defined above. Field tests were carried out by comparing the uncoated mold against the current Lafer solution on the market (TiAlCrN), based on the number of compliant produced parts.

Subsequently, a new TiCn-based coating deposited with arc technology was developed: the various tests led to a reduction of the friction coefficient and coating wear rate and increase of its fatigue resistance, measured through multiple impacts technique.

A molding comparison between the new and the actual solutions was carried out: the new coating led to a reduction in lubricant consumption and a significant increase in the number of produced parts.

Future developments will investigate the joint effect of a surface hardening process underneath the newly developed PVD coating and its performances with different types of metal sheet materials.
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homogeneous coverage of 3D intricate parts (thus able to match the low tolerances required for micromachining) makes this technology ideal for these applications. The tested coatings are based on Si- and B-containing AlTiN and were deposited in different sets of tools, according to their specific requirements, attaining hardness values of 35 GPa and good adhesion. Moreover, oxidation studies were performed to determine the stability of these coatings, analysing, and comparing the results in terms of SEM, TEM, and XRD, observing a greater oxidation resistance for the Al containing coatings.

c) Machining tests, which, in addition to mechanical properties analysis, provide information regarding the performance of the coatings under operation conditions. The materials selected for machining are Hardened Steel (HR60) and Ti6AlV4 alloy, and the finishing of the machined parts, as well as the wear suffered by the tool is analyzed.

Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-3-WeM

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

Moderators: Gustavo Garcia-Martín, REP-Energy Solutions, Spain; Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK; Eli Ross, Pratt & Whitney, USA

8:00am MA1-3-WeM-1 Characterization and Evaluation of Physical-Chemical Properties of Novel Ternary and Quaternary Molten Salts and Their Economic and Environmental Impact in Parabolic Trough Technology: Corrosion Effects, M. Lombrecht, D. Maria Teresa, L. Maria Isabel, Gustavo Garcia Martin, J. Chaves, F. Perez Trujillo, Universidad Complutense de Madrid, Spain; P. Audigie, A. Aguero, INTA, Spain

Only molten salt combinations are used as a heat storage medium in CSP to date. Alkaline nitrates and nitrates have been successfully utilized as heat transfer fluids (HTF) and heat storage medium (HSM) in concentrated solar power (CSP) plants. Particularly, the binary mixture combination 60%NaNO3 - 40%KNO3 well known as Solar Salt with a freezing point around 220°C and thermal decomposition at 560°C [1]. Separately, there is a synthetic thermal oil that comprises the commercial parabolic trough (PT) technology to capture the heat of solar radiation. This costly HTF with a melting point around 12°C and high environmental impact yields the heat to Solar Salt by means of exchangers. The maximum thermal energy storage temperature reached is about 390°C, their energy power is thus limited by the organic heat carrier fluid. There are investigations aiming to increase the working temperature range a long with a unique molten salt (MS) as heat capture and storage medium. Ternary and quaternary low melting point mixtures with addition of LiNO3 and Ca(NO3)2 have been presented as direct systems candidates according to their better physic - chemical properties than Solar Salt but, nonetheless, these previous investigations have deemed a full properties study with additional environmental and economic aspects to weigh the best selection criterion to envisage alternative fluids.

This investigation evaluates the important properties (melting point, degradation temperature, specific heat capacity, density and energy density) of the novel mixtures46% wt.NaNO3-19%wt.Ca(NO3)2 - 35%wt.LiNO3 (T1) and 33%wt.NaNO3-22%wt.KNO3-29%wtCa(NO3)2-16% wt.LiNO3 (Q-1). Life Cycle Assessment (LCA) has been used to calculate the environmental impact of the mixtures through the software tool Simaprog in comparison with the Solar Salt. Likewise, an economic simulation of their usage in a direct and indirect parabolic through (PT) configuration has also been estimated by means of Levelised Cost of Energy (LCOE) parameter, which was customized for the TES facility, (LCOE). The effects of molten salts chemical composition in the high temperature corrosion of metallic materials and coatings will be analyzed.

In this study, a 50 MW and 6 hours heat storage capacity PT plant has been considered for LCOE estimation. This parameter was assessed by means of an in-house method from articles references and data extrapolation to simulate price variations by replacing novel multicomponent fluids by Solar Salt as HSM.

8:20am MA1-3-WeM-2 Influence of the BN Content on the Microstructure and the Mechanical Properties of Cr2C3-NiCr-BN Composite Coatings Prepared by a Novel HVOF Process Using Ethanol as a Fuel, S. Liu, UTBM, France; M. Arab Pour Yazdi, Pavel Sedmid, J. Nohava, Anton Paar, Switzerland; M. Moliere, H. Liao, UTBM, France

Cr2C3-NiCr-BN composite coatings were thermal sprayed on 304 stainless steel substrates using an ethanol-fueled High-Velocity Oxygen Fuel (HVOF) process. We examined the effect of varying Boron Nitride (BN) contents (ranging from 0 wt% to 15 wt%) in the feedstock on the microstructure and mechanical properties of the resulting coatings. Our findings reveal that the different BN contents significantly influence the microstructure, interlayer porosity, nanohardness, scratch resistance, and sliding wear resistance of the composite coatings. As the BN content increased, the interlayer porosity of the coatings increased and the BN content also contributed to an increase in the nanohardness of the films. In addition, a higher BN content resulted in a reduction in the coefficient of friction, but at the expense of an increase in the wear rate and a decrease in the scratch resistance.

Notably, when the BN content reached 15%, the composite coating exhibited its lowest coefficient of friction. However, the wear rate was simultaneously increased due to the higher interlayer porosity of this particular coating. These results provide valuable insight into the optimization of BN content to achieve the desired balance of mechanical properties in Cr2C3-NiCr-BN composite coatings.

8:40am MA1-3-WeM-3 Oxidation Behavior of Si-Based Coatings on Refractory Multi-Principal Element Alloys, Brady Bresnahan, D. Poerschke, University of Minnesota, USA

The large design space for refractory multi-principal element alloys (MPEAs) provides opportunities to tune alloy chemistry to simultaneously optimize the bulk and surface properties. This investigation studied Si-based coatings to improve the oxidation resistance of refractory alloys. A set of MPEAs systematically exploring composition variables related to silicide formation were produced by arc melting and coated by pack cementation and slurry processing. The effects of alloy and coating compositions on coating microstructure were studied to understand refractory metal partitioning between silicide phases. The phase evolution after oxidation was similarly explored where the tendency to form protective oxides and mass change were used to evaluate the composite material performance and understand alloy and coating composition effects. These insights will enable coupled alloy and process design to improve oxidation resistance while taking advantage of the superior high temperature yield strengths of refractory MPEAs for aerospace applications.

9:00am MA1-3-WeM-4 Multifunctional Nanostructured ZrN-Cu Coating for Maritime Applications, Jose D. Castro, University of Coimbra, Portugal; M. Lima, I. Carvalho, University of Minho, Portugal; J. Sánchez-López, Instituto de Ciencia de Materiales de Sevilla (ICMS), Spain; R. Escobar-Galindo, University of Sevilla, Spain; C. Rojas, Instituto de Ciencia de Materiales de Sevilla (ICMS), Spain; S. Carvalho, University of Coimbra, Portugal

Ships are essential to globalisation since they are the primary mode of transportation for goods worldwide. Any potential ship issue could affect the global economy. Corrosion and biofouling are prevalent problems linked to maritime elements. From this angle, the most widely used product was paint made of tributyltin (TBT), which was outlawed in 2008. Given this requirement, multifunctional coatings appear to be a great alternative to TBT. Magnetron sputtering technology can obtain nanoarchitectures to gather different materials and enhance characteristics. The present work presents an insight into a nanostructured film with ZrN and Cu (obtained via Deep Oscillation and DC magnetron sputtering, respectively). S5316L was used as the substrate, widely used in the naval industry. ZrN coating without copper was employed as a control sample. SEM, EDS, XRD, TEM, Nano-indentation, scratch tests, and tribology measurements assessed the characteristics of the films. Electrochemical impedance spectroscopy (EIS) until 30 days and potentiodynamic polarisation measurements were conducted in a 3.5 wt. % NaCl solution to replicate the work regime. The halo test evaluated the inhibition of microorganisms. The results demonstrate that Cu migration towards the surface (with chemical activation using NaOCl solution) reduces bacterial growth. Besides, inductively coupled plasma optical emission spectrometry (ICP-OES) and transmission electron microscopy (TEM) show that the ZrN nanolayers (~ 6nm thick) control the embedded copper nanoparticles (~ 12 nm thick) release. On the other hand, the chemical activation decreases the film corrosion resistance, the mechanical properties and the tribological
During the MAO treatment, due to the deposition effect, the coating enhanced corrosion resistance, and are also more environmentally friendly. One of the most effective and emerging methods for forming inorganic environmentally friendly surface treatment technology must be developed. Corrosion, which may cause serious consequences, so a simple and effective corrosion inhibition technology is in great demand. Lien and Po, National Taipei University of Technology, Taiwan, U.S.A.

10:45am MA1-3-WeM-11 Characteristics of High-temperature Resistant Coatings Prepared by the Liquid Spray Technique, Yan-Rui Chen, National Taipei University of Technology, Taiwan; T. Wu, Researcher of National Chung-Shan Institute of Science & Technology, Taoyuan city, Taiwan; Y. Yang, Distinguished professor of National Taipei University of Technology, Taiwan; Y. Wu, Professor of National Taipei University of Technology, Taiwan

In the coating technology, liquid spray (LS) is different from the traditional thermal spraying technology. The liquid spray coating is made by using compressed air. The spray liquid sprayed from the nozzle is subjected to high pressure and collides with the still air at high speed. The liquid spray splits and slows down due to air resistance, and turns into mist to form a coating which can keep the original characteristics of the material during the spraying process and have a denser coating. Refractory metals, boride (Xb), has good performance at high temperature, used in the electronics industry, aviation and defense. This study used liquid spray to prepare refractory metals boride (Xb), high temperature resistant coating, discusses the liquid spray under different process parameters (working distance, solidification conditions) affected the microstructure changes of the coating and its mechanical properties, such as porosity, hardness, tensile strength, etc.

11:40am MA1-3-WeM-12 Development of Tantalum Bond Coating for Thermal Barrier Coating by the Cold Spray, Wei-Chie Hung, National Taipei University of Technology, Taiwan; W. Li, Y. Chung, Researcher of National Chung-Shan Institute of Science & Technology, Taiwan; Y. Yang, Y. Wu, National Taipei University of Technology, Taiwan

In the coating technology, cold spray(CS) is different from the traditional thermal spraying technology. The cold spray coating is formed by plastic deformation without high temperature melting, which can keep the original characteristics of the material during the spraying process and have a denser coating. This study we focus on depositing tantalum(Ta) as the protecting coating and also the bond coat for the thermal barrier coating on differentcurvature shape to simulate curved shell of an actual aircraft by using cold spray process. The results show that the cold spray coating can cause the powder to have good plastic deformation as the chamber pressure, temperature and closer working distance increase, so it has lower porosity and forms a dense coating. The Ta bond coat is well bonded with the substrate and atmospheric plasma spraying is used to prepare the YSZ top coat.

10:45am MA1-3-WeM-11 Characteristics of High-temperature Resistant Coatings Prepared by the Liquid Spray Technique

11:40am MA1-3-WeM-12 Development of Tantalum Bond Coating for Thermal Barrier Coating by the Cold Spray

Protective and High-temperature Coatings Room Town & Country C - Session MA4-1-WeM

High Entropy and Other Multi-principal-element Materials

11:00am MA1-3-WeM-10 Study on the Characterization of Adding CeO₂ Particles on Micro-arc Oxidation Coated AZ91D Magnesium Alloys, Po-Wei Lien, MING Chi University of Technology, Taiwan

AZ91D magnesium alloy has the advantages of low density, high tensile strength, high elongation, and easy processing. Compared with other light metal magnesium alloys are lighter. And it has been widely used in our daily life. Unfortunately, aluminum-magnesium alloys are prone to corrosion, which may cause serious consequences, so a simple and environmentally friendly surface treatment technology must be developed.

Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation, is one of the most effective and emerging methods for forming inorganic ceramic layers on various light metals. Compared to the traditional anodizing process, MAO coatings exhibit higher mechanical properties, enhanced corrosion resistance, and are also more environmentally friendly. During the MAO treatment, due to the deposition effect, the coatingsolidifies and contracts, resulting in surface structural defects such as microracks. Hence, the addition of CeO₂ particles in the electrolyte aims to seal micro-pores and introduce self-healing capabilities.

This study uses AZ91D was utilized as the research substrate, and CeO₂ was introduced into the electrolyte. The investigation aimed to observe the presence of CeO₂ particles within the micro-pores on the MAO surface and evaluate the self-healing functionality during salt spray experiments.

8:00 PM MA4-1-WeM-1 Growth and Properties of Epitaxial High-Entropy Alloy Thin Films, Thomas Seyller, Chemnitz University of Technology, Germany

High-entropy alloys (HEAs) are discussed for applications in the fields of corrosion and wear protection as well as electrocatalytic. Although the surface properties of HEAs play a central role in these applications, they are still largely unexplored. This is at least to a certain extend - caused by the unavailability of single-crystalline samples. In this presentation, recent progress is reported on the growth and subsequent characterization of epitaxial CoCrFeNi films [1]. The films were deposited by DC magnetron sputtering from spark-plasma sintered targets [2] using single-crystalline oxide substrates. A characterization of structural, chemical and electronic properties of the films was performed by different techniques including X-ray diffraction (XRD), scanning electron and transmission electron microscopy (SEM, TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), angle-resolved photoelectron spectroscopy (ARPES), low-energy electron diffraction (LEED) and, more recently, by scanning tunnelling microscopy (STM). It is demonstrated that epitaxially grown HEA films have the potential to fill the sample gap, allowing for fundamental studies of properties of and processes on well
defined HEA surfaces over the full compositional space.


9:20am MA4-1-WeM-5 Effect of Elemental Additions [X: Pt, Al, Ti, and Ag] on the Microstructure and Electrical Properties of CrMnFeCoNi-Based High-Entropy Alloy Thin Films, Salah-eddine Benrazzouq, J. Ghonbaja, S. MIGOT, A. Nominé, J. Pierson, V. Milichka, Institut Jean Lamour - Université de Lorraine, France

High-entropy alloys (HEAs) have garnered significant attention across various research and industrial fields owing to their exceptional properties, which originate from their complex multiprincipal element composition. This study delves into the phase evolution, microstructure, and electrical properties of the Cantor alloy (CrMnFeCoNi) enhanced by the incorporation of additional elements such as Pt, Ti, Al, and Ag. The deployment of DC magnetron co-sputtering has been crucial in achieving homogeneous films with precise stoichiometric and morphological control. This technique has enabled the systematic investigation of the structural evolution between crystalline phase (FCC, BCC) and amorphous states and their subsequent impact on the properties of the films. We carried out comprehensive characterization using X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), resistivity measurements, and optical reflection measurements to assess the films’ structural, microstructural, electrical, and optical attributes. Abundant nanotwins were observed in the CrMnFeCoNi and CrMnFeCoNiPt films, both of which possessed a single FCC crystalline structure. The CrMnFeCoNieAl films transitioned from a single FCC phase to a duplex FCC + BCC phase structure, eventually stabilizing as a single BCC structure. The duplex FCC+BCC phase exhibited a low degree of nanotwins with larger grains of each phase. The CrMnFeCoNiTi films displayed an amorphous structure at various percentages, whereas the CrMnFeCoNiAl films exhibited a multiphase structure comprising single Ag and CrMnFeCoNiAg phases. Notably, Ag formed precipitates zone within the Cantor matrix. The observed phases were consistent with predictions made using thermodynamic criteria, despite the far-from-equilibrium conditions.

The study reveals that altering the concentration of elements such as Al and Pt significantly impacts the films’ crystallographic structure and microstructure. Specifically, the electrical resistivity increased with the addition of elements in the single-phase region. Notably, values of electrical resistivity were even higher in the duplex phase for the Al-doped samples due to the additional scattering effects of FCC/BCC phase boundaries in the alloys. The incorporation of silver was found to decrease the material’s resistivity, likely because of the increased precipitation of silver within the Cantor matrix. Furthermore, optical reflectance and tempearture-dependent electrical resistivity measurements confirm the metallic behavior of our alloys.

9:40am MA4-1-WeM-6 Property Evaluation of Nd Doped NiCoFeAlTi Non-equiaxiomt High Entropy Alloy Films and the Influence of Post-annealing Treatment, Chia-Lin Li, Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan

The effects of Nd addition on the microstructures and mechanical properties of non-equiaxial NiCoFeAlTi high entropy alloy films (HEAfs) were studied in this work. A series of NiCoFeAlTi HEAfs doped with Nd, ranging from 0 to 8.7 at.% Nd, was prepared by magnetron co-sputtering. Subsequently, a post-annealing treatment at 700°C was executed to investigate the changes in microstructure and mechanical properties.

With the additions of Mo and Ti, the maximum yield strength of 5.87 GPa and hardness of 11.96 GPa were obtained at MoTi70 and then decreased with the higher Mo content. The addition of small amounts of Mo and Ti strengthened the CoCrNi MEAFs due to solid solution strengthening and grain boundary strengthening.

To further enhance the crystallinity and mechanical properties, MoTi90 medium entropy alloy films with amorphous were deposited on 304 steel substrates, and the post-annealing treatment was conducted to investigate the effects of different annealing temperatures on the microstructures and mechanical properties of the films. The crystallinity increased with the increasing annealing temperature. The hardness and Young’s modulus were measured by nanoindentation and micro-pillar compression tests. Therefore, the moderate post-annealing treatment was beneficial in promoting the formation of stacking faults and strengthening the mechanical properties. Our findings suggest that these MEAFs hold promise for lightweight and high-strength material applications in various industries.

11:20am MA4-1-WeM-11 Effect of Substrate Temperature on Properties and Microstructure of High Entropy Alloy Thin Films Deposited by Magnetron Sputtering Systems, Yi-Jun Yan, F. Ouyang, National Tsing Hua University, Taiwan

In recent years, high-entropy alloy thin films have attracted much attention because of their higher strength and lower cost than bulk materials. This study used magnetron sputtering to prepare Ni52Co42Fe10Cr10Al30Ti high-entropy alloy (HEA) thin film on a Si substrate. We investigated the effect of substrate temperature on the properties and microstructure of HEA thin films, including nanotwin formation, grain growth, hardness, and roughness. The composition of the film is uniformly distributed, and different substrate temperatures did not cause significant changes in the concentration of film elements. The thin film fabricated at low substrate temperature has a highly (111)-oriented columnar grain structure, and the nanotwin boundaries are parallel to the substrate surface with average twin spacing of 1.4 nm. As the substrate temperature increased, the columnar grain structure gradually disappeared and transformed into a BCC+FCC dual-phase polycrystalline structure. The hardness of thin film possesses a maximum hardness of 1.92 GPa at the substrate temperature of 100 °C, but as the substrate temperature rises, the grain growth and detwinning cause the hardness to decrease. The resistivity of HEAs is about 105 uΩ-cm, and there is no obvious correlation with the substrate temperature. The HEA thin films also exhibit a flat surface morphology with a root mean square roughness value of 0.5 nm at low substrate temperature. But the root mean square roughness value increased to 1.5 nm as substrate temperature
Wednesday Morning, May 22, 2024

increased, which is due to the grain growth inside the films. The residual stress of the film changed from compressive stress to tensile stress as the substrate temperature increases. The results of this study show that the substrate temperature greatly influences the microstructure, twin crystal growth, hardness, and residual stress, and corresponding mechanism will be discussed in the talk.

11:40am MA4-1-WeM-12 A Combinatorial Approach to Developing Sputter-Deposited AuBiTaW High-Entropy Alloy Films for Inertial Confinement Fusion Applications, Daniel Goodelman, D. Strozzi, S. Kucheyev, L. Bayu Aji, Lawrence Livermore National Laboratory, USA

After achieving inertial confinement fusion (ICF) ignition in December 2022, further optimization of material properties and experimental protocols are required to increase the fusion energy gain. To accomplish this goal, we are designing a new generation of hohlraums. Typically fabricated via magnetron sputtering, hohlraums are centimeter-scale spherocylindrical cans made from Au or depleted U with a wall thickness of >10 μm, serving as the outer housing for fusion fuel capsules. They must balance design constraints including high laser light-to-x-ray conversion efficiency, mechanical and corrosion stability, and electrical resistivity for magnetically assisted implosion. Here, we present results of a combinatorial magnetron co-sputtering study, aimed at developing a family of AuBiTaW films to address these outstanding challenges. Effects of the alloy composition and deposition process parameters on the microstructure, residual stress, mechanical properties, and electrical transport will be considered, as well as implications for ICF applications.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344 and was supported by the LLNL-LDRD Program under Project No. 23-ERD-005.

12:00pm MA4-1-WeM-13 Tungsten-Based Complex Concentrated Alloys for Fusion Applications, M. Vigil, University of Wisconsin—Madison, USA; Sabine Faulhaber, M. Patino, D. Nishijima, A. Založnik, M. Simmonds, T. Lynch, M. Baldwin, K. Vecchio, G. Tynan, University of California San Diego, USA

A complex concentrated alloy (CCA) has been identified as a promising candidate material for use in nuclear fusion applications. Previously, tungsten-based complex concentrated alloy thin films have been found to exhibit high radiation resistance [1].

This work represents the first study of fuel retention in bulk W-based complex concentrated alloys as plasma-facing components. A bulk W-based CCA was synthesized by spark plasma sintering (SPS) and characterized by x-ray diffraction (XRD), scanning electron microscopy / x-ray dispersive x-ray spectroscopy / electron backscatter diffraction (SEM/EDS/EBS/D) and Auger electron spectroscopy (AES) before and after exposure to fusion-relevant plasma at deuterium-ion fluences of 2·10^20 m^-2.

During plasma exposure optical emission spectroscopy (OES) was used to measure elemental sputtering; transient grating spectroscopy (TGS) was employed to measure the changes in thermal diffusivity and thermal desorption spectroscopy (TDS) allowed measurement of deuterium retention.


Functional Thin Films and Surfaces
Room Town & Country D - Session MB2-1-WeM

Thin Films for Electronic Devices I
Moderators: Claudia Falubi, Evatec AG, Switzerland, Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, Panos Patsalas, Aristotle University of Thessaloniki, Greece, Jörg Patscheider, Evatec AG, Switzerland

8:40am MB2-1-WeM-3 Strain-Induced Self-Rolled-Up Thin Films for Extreme Miniaturization and Integration of Passive Electronic Components, Xuiling Li, The University of Texas at Austin, USA INVITED

The fundamental physical principle underlying self-rolled-up membrane (S-RuM) nanotechnology is the strain-driven spontaneous deformation of 2D membranes into 3D architectures. S-RuM technology offers a unique solution for achieving 3D functional hierarchical architectures without the challenges associated with processing in three dimensions. Through strain engineering, it opens up new possibilities by facilitating the creation of practically unlimited complexity in L-C circuits, integrated photonics, and lab-on-a-chip integration of soft and hard materials. Importantly, these advancements are achieved through the utilization of well-established CMOS-compatible planar processing techniques.

In this talk, I will present examples of S-RuM based passive electronic components, including on-chip inductors, transformers, L-C networks. I will discuss how S-RuM technology can potentially break the constraints of size, weight, and performance of RFICs and power electronics.

9:20am MB2-1-WeM-5 Enhanced Synaptic Characteristics Under Applied Magnetic Field in V_2O_5-Ni-Mn-In Based Switching Device for Neuromorphic Computing, Kumar Kaushlendra, D. Kaur, Indian Institute of Technology Roorkee, India

The present study reports a memory structure Al/V_2O_5-Ni-Mn-In on a flexible stainless-steel (SS) substrate for neuromorphic applications. The fabricated device exhibits gradual SET and RESET switching characteristics with an Off/ON resistance ratio of ~100, good consistency of 4500, and excellent retention capability up to 6000 s. The current-voltage (I-V) study supports an Ohmic conduction mechanism in the low resistance state (LRS). In contrast, the trap-controlled modified space charge conduction mechanism demonstrated the high resistance state (HRS). The resistance versus temperature measurement (R-T) in the LRS and HRS of the device signifies that oxygen vacancies form the conduction filament. We further analyze the synaptic functioning by applying identical consecutive voltage pulses, and the device’s conductance change has been observed. These characteristics show a good representation of the biological memory synapse in terms of the artificial memory device. Long-term potentiation (LTP) and long-term depression (LTD) show nonlinear and asymmetry behavior, which is substantial for neuromorphic applications. A considerable shift in LTP and LTD was detected by applying external temperature and magnetic field. This is explained via temperature and magnetic field strain in the functional Ni-Mn-In bottom electrode of the fabricated device. The mechanical flexibility of the memory structure was tested by exploring the switching characteristics with various bending angles and bending cycles. Therefore, the present study offers new avenues for flexible devices with high data storage capability for futuristic neuromorphic applications.

9:40am MB2-1-WeM-6 Electrolyte Gated Transistors for Neuromorphic Signal Processing and Biosensing, Luke Sylvander, P. Le, C. Tan, H. Tran, RMIT University, Australia; D. McKenzie, University of Sydney, Australia; D. McCulloch, J. Partridge, RMIT University, Australia

An Ar plasma immersion ion implantation (PIII) process has been employed to introduce free-radical covalent binding sites in spin-on polymer layers. These layers have been incorporated as dielectric layers into lateral electrolyte-gated transistors (EGTs) with characteristics resembling those of biological synapses. Specifically, if the gate electrode of the EGT is taken to be the pre-synapse and voltage pulses are applied, the resulting source-drain output mimics aspects of postsynaptic signals. Notably, this postsynaptic output is sensitive to the dynamics of the double layers (DLs) that are formed at the two polymer/electrolyte interfaces when the presynaptic voltage is applied. If biomolecules are covalently immobilised on the PIII-treated polymer dielectric layer, the dynamics of the DL formation/decay are altered, as are the postsynaptic signals. This provides a neuromorphic detection signal and enables the EGTs to be used as artificial sensory synapses. This talk will cover the PIII treatment of the polymer layers, device fabrication/characterisation and biosensing measurements from the EGTs.

11:00am MB2-1-WeM-10 Investigation Of Piezoelectric Properties And Defect Structure In Vanadium Doped ZnO Thin Films, Y. Chang, Yu-Tsong Lin, S. Brahma, J. Huang, National Cheng Kung University (NCKU), Taiwan

Zinc oxide (ZnO) is a II-VI group semiconductor characterized by high thermal stability and a relatively wide direct bandgap (~ 3.37 eV). The bandgap width conveniently falls within the ultraviolet (UV) light spectrum, making ZnO an excellent candidate for optoelectronic thin film materials which are capable of efficient UV light emission. In comparison to other wide bandgap semiconductors, ZnO exhibits a higher exciton binding energy (approximately 60 meV), resulting in enhanced luminescent efficiency, making it well-suited for applications as a fluorescent material. In general, ZnO with wurtzite structure has a strong polarity along the c-axis direction, so it is also a piezoelectric material with excellent piezoelectric properties. With this asymmetry structure, ZnO can be applied in many fields, such as, surface acoustic wave (SAW) device, piezoelectric micro mechanical system (MEMS) device or even new generation energy
harvesting systems. However, the piezoelectric coefficient (d33) for pure ZnO is low (12.4 pc/N) due to its intrinsic defects like oxygen vacancies and Zn interstitials.

Doping transition metals is one of the most effective ways to improve ZnO's piezoelectric properties. Compared with other TM dopants which have been reported in many research, V doping stands out for its great contribution. The improved piezoelectric coefficient (d3) can be attributed to the switchable spontaneous polarization induced by the vanadium, which also results in the increase of the relative permittivity.

In this work, we investigate the effect of defect structure over the piezoelectric properties of ZnO and V doped ZnO thin films by resonant Raman and photoluminescence spectroscopy. ZnO/V doped ZnO are deposited on p-type Si(111) substrates through RF magnetron sputtering under Ar(20scm) oxygen(10scm) atmosphere at 250°C. All the films exhibit wurtzite structure with strong [0002] preferential orientation. In addition, variation of oxygen flow rate significantly affects the crystal quality of ZnO by the generation of oxygen defects. The deposition of V doped ZnO is carried out at 250°C under argon(20scm) atmosphere and the thickness is maintained for 1000 nm. Vanadium generally shows V3+ and V5+. As the vanadium doping concentration increases (50W), more V3+ will doped into ZnO and enhance the polarity as well as the piezoelectric coefficient(29.52 pm/V). Combining the defect structure (oxygen flow rate 10 scm) and vanadium doping (50W), the piezoelectric coefficient of V doped ZnO is improved to 113.37 pm/V.

11:20am MB2-1-WeM-11 Tracking the Metal-Insulator Transition at YTiO3/LaTiO3 Interfaces Grown by the Soft Chemical Method, Alexandre Simoes, UNESP, Brazil

In the last couple of years, perovskites and transition metal oxides have demonstrated high potential for energy storage/processing applications. Materials usually used in random access memory devices, such as perovskites and transition metal oxides (TMO), have shown potential to be applied in the fabrication of other types of nonvolatile memories. Correlated electron random access memories (CeRAMs) were recently developed for exhibiting partially filled bands in addition to showing resistive switching as a result of strong electronic correlations. It is worth mentioning that the band structure of related electronic materials depends not only on the d-orbitals of the transition metals, but also on the p-orbitals of neighboring oxygen atoms. In this work, oxide interfaces with piezoelectric, magnetic and metal-insulator transition based on YTiO3/LaTiO3 heterostructured films were investigated. The Mott insulator, YTiO3, was deposited onto a Mott insulator, LaTiO3, via polymeric precursor method. Spin coating was performed to obtain a YTiO3/LaTiO3 heterostructured thin films deposited onto Pt/YSZ/Si/Si substrate. Structure, morphology, and electrical properties of the films were assessed. The YTiO3/LaTiO3 heterostructures exhibit ferromagnetic and piezoelectric behavior (d31≈11 pm/V), which may be attributed to smaller grain (average grain size=20.00 nm) and, thus, a higher grain boundary density, and stress in the film plane due to the different properties of the interface. The dielectric permittivity and dielectric loss at 1 KHz were found to be 70 and 0.41, respectively. I-V measurements on different electrode areas confirmed a metal-to-insulator transition, indicating a potential application in correlated electron random access memory (CeRAM).

11:40am MB2-1-WeM-12 Combining a Hybrid-Aln Buffer Layer in the Epitaxial Growth and Characterization of GaN Thin Films on Graphene/Sapphire Substrate, Soloman Teklahymanot Tesfay, Ming Chi University of Technology, Taiwan; K. Wen-Cheng, National Taiwan University of Science and Technology, Taiwan

This work explores the potential of utilizing a hybrid AlN buffer layer (BL) to grow superior-quality GaN thin films on a few-layer graphene (FLG)/sapphire substrate. To create the hybrid AlN BL, the low-temperature AlN nucleation layer (LT-AlN NL) and the high-temperature AlN BL were grown using sputtering and metal-organic chemical vapor deposition (MOCVD), respectively. GaN films grown without the hybrid AlN BL contained a high density of threading dislocations (TD), creating current leakage channels and resulting in a symmetric, temperature-independent I-V characteristic curve for a Ni-based Schottky contact. Sputtering LT-AlN NL on the FLG layer with great adhesion and uniform coverage can avoid the heat etching of graphene during the MOCVD epitaxial process and solve the nucleation problem. GaN thin films produced on a hybrid AlN BL/FLG/sapphire substrate can have much lower edge-type TD densities and carbon concentrations, which results in less intense blue, green, and orange luminescence on a 17-K photoluminescence spectrum. The Ni-based Schottky contact shows that high-quality GaN thin films will be grown onto FLG substrate by inserting a hybrid AlN BL. It has a barrier height of 0.69 eV and a leakage current density of 4.38×10^-6 A/cm².

A hybrid thin film deposition system (Swiss Cluster) was used to create the samples by combining atomic layer deposition (ALD) and physical vapour deposition (PVD) [1]. Sequential deposition of approx. 1 μm thick multilayers were separated by 10 nm thick Al2O3 interlayers. The initial 100-250 nm grain size was increased by extensive heat treatment (@800°C for 4h under Ar atmosphere, Fig. 1a). Such final specimen was quite challenging to create without porosities or major delamination from the substrate after heat treatment.

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Afterwards, micropillars were fabricated using focused ion beam (FIB) milling close to the edge of the bulk sample (Fig.1b). These micropillars were then compressed at various strain rates (0.1-1000/s) using a nanodeformation setup (Aleennis AG). High (angular) resolution electron backscatter diffraction (HR-EBSD) was applied to study the geometrical necessary dislocation (GND) density distribution after low and high strain rate deformations. Sequential FIB-slicing [2] was applied to create 3D reconstructions of the deformed volumes.

References

8:40am MB2-2-WeM-3 Assessing Brittleness of Indium Tin Oxide Layers on Glass Substrates with Nanoindentaion, Kurt Johanns, S. Vorma, J. Hay, B. Crawford, KLA-Tencor, USA

Many of the materials used in manufacturing semiconductors are susceptible to cracking, i.e., exhibit brittle failure during processing and in application. While the definition of brittle is well understood, assigning a “brittleness” value to a given material or system of materials is not easy as “brittleness” is not a material property. Here, we define a simple set of nanoindentation experiments in an effort to assess the brittleness of Indium Tin Oxide (ITO) layers and provide feedback to semiconductor manufacturers on how to mitigate latent defects that may initiate and propagate during processing. Multiple ITO film thicknesses in different residual stress states of ITO are tested. Results show that indentation testing is capable of assessing the brittleness of ITO on glass when experimental and material system artifacts are taken into account. Multiple examples of nanoindentation and nanoscratch testing are provided with a focus on advantages and improved sensitivity over related techniques.
The binary refractory metal nitride, Mo-Ta-N, coatings were fabricated and characterized in this study. The relationship between its microstructure and mechanical properties of the magnetron sputtering Mo-Ta-N coatings were investigated. The coatings were deposited using radio frequency reactive magnetron sputtering with input powers of 150 W. Ta-N thin films were prepared under a fixed inert gas Ar/N$_2$ ratio and input power of 12/8 sccm/scm and 150 W on Mo, respectively. The input power of Ta was tuned from 50 to 150 W to adjust the microstructure and composition. The addition amount of Ta and the deposition rate increased monotonically from 3.7 to 16.8 at.% and from 5.4 to 6.7 nm/min, respectively, as a function of Ta input power, while the (Mo+Ta)/N ratio kept a steady value around 1.0. The Mo-N film showed well-defined Mo-N (111) and (200) facets with minor MoN (111) and (220) reflections. The Mo-Ta-N coatings exhibited a polycrystalline microstructure with MoN(111), Mo(N111), Mo(200), TaN(111), TaN(200) and TaN(220) multiple phases and showed the nano-crystalline structure according to the broadened diffraction peaks. A maximum hardness of 18 GPa was found for the Mo-Ta-N coating deposited at an input power of 150/100 W/W. A sufficient adhesion was revealed and a better wear resistance was realized for Mo-Ta-N coatings with 6.8 and 10.4 at.% Ta and nanocrystalline multiple phase feature.

Keywords: refractory metal nitride, Mo-Ta-N, co-sputtering, multiple phase, nanocrystalline.
substance material thanks to the electrochemical reactions driven by the ions exchange between the substance and electrolyte. Thus, not only the selection of proper electrolyte and MAO process conditions is important, but also microstructure of the substance material. The plastic deformation of the substance material may also affect the mechanisms of the oxide formation. Grain refinement and formation of higher density of low angle (LAGB) and high angle grain boundaries (HAGB) allows many more sites for the nucleation of oxides to be formed which results in a finer oxide coating. Application of severe plastic deformation techniques such as hydrostatic extrusion provided amazing results in terms of strengthening of metallic materials such as titanium, allowing for its widespread application, especially as future dental implants. Owing to the hydrostatic extrusion characteristics microstructure refinement down to the nanometric scale may be achieved, increasing strongly the density of LAGB and HAGBs, also having a huge impact on eventual surface modification with the methods like MAO. However, there is a lack of information about microstructure and tribological properties of the MAO coatings deposited on the surface of hydrostatically extruded titanium. In this work, titanium grade 4 substrates was subjected to 3-pass hydrostatic extrusion and subsequent rotary swaging reducing the initial diameter from 50 mm down to 5 mm. The rods were cut into diameter and subjected to MAO process in phosphate-based electrolyte with the help of the bipolar pulsed power supply. Such power supply allows for far better control of the electrochemical reactions during the deposition process than direct current or unipolar pulsed ones. Before the MAO coatings deposition, the cp-Ti substrates were thoroughly investigated in terms of determination of the HAGB and LAGB density with the SEM/EBSD method in order to determine their influence on the properties of the forming oxide surface layer. The microstructure observations (SEM/TEM) supported by phase and chemical analysis (XRD, SAED, EDS) allowed us discuss the mechanisms of oxide coating formation and correspond to their tribological behavior.

Acknowledgement: This research was funded by the National Science Centre of Poland, grant number UMO-2020/39/D/ST8/01783.

11:40am MC2-2-WeM-12 Effect of Ultrasonic-Assisted Machining for Surface Functionalization of Innovative Work-Hardening Multi-Principal-Element Alloys, Marcel Giese, D. Schroeper, M. Rhode, Bundesanstalt für Materialforschung und -prüfung, Germany; B. Preuss, T. Lindner, N. Hansisch, T. Lampke, Institute of Materials Science and Engineering (IWW), Chemnitz University of Technology, Germany

Multi-principal-element alloys (MPEAs) are an alloying concept consisting of at least two main alloying elements resulting in unique microstructures and potentially superior physical, mechanical and chemical properties, for instance a high work hardening capacity. These characteristics are determined by four core effects: sluggish diffusion, severe lattice distortion, high-entropy and cocktail effect. The development of MPEAs is a promising approach to extend the range of applications of conventional alloys by exploiting these core effects. In the present study, as reference to the conventional high-manganese steel X120Mn12 (ASTM A128), characterized by particularly high work hardening capacity generating exceptional mechanical properties, work-hardening MPEAs based on the equiatomic composition CoFeNi in combination with Mn and C were developed. Specimens were produced as bulk material by melting via an electric arc furnace. In a second step the specimens undergo a surface finishing via milling process. Therefore, a hybrid milling process was used which, in addition to producing defined surfaces, also has the potential to reduce tool wear and increase surface integrity by introducing compressive stresses and increasing hardness through pronounced work hardening in comparison to conventional machining. The so-called ultrasonic-assisted machining (USAM) is characterized by an axial oscillation of the tool during the milling process. The machining parameters were varied to analyze the effect on work hardening together with process forces during milling and resulting surface integrity. Subsequently, microstructure evolution, hardness as well as resulting wear resisting capacity were investigated and correlated with the composition and the USAM parameters. For the MPEA CoFeNi-Mn12C1.2 a pronounced lattice strain and grain refinement due to the plastic deformation during the USAM was recorded, especially at high USAM amplitude and lower cutting speed due to the greater number of tool oscillations per cutting engagement. Consequently, a hardness increase of up to 380 HV0.025 was induced for the aforementioned MPEA exhibiting a higher wear resistance compared to the X120Mn12. This shows the promising approach for the development of work-hardening materials based on new alloy concepts such as MPEAs allowing also coatings required for applications in tribological systems. As conventional hard and wear-resistant coatings are challenging in machining due to massive tool wear this approach of functional coating materials with high hardening capacity during USAM have the potential to reduce tool wear and ensure a adequate surface integrity and wear resistance.

Plasma and Vapor Deposition Processes

Room Palm 3-4 - Session PP3-WeM

CVD Coating Technologies

Moderators: Hiroki Kondo, Kyushu University, Japan, Frederic Mercier, University of Grenoble Alpes, France

8:00am PP3-WeM-1 Area-Selective Deposition of DLC Using Optoelectronic-Controlled Plasma CVD Method, Susumu Takabayashi, National Institute of Technology, Ariake College, Japan; B. Preuss, T. Lindner, N. Hansisch, T. Lampke, Institute of Materials Science and Engineering (IWW), Chemnitz University of Technology, Germany

Diamond-like carbon (DLC) is an amorphous carbonaceous material composed of sp2 carbon, sp3 carbon and hydrogen. We propose a controlled DLC film synthesis by photoemission-assisted plasma-enhanced chemical vapor deposition (PA-PECVD). A-PECVD is a DC discharge plasma with the aid of photoelectrons from the substrate on which a deep UV light irradates. The current flows only in the UV-irradiated area and the starting voltage of the glow discharge, called photoemission-assisted glow discharge (PAGD), becomes stable owing to plenty of photoelectrons as initial electrons. The discharge before starting PAGD occurs is photoemission-assisted Townsend discharge (PATD). The current in PATD is around 10,000 time larger than that in conventional Townsend discharge. The substrate is not subject to the sheath electric field, so minute and precise synthesis with a rate of nmand min. is realized in PATD. With PAGD, we actually succeeded to fabricate a graphene field effect transistor (GFET) with a DLC top-gate dielectric and synthesize oxygen and nitrogen-doped DLC films on the order of nm thickness. With PA-PECVD, we are developing and exploring application of DLC in nano-electronics and science.

8:40am PP3-WeM-3 Advanced and Economical Hot-Filament CVD Diamond Coating Technology for Deposition of High-Performance Diamond Coatings on Tungsten Carbide Tools, Frank-R. Weber, Weber Technologies GmbH, Germany

Diamond coating systems at Weber Technologies utilize a unique activation mechanism in hot-wire CVD diamond coating technology for the deposition of high-performance diamond coatings. The area of application of this coating technology ranges from wear protection to electronic and medical applications as well as semiconductor technology. High growth rates with low energy consumption have increased the cost-effectiveness of the diamond coating process. The crystallite size and the coating morphology of the diamond layers can be specifically adapted by varying the process parameters. This enables the deposition of 10 to 20 nm ultrananocrystalline monolayers as well as microcrystalline layers with crystallite sizes between 1 to 10 n. Due to our innovative CVD diamond coating process for deposition of high-performance diamond coatings, we can adjust optimal coating structure and scalable crystallite sizes in relation to the respective machining application, e.g., specific application-optimized gradient diamond coatings. The ultra-nanocrystalline diamond coatings are dense and tight from layer thicknesses of 1 to 2 µm. Diamond coating solutions with outstanding coating performance have been optimized for the respective machining application in various materials (CFRP, CFC, graphite, ZrO2 ceramics and Al alloys). Various examples of increased performance when machining with diamond-coated tools in different materials will be presented.

9:00am PP3-WeM-4 CVD Diamond Coating Technology for Cutting Tool Applications, Marvin Wegh, M. Woda, W. Puettz, O. Lemmer, C. Schiffers, CemeCon AG, Germany

In addition to a variety of DLC-based coatings for machining applications and other tribological applications, pure polycrystalline diamond has been established as an excellent coating material in the industrial cutting market for hard to machine materials such as carbon fiber reinforced plastics (CFRP), zirconium oxides, cemented carbide, aluminum silicon alloy and graphite. Modern industrial machining operations often require complex tool geometries with tailored coatings for specific cutting applications. The well-established filament assisted CVD diamond coating technology offers a solution to this challenge while combining complex geometries with extreme mechanical thin film properties. This presentation shall give an insight into the basic principle of Hot Filament CVD diamond deposition on cemented carbide cutting tools on an industrial scale. Furthermore, results
These coatings were evaluated by turning tests of alloy steel (AISI:4140). As a result, cutting performance of MT-TiZrCN coatings was superior to conventional TiCN. It seems that higher hardness of MT-TiZrCN enhances the cutting performance.

11:00am PP3-WeM-10 New Perspectives of Atmospheric Pressure Dielectric Barrier Discharges for the Deposition of Thin Films: From Uncontrolled Amorphous Plasma-Polymer Layer to Chemically Patterned and Crystalline (In)Organic Coatings, François Reniers, Université libre de Bruxelles, Belgium

For more than a century, atmospheric pressure dielectric barrier discharges (DBDs) have been used industrially for gas conversion, the Siemens ozone process dates from 1857 [1], and for surface treatment. Deposition of coatings remained confidential, due to the poor control of the quality of the films. Indeed, the very small mean free path at atmospheric pressure leads to plasma efficiently interacting with very low energies, and random processes due to moving filaments often occur.

We show that, nowadays, starting with organic precursors, DBD can lead to chemically well controlled and tunable thin films, with a variety of properties (hydrophilic/hydrophobic). We establish correlations between the gas phase chemistry (analyzed by mass spectrometry) and the coating chemistry [characterized by XPS and IR-spectrometry][2]. The effect of the nature of the carrier gas (Ar or He) on the roughness and chemistry of the deposited coating is evidenced and explained[3]. With the improvement of the understanding of the plasma chemistry, amorphous inorganic coatings (SiOx, TiOy) can now be easily deposited. By controlling the substrate temperature and the plasma parameters, pure and dense crystalline TiO2 can now be deposited by APDBDs [4]. By modifying the gas composition, introducing ammonia into the plasma, N-doped TiO2, photocatalytic (and antiviral) under visible light can now be synthesized in one single step [5].

Very recently, one could immobilize streamers in a DBD and use them to deposit, in one simple step, locally chemically patterned organic films. The local chemistry (analyzed by µXPS) is depending on the gap between the electrodes, the power impulsion mode (continuous vs pulsed), the precursor flow. A physico-chemical interpretation is proposed [6,7].

Finally, injecting a precursor for inorganic coating in such discharges with immobilized filaments, in appropriate substrate and plasma streamer conditions, crystalline spots, with multi-micron length crystal needles were for the first time synthesized.

References:
5. A. Chauvin et al, Surface and Coatings Technology 472 (2023), 129936

11:40am PP3-WeM-12 Novel Metal Boride Coatings in the System Zr-Hf- Ti-B by LPCVD, Mandy Höhn, M. Krug, S. Höhn, B. Matthey, Fraunhofer Institute for Ceramic Technologies and Systems IKT, Germany

The synthesis of metal boride thin films is recently attracting large interest. Boron forms binary compounds with most metals. These materials in general are high-melting, extremely hard solids with high degrees of thermal stability and chemical inertness. In this work the preparation of mixed metal boride coatings with Me = Zr, Hf, Ti by chemical vapor deposition (CVD) is described. A low-pressure CVD (LPCVD) process using the metal tetrachlorides MeCl3 (Me = Zr, Hf) and/or Ti as precursors as well as BCl3, H2 and Ar is applied. At a deposition temperature of 850°C and a deposition pressure of 6 kPa boride layers were prepared. The coatings were characterized with respect to phase composition, crystal structure, hardness and wear behaviour. Layers were deposited in the binary systems HfTiB2, ZrTiB2 and HfZrB2, as well as in the ternary system HfZrTiB2. The deposited diboride layers show crystalline structures with a high hardness of up to 38 GPa. Depending on the precursor ratio layers with single phase diboride composition or a mixture of different metal diborides were obtained. Phase composition and structure were examined using SEM, EDX and EBSD-analysis. The measured tensile stress in the obtained coatings depends on the deposition conditions and varies between 300 MPa and 800 MPa.
A strong adherence on hardmetal inserts is achieved by using a thin TiN bonding layer prior the diboride deposition. Scratch test measurements showed critical loads of about 90 N. In cutting tests a high performance of the CVD diboride coatings was observed. HfZrTiB; coated inserts showed a higher lifetime in comparison with state-of-the-art CVD-TiB$_2$-coatings in face-milling of TiAl6V4.

**Plasma and Vapor Deposition Processes**

**Room Town & Country A - Session PP4-1-WeM**

**Deposition Technologies for Carbon-based Coatings I**

**Moderators:** Ivan Kolev, IHI Hauzer Techno Coating B.V., Netherlands, Biplab Paul, PLATIT AG, Switzerland

8:00am **PP4-1-WeM-1 Molecular Dynamics Study of Interfacial Phenomena in Diamond-Like Carbon Films, Kwang-Ryeol Lee, Korea Institute of Science and Technology (KIST), Republic of Korea; X. Li, Chinese University of Mining and Technology, China**

**INVITED**

Due to the experimental limitations in precisely characterizing the complicated evolution of a-C film deposition and their physical and chemical properties, molecular dynamics simulation has been widely employed for atomistic understanding of the structural evolution and investigating structure-property relationship. Especially, much attention has been drawn to reactive molecular dynamics simulation technology that can include the chemical reaction during the atomic scale structure evolution. We compared various reactive force field (ReaxFF) models in terms of the structural properties of the simulated a-C films prepared by atom-by-atom deposition approach. By linking the structural properties of the film with the difference in the parameter sets of the ReaxFF models, we reveal that the carbon triple bond stabilization energy in the ReaxFF model, $v_{\text{tr}}$, significantly affects the growth dynamics and structural evolution of the simulate a-C films. Tribological behavior of amorphous carbon surface was extensively investigated in atomic or molecular scale by the reactive molecular dynamics simulation. Simulational study of friction in hydrogenated surface of a-C revealed that hydrogenating the a-C surface only improved the friction property drastically while not deteriorating the intrinsic properties of a-C films. The analysis of interfacial structure demonstrated that being different with a-C:H cases, the competitive relationship between the stress state of H atoms and interfacial passivation caused by H and C=C structural transformation accounted for the evolution of friction coefficient with surface H content. This disclosed the friction mechanism of a-C with surface hydrogenated modification and provides an approach to functionalize the carbon-based films with combined tribological and mechanical properties for specific applications. The reactive molecular dynamics simulation resulted in fundamental understanding of low-friction mechanism. We comparatively investigated the friction property and structural information of contacting interface under different passivated or graphitized states. For the passivation mechanism, the low friction behavior attributes to the reduction of both the real contact area and shearing strength of graphitized sliding interface due to the passivation of a-C dangling bonds. However, the graphitization mechanism strongly depends on the size and layer number of graphitized structure, causing the transition of sliding interface from a-C/a-C, a-C/G to G/G, which is followed by the low-friction mechanism evolved from passivation synergistic effect between graphitization and passivation to graphitization mechanism.

8:40am **PP4-1-WeM-3 Study of ta-C Thick Film Deposition Using FCVA-Based Hybrid Coating System, Jongkuk Kim, J. Kim, J. Jang, Y. Jang, Korea Institute of Materials Science, Republic of Korea**

Tetrahedral amorphous carbon (ta-C) coating film has a high sp$^3$ content and excellent wear resistance and heat resistance even without hydrogen, so it is used in various industrial fields such as cutting tools, automobiles and molds.

In the vacuum arc process using a carbon target, coating is difficult for a long time due to the unstable movement of the arc spot inside the carbon target, resulting in poor thickness and an enlarged coating area. In addition, the Ta-C coating film deposited by this method has high internal stress, making it difficult to increase its thickness.

We controlled the electric and magnetic fields to stabilize the arc spot movement of the carbon cathode for a long period of time, allowing the carbon arc target to be used stably for up to 24 hours at a discharge current of 160 A.

The designed hybrid coating system consists of 1) anode-layer ion source (ALIS) for the etching processes, 2) an unbalanced magnetron sputter (UBM) for the interlayer deposition, 3) a filtered cathodic vacuum arc (FCVA) source for the ta-C film deposition, and 4) pulsed bias power.

To apply the designed hybrid coating process, a system consisting of a single ALIS, two UBMs, and eight FCVAs with a maximum deposition area of 900 mm in diameter and 500 mm in height was built to deposit a 7 µm coating film on a piston ring used in an automobile engine.

We have also built a smaller machine with similar capabilities that can deposit rainbow coatings (up to 0.7 um) and black coatings (0.7-3 um) on non-ferrous cutting tools for a variety of applications, depending on their thickness.

9:00am **PP4-1-WeM-4 Diamond-Like Films of Tetrahedral Amorphous Carbon Deposited by Anodic Arc Evaporation of Graphite, Bert Scheffel, O. Zywitzki, Fraunhofer IEP, Germany**

A physical vapor deposition process using anodic arc evaporation in combination with a hollow cathode arc discharge was applied to the evaporation of graphite for deposition of hydrogen-free carbon layers. The diamond-like carbon (DLC) films deposited on 100Cr6 steel substrates were investigated by nanindentation, Raman spectrometry, FE-SEM, AFM and spectroscopic ellipsometry. The relationships between the process parameters and the coating properties are discussed. Coatings deposited without bias voltage at substrate temperatures < 200°C are very hard (61-75 GPa) with also very high Young's modulus (588-685 GPa). The evaluation of the Raman spectra indicated a high proportion of tetrahedral sp3 bonds in the range of 70-88 %. The coatings proved to be completely droplet-free and have a very low surface roughness as confirmed by FE-SEM and AFM. The deposition rates in the range of 4-18 nm/s are exceptionally high for such ta-C coatings, which is a good prerequisite for industrial applications.

9:20am **PP4-1-WeM-5 Constitution and Properties of TiCl$_3$-x:H/a-C:H Nanocomposite Thin Films Prepared by HIPIMS Processes at Low and Elevated Temperature, Sven Ulrich, C. Pottorak, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany; H. Sternschulte, J. Grau, Technical University of Applied Sciences Augsburg, Germany; J. Julien, T. Sajavaara, Radiate, University of Jyväskylä, Finland; A. Bergmaier, University of the Bundeswehr Munich, Germany; K. Seemann, M. Dürrschmied, M. Stüber, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany**

Carbon-based nanocomposites with tunable multifunctional properties are suitable candidates for diverse fields of applications like tribology or biological, medical and energy technologies. Reactive HIPIMS is selected as a coating process with a Ti-target, an average target power of 5 kW, 50 µs pulse length, 550 µs cycle duration, working gas pressure of 0.3 Pa, 300 sccm Ar working gas flow and up to 40 sccm CH$_4$ reactive gas flow as well as 200°C and 400°C substrate temperatures. HIPIMS show a high ion fraction of the film-forming particles and the deposited energy by ion bombardment during film growth can be adjusted precisely. The constitution and microstructure war determined by a combination of several analytical techniques: EPMA, ERDA, Raman spectroscopy, XRD, TEM and HRTEM. It is shown that by varying the methane reactive gas flow, the following structures can be adjusted: Ti, TiC$_x$-H$_y$ and TiC single layer coatings as well as TiC:H/a-C:H nanocomposites. A clear correlation is identified between the constitution and microstructure with the mechanical properties.

9:40am **PP4-1-WeM-6 Effect of Deposition Temperature and Nitrogen Concentration on Highly Conductive a-C:H/N Films Obtained by Means of DC PACVD, Manuel Schachinger, University of Applied Sciences Upper Austria; F. Definin, University of Applied Sciences Upper Austria, Argentina; C. Forsich, D. Heim, University of Applied Sciences Upper Austria; B. Rübig, T. Müller, C. Dipolff, Rubig GmbH & Co KG, Austria**

a-C:H films are known for their distinct properties such as excellent wear resistance, chemical inertness and a low coefficient of friction. However, these films are typically highly electrically insulating materials. In view of the constantly increasing demands on technical components, it is critical to further expand the areas of application of a-C:H coatings by combining...
their desired and well-established material properties with low electrical resistivity. One way to decrease the specific electrical resistance of DLC films substantially is via the utilization of high-temperature DC PACVD. For further optimization of the electrical properties, nitrogen doping may be applied. In this work, a-C:H:N films were deposited at 450°C and 550°C via DC PACVD on steel and titanium substrates, employing C2H2 and an additional N2 flow. This resulted in an N2 concentration of 0-63 vol.-% in the gas mixture. Subsequently, film characterization was carried out via nanoindentation, density measurement, calotest, the van der Pauw method, GDOES and Raman spectroscopy. Nanoindentation showed that hardness was increased at higher deposition temperatures and continued to increase with nitrogen gas concentrations up to a certain point. Thereafter, a trend inversion was observed. Density was higher for 550°C deposition compared to the 450°C process and increased for both temperatures with higher N2 gas concentrations up to 31 vol.-%. Thereafter, a trend reversal was observed, pointing towards an increased fraction of terminating structures such as C-H or CN triple bonds and a lower fraction of C-C sp3 bonding in the material. Coating thickness decreased from 40 µm to 14 µm at 450°C and from 32 µm to 12 µm at 550°C with increasing nitrogen flow following an exponential function. Specific resistivity reached an average minimum of 1688 µΩ cm at 31 vol.-% N2 for 550°C, which approximates the conductivity of compressed graphite powders. In addition, it decreased by several decades at 450°C, reaching an average minimum of 45 000 µΩ cm. GDOES analysis showed that nitrogen concentrations in the films were markedly low ranging from 0,08 to 1,3 at.-% on average. Raman analysis indicates that nitrogen incorporation induces disordering effects in the film structure, combined with a rise in the number and size of aromatic clusters. In summary, the addition of nitrogen as a process gas successfully enhanced the properties of the film, resulting in materials that exhibited higher hardness than martensitic steels with an electrical resistivity equivalent to that of compressed graphite powders.
Protective and High-temperature Coatings
Room Town & Country C - Session MA4-2-WeA
High Entropy and Other Multi-principal-element Materials II

Moderators: Erik Lewin, Uppsala University, Sweden; Jean-François Pierson, IJL - Université de Lorraine, France

2:00pm MA4-2-WeA-1 Effect of Bilayer Periodic Thickness Ratios on the Mechanical Properties and Corrosion Resistance of TiZrNbTaFeN/TiN High Entropy Alloy Nitride Multilayer Thin Films, Sheng-Yuan Hung, Ming Chi University of Technology, New Taipei, Taiwan; B. Lou, Chang Gung University, Taoyuan, Taiwan; J. Lee, Ming Chi University of Technology, New Taipei, Taiwan

Due to the excellent mechanical and physical properties of high entropy alloy thin films, they have attracted extensive attention and research from the global industry, academy, and research institutions in recent years. In this study, an equimolar TiZrNbTaFe high entropy alloy target and Ti target were used to deposit TiZrNbTaFeN/TiN multilayer films on AlSi304 stainless steel, AISI420 stainless steel, and silicon wafers substrates by a high power impulse magnetron sputtering (HIPIMS) system. The bilayer period thickness ratios of TiZrNbTaFeN and TiN layers were adjusted from 1:1 to 1:2 and 2:1. The cross-sectional morphology of each thin film was observed with a field emission scanning electron microscope. The crystal structure of the multilayered film was analyzed with an X-ray diffractometry. A nanoindenter, scratch tester, and pin-on-disk wear tester were used to measure the hardness, elastic modulus, adhesion, and wear resistance. The corrosion resistance of multilayered thin films in 0.1 M sulfuric acid aqueous solution was tested by the electrochemical worktest. Effect of bilayer periodic thickness ratios on the microstructure, mechanical properties, and corrosion resistance of TiZrNbTaFeN/TiN multilayer films will be explored.

2:20pm MA4-2-WeA-2 Enhanced Mechanical Properties of Nitrogen-Supersaturated High-Entropy Alloys via Phase Manipulation, Yujie Chen, University of Adelaide, Australia

N-supersaturated Fe3Mn5Co4Cu1Cr10 high-entropy alloys (HEAs) were prepared via magnetron sputtering at various Ni flow rates (RNi) of 4, 8, 10, 15 and 20 sccm, denoted hereafter as N4, N8, N10, N15 and N20, respectively. It was found that the content rose up from 6.5 to 28.9 at.% when RNi increased from 4 to 20 sccm. Both N4 and N8 exhibit a face-centred cubic (FCC) structure. An increase in RNi to 10 sccm and 15 sccm resulted in the formation of an FCC and hexagonal closed-packed (HCP) dual-phase structure. The volume fraction of the FCC phase increased with a further increase in RNi, leading to a predominant FCC structure in N20. Despite their unusually high N concentration of up to 28.9 at.%, the HEAs comprises solid solution phases without nitrogen formation. Notably, the N15 HEA with 21.8 at.% N shows an impressive hardness of 20 GPa, comparable to ceramics, while demonstrating exceptional damage-tolerance with considerable plasticity. The excellent combination of high hardness and damage-tolerance is believed to stem from 1) massive solid solution strengthening caused by a high level of Ni intake, 2) a dual-phase FCC and HCP structure supposedly due to the low stacking fault energy, and 3) stress-induced FCC to HCP phase transformation. These findings demonstrate that, in contrast to the high brittleness as seen in nitrides, N-supersaturated HEAs can undergo large plastic deformation like pure metallic materials, thus opening up a new avenue for enhancing the mechanical properties of advanced alloys for applications under extreme loading conditions.

2:40pm MA4-2-WeA-3 Super-Hard (MoNbTaW)N Coatings: Impact of Deposition Temperature on Structural and Mechanical Properties, S. Kata, Venkata Girish Kotnur, University of Hyderabad, India

This study presents the deposition of (MoNbTaW)N coatings on Silicon wafers using reactive direct current (DC) magnetron sputtering, emphasizing the influence of deposition temperature on their structural and mechanical properties. The coatings were deposited under controlled conditions with an Argon flow of ~21 sccm, a Nitrogen flow of ~45sccm, and a deposition pressure of 0.3Pa. The deposition temperature was varied from ambient to 500°C. The characterization of these films was conducted using X-ray diffraction (XRD), Scanning Electron Microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), Atomic force microscopy (AFM), and nanindentation. SEM analysis demonstrated that all coatings were fine-grained with a uniform and dense morphology. The thickness of the films is in the range of 640-710 nm. XRD results confirmed that all coatings face a centred cubic (FCC) crystal structure. A notable decrease in the 111/200 intensity ratio with rising deposition temperature was observed, indicating changes in crystallographic texture.

AFM imaging provided insights into grain size distribution, revealing a decrease in average grain size from 11nm to 5nm as the deposition pressure increased, indicative of grain size refinement. This microstructural evolution with temperature is crucial for understanding the mechanical properties of the films.

Nanoindentation studies revealed that films deposited at temperatures above 300°C exhibited exceptional hardness values exceeding 40 GPa, classifying them as super-hard coatings. The relationship between the hardness and Young’s modulus (H/E) and the plasticity index (H/E^2) was analysed. The highest values of these ratios, 0.2 for H/E and 2.2 for H/E^2, were achieved in coatings deposited above 300°C. These ratios are critical indicators of wear resistance in coatings. The hardness value, 46 GPa, obtained in the present work is the highest ever reported for (MoNbTaW)N coatings.

In conclusion, the (MoNbTaW)N coatings deposited on silicon wafers display significant variation in grain size and mechanical properties with deposition temperature. Films deposited at higher temperatures show promising characteristics for use as super-hard, wear-resistant coatings, highlighting their potential in demanding industrial applications.

3:00pm MA4-2-WeA-4 Structure and Mechanical Properties of (Al,B,Cr,Si, Ti)-based Thin Films, Alexander Kirnbauer, P. Koncny, TU Wien, Institute of Materials Science and Technology, Austria; R. Hahn, Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; S. Kolozsvari, Plansee Composite Materials GmbH, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Ceramics based on the high-entropy concept usually consist of refractory metals such as Ta, Hf, Zr, W, V etc. These metals are good nitride and carbide formers which is why they are mainly used especially for PVD coatings. Nevertheless, the production of these elements needs a lot of energy input due to their very high melting points. Furthermore, these elements are very heavy which in consequence makes them hard to process and rather expensive. In this study we want to focus on a material system consisting of Al, B, Cr, Si, and Ti which are comparably light and cheap elements and the production of a corresponding compound target consumes less energy. To get an idea of the properties of coatings based on this material system we investigated “metallic” coatings as well as nitrides and oxides. The coatings were synthesised by magnetron sputtering using a single composite target with an appropriate composition and different gas mixtures. All the targetings produced show XRD amorphous diffraction patterns without any indication of crystalline phases. Also, SEM images of fracture cross-sections do not show the, usually characteristic, columnar growth which further underpins the results obtained by XRD measurements. The hardness and indentation modulus of the coatings range from ~10 to 22 GPa and from ~170 to 260 GPa, respectively, depending on the character of the coating. To get information of the bonding state, XPS measurements were carried out. Furthermore, in-situ cantilever bending tests were done to investigate the fracture toughness of the coating depending on their either “metallic”, nitride, or oxide character.

3:20pm MA4-2-WeA-5 Synthesis and Characterization of High Entropy Ceramic Coatings from Cr-Hf-Mo-Ta-W Refractory Metal System, S. Debradová, T. Stasiak, V. Buršíková, Masaryk University, Czechia; Z. Cigány, K. Balázsi, HUN-REN Centre for Energy Research, Hungary; S. Lin, N. Koutná, Technische Universität Wien, Austria; Pavel Souček, Masaryk University, Czechia

High entropy alloys (HEAs) are multicomponent materials containing at least five principal elements with contents ranging between 5 and 35 at.%. The high entropy concept also extends to ceramics, such as oxides, nitrides, borides and carbides. High entropy materials can exhibit high strength and hardness at low as well as high temperatures, outstanding structural stability, wear, corrosion and oxidation resistance. This makes them promising candidates for next-generation replacements of traditional materials in many areas of the industry.

Wednesday Afternoon, May 22, 2024
In this contribution, we are examining the formation of single-phase high entropy nitrides and high entropy carbides NaCl-type fcc structure from the Cr-Hf-Mo-Ta-W system. Magnetron sputtering was used for all depositions. An ambient temperature was used for the first deposition set, while an elevated temperature of 700°C was used for the second to observe the influence of the temperature on the crystallization. Argon/nitrogen gas admixture was used in nitrides, while argon/acyetylene was used in carbides. This resulted in the first difference in reaching different nitrogen/carbon content in the coatings. While sputtering in nitrogen is a typical representative of reactive magnetron sputtering and nitrogen content never exceeded 50 at.%, sputtering in acetylene belongs to the hybrid PVD-PECVD deposition processes, also known as unsaturated reactive sputtering, and much higher carbon content in the coatings is reached. The deposition rate did not significantly decrease for all reactive gas flows.

The structure and mechanical properties of the coatings were heavily influenced by the reactive gas flow for both systems. In films deposited without acetylene flow, a bcc metallic phase was observed. Increasing reactive gas flow first showed an amorphous structure and then an fcc monoclinic phase in the structure. Therefore, the ability of the system to form either metallic or ceramic nitride and carbide single phases was confirmed. Amorphous coatings exhibited a dense microstructure, while crystalline films were more columnar with multilayered structure at the nanoscale given by the deposition process geometry. The mechanical properties of the deposited films were good, exhibiting a hardness of up to 25 GPa, while the majority of the coatings were around 20 GPa. There was no great difference between the hardness of the corresponding nitrides and carbides.

This research was supported by project LM2018097, funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA23-059475 financed by the Grant Agency of the Czech Republic.

3:40pm MA4-2-Wea-5 Mechanical and Oxidation Properties Evaluation of Equimolar and Non-Equimolar High Entropy Alloy Boron Carbonitride Coatings, Igamcha Moirangthem, National Taiwan University of Science and Technology, Taiwan; B. Lou, Chang Gung University, Taiwan; C. Wang, National Taiwan University of Science and Technology, Taiwan; J. Lee, Ming Chi University of Technology, Taiwan.

In recent studies, high entropy alloy (HEA) nitride and carbide coatings have shown improved chemical and mechanical properties as compared to conventional alloy nitride and carbide coatings. Various combinations of transition metals in equimolar ratio as well as non-equimolar ratio carbide and nitride coatings have been explored. The first difference in reaching different multilayered structure, hardness, and wear resistance of TiZrNbTaFeBCN high entropy coatings was confirmed in this study, an equimolar TiZrNbTaFe alloy target and a non-equimolar AlCrNBsiTi alloy target were used to fabricate their boron carbonitride phases using superimposed high power impulse magnetron sputtering. A radio frequency (RF) power source was used for the boron target. The coatings were deposited on p-type Si (100), AISI 304, and AISI 420 stainless steel substrates. The nitrogen flow was maintained at a constant rate, and the acetylene flow rate was varied. The microstructures, phases, and surface roughness of the HEA boron carbonitride coatings were investigated by a field emission scanning electron microscope, X-ray diffractometer, and atomic force microscope, respectively. The nanohardness was measured using nanoindentation. A pin-on-disk tribometer was used to study the wear characteristics of these coatings. The effects of heat treatment, oxidation, and potentiodynamic polarization of these coatings were also examined. The mechanical, chemical, and oxidation properties of TiZrNbTaFeBCN and AlCrNbSiTiBCN boron carbonitride coatings were explored in this work.

4:00pm MA4-2-Wea-7 Research on the Effects of Various Acetylene Contents on the Mechanical Properties of TiZrNbTaFeBN High Entropy Alloy Films, Meng-Hsueh Chuang, National Taiwan University of Science and Technology, Taiwan; B. Lou, Chang Gung University, Taiwan; J. Lee, Ming Chi University of Technology, Taiwan; C. Wang, National Taiwan University of Science and Technology, Taiwan.

The conventional alloys are made of one primary element with the addition of small or moderate amounts of alloying elements to yield an alloy with specific properties. However, in 2004, Professor Jien-Wei Yeh from National Tsing Hua University, Taiwan, and Professor Brain Cantor from the University of Oxford, UK, independently introduced innovative material systems known as multicomponent alloys and high entropy alloys (HEAs). These breakthroughs garnered significant attention and research interest from the global academic, industrial, and scientific communities and led to a new distinct branch in materials research. The effects of various acetylene gas flow rates on the chemical composition, microstructure, phase structure, hardness, and wear resistance of TiZrNbTaFeBCN high entropy alloy films were investigated. The HEA thin films were prepared by co-sputtering an equimolar TiZrNbTaFe high entropy target and a TiB target onto the surfaces of AISI420 stainless steel, AISI304 stainless steel, and P-type (100) silicon wafer substrates using fixed nitrogen gas flow rate and different acetylene flow rates. The structures of thin films were determined by X-ray diffraction. The cross-sectional morphologies of thin films were examined by field emission scanning electron microscopy (FE-SEM). A nanoindenter and scratch test were used to evaluate the hardness and adhesion properties of thin films, respectively. Effects of carbon contents on the mechanical properties of TiZrNbTaFeBCN HEA thin films will be discussed.

4:20pm MA4-2-Wea-8 Influences of Target Poisoning on the Mechanical Properties of AlCrNbSiTiBCN Thin Films Grown by a Superimposed Highpower Impulse and Medium-Frequency Magnetron Sputtering. Tse Wei Chen, J. Lee, Ming Chi University of Technology, Taiwan; B. Lou, Chemistry Division, Center for General Education, Chang Gung University, Taiwan.

High entropy alloy (HEA) materials have been widely studied since reported by Prof. Yeh in 2004 due to their outstanding mechanical and physical properties. HEAs refer to alloys consisting of a minimum of five elements, with each element’s content not exceeding 35 at.%. This compositional constraint prevents any single element from dominating the material’s behavior, resulting in unique characteristics arising from the collective contribution of multiple elements. Compared with traditional binary or ternary alloy nitride coatings, HEA coatings have more excellent properties, such as high hardness and good wear resistance, excellent corrosion resistance, and good thermal stability. In this study, the AlCrNbSiTi and TiB2 targets were used to deposit AlCrNbSiTiBCN thin films by the superimposed HiPIMS-MF system using nitrogen and acetylene gases on 420 stainless steel, 304 stainless steel, and silicon wafer substrates. During sputtering, the N2 gas flow was fixed, and the acetylene gas flow rate was precisely controlled by a plasma emission monitoring (PEM) control system. The target poisoning ratio was changed from 10 % to 80 % to grow five thin films with different carbon contents. The cross-sectional morphology of each film was observed using field emission scanning electron microscopy (FE-SEM). X-ray diffraction analysis was used to examine the crystal structure of thin films. The hardness, elastic modulus, adhesion, and wear resistance of thin films were evaluated using a nanoindenter, scratch tester, and pin-on-disc wear tester. The influence of the target poisoning rate on the mechanical properties of AlCrNbSiTiBCN high entropy alloy boron carbonitride films was explored in this study.

Keywords: AlCrNbSiTiBCN, high power impulse magnetron sputtering (HiPIMS), hardness, target poisoning, acetylene, plasma emission monitoring.

4:40pm MA4-2-Wea-9 Mechanical and Anticorrosive Properties of Laminated (NbTaMoW)N Films, Yan-Zhi Liao, Y. Chen, National Taiwan Ocean University, Taiwan (NbTaMoWN)N films were prepared through co-sputtering with four element targets. The distinction in characterization between the laminated nitride films fabricated at substrate holder rotation speed R0 of 2 and 10 rpm and homogeneous high-entropy alloy nitride films prepared at R0 of 30 rpm were evaluated. The nitrogen flow rate [fN2 = [N2/(N2+N4+Ar)] during the sputtering process was set at 0.1, 0.2, and 0.4, respectively. The deposition rate decreased from 43.8 to 33.7 nm/min with increasing fN2 from 0.1 to 0.4 at R0 of 2 rpm due to the target poisoning effect, whereas the deposition rate decreased from 46.4 to 34.8 nm/min at R0 of 10 rpm. The phase structures and mechanical and anticorrosive properties of the (NbTaMoWN)N films were studied. The results indicated that a metallic phase dominated structure was observed for the films prepared at fN2 of 0.1, whereas nanocrystalline and face-centered cubic nitride phases were obtained for films fabricated at fN2 of 0.2 and 0.4, respectively. The films deposited at fN2 of 0.4 exhibited hardness values of 25.2 and 26.1 GPa for the films prepared at R0 of 2 and 10 rpm, respectively, which were lower than 29.9 GPa for the films prepared at R0 of 30 rpm. Potentiodynamic polarization tests were conducted out for evaluating the anticorrosive properties of the films on SUS420 substrate.
Wednesday Afternoon, May 22, 2024

Functional Thin Films and Surfaces
Room Town & Country D - Session MB2-2-WeA
Thin Films for Electronic Devices II
Moderators: Claudiu Falub, Evatec AG, Switzerland, Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solution AG, Lichtenstein, Panos Patsalas, Aristotle University of Thessaloniki, Greece

2:00pm MB2-2-WeA-1 Electro-optic Thin Film Switch for Silicon Photonics Quantum Computer, Vimal Kamineni, PsiQuantum Ltd., USA INVITED

A general-purpose quantum computer has a broad range of applications from finance, healthcare, climate, security, computing, materials, to other industry verticals as companies continue to explore the possibilities. PsiQuantum is on a mission to build and deploy the world’s first useful quantum computer utilizing integrated silicon photonics. Photonic qubits uniquely overcome the scaling challenges associated with error correction for implementing a large-scale fault tolerant quantum computer. These photonic qubits are implemented in an integrated custom process stack, co-developed with our semiconductor foundry partners. The talk will cover our development towards building a scalable integrated silicon photonics platform with focus on a high performance electro-optic thin film switch. Our linear optics operations are probabilistic, and efficiency of successful events is boosted by multiplexing using an electro-optic switch. The electro-optic material induces an optical phase shift when voltage is applied, and it is fabricated using barium titanate (BTO). Thin film BTO was downselected for our application as it offers the highest Pockels coefficient at room temperature when grown epitaxially as a thin film on silicon substrates. BTO enables high speed phase shifters with low loss and power consumption which are critical metrics for a quantum computer.

KEYWORDS
Silicon photonics, quantum computing, qubit, electro-optic switch, barium titanate

2:40pm MB2-2-WeA-3 Growth and Characterization of Thermoelectric–Topological Insulator Bi$_{x}$Se$_{x}$Te$_{1-x}$ (X = 0, 1.5, 2, 3) Films Grown Using Pulsed Laser Deposition, Phuoc Huu Le, Ming Chi University of Technology, Taiwan, Viet Nam; N. Quyen, L. Tuyen, National Yang Ming Chiao Tung University, Taiwan, Viet Nam; S. Jian, I-Shou University, Taiwan; C. Luo, J. Lin, National Yang Ming Chiao Tung University, Taiwan; J. Lee, Ming Chi University of Technology, Taiwan

Bismuth chalcogenides have been intensively studied for their high-performance thermoelectric (TE) properties and novel topological surface states, which can significantly benefit novel applications in fields such as TE devices, spintronics, and quantum computing. In this study, Bi$_{x}$Se$_{x}$Te$_{1-x}$ films (x = 0, 1.5, 2, 3) films were grown on Al$_2$O$_3$ (0001) substrates at the same conditions (i.e., T$_s$ = 280°C, P$_w$ = 30.7 Pa, 5 Hz and 30 min) using Bi$_2$Te$_3$, Bi$_2$Se$_3$, Te$_2$ and Bi$_2$Se$_3$ targets. The grown thin films exhibit rhombohedral structures of Bi$_2$Te$_3$, Bi$_2$Se$_3$, Bi$_2$Se$_3$, and Bi$_2$Te$_3$ with highly c-axis preferred orientations, and near stoichiometric compositions of the phases. XPS results present the surface composition and oxidation status of the films after a month of atmospheric exposure. The films exhibit granular morphologies with different surface features of triangular-, rice-like-, and hexagonal grains. Hardness (Young’s modulus) of the films are 2.3 GPa (39.4 GPa) for Bi$_2$Te$_3$, 2.5 GPa (74.5 GPa) for Bi$_2$Se$_3$, 3.2 GPa (80.4 GPa) for Bi$_2$Se$_3$, and 3.6 GPa (91.8 GPa) for Bi$_2$Se$_3$. In addition, TE power factor of the Bi$_2$Se$_3$Te$_3$ (x = 0.0, 1.5, 2, 3) films were 10.1 µW/cm.K$^2$ (x = 0), 2.84 µW/cm.K$^2$ (x = 1.5), 3.98 µW/cm.K$^2$ (x = 2), and 2.77 µW/cm.K$^2$ (x = 3). Moreover, the films show 3D weak antilocalization magnetoresistance at low temperatures (T < 10 K), suggesting for presence of topological surface states in the films. Furthermore, we report the ultrafast dynamics of electrons and phonons in the Bi$_2$Se$_3$Te$_3$ (x = 0.0, 1.5, 2, 3) films studied by the time-resolved pump-probe spectroscopy. Keywords: Bismuth chalcogenides; Pulsed laser deposition; nanointerdentation; Magnetotransport; Time-resolved pump-probe spectroscopy

3:00pm MB2-2-WeA-4 Stoichiometric Engineering of Rotary Metal Oxide Targets for Thin Film Applications: A Focus on Zinc Oxide Based Alternatives, Jing Yang, SCI Engineered Materials, Inc., USA

Indium Tin Oxide (ITO) is the most widely used transparent conductive oxide (TCO) for flexible electronics. With its demand increasing for applications such as liquid crystal displays, smart windows, thin film photovoltaics, architectural windows, and polymer-based electronics, the historically volatile pricing of Indium presents a concern for manufacturers. Zinc Oxide based materials, given Zn’s abundance in Earth’s crust, emerge as a cost-effective alternative for thin film applications.

Zinc Tin Oxide (ZTO), a potential candidate as the TCO layer in OLED, the channel layer in Thin Film Transistor (TFT), and the interlayer for low-E glass, faces challenges in DC sputtering due to the spinel structure of Zinc Stannate. One solution is to employ reactive sputtering of Zinc and Tin metal targets. This approach introduces difficulty in terms of precise stoichiometric control and overall quality of finished film. Alternatively, RF sputtering of a ZTO target may be employed, but the film growth rate is very slow.

In this study, we explore the use of a conductive, sintered oxide target as the solution that offers controlled DC sputtering and high-quality film production. We demonstrate compounding various ratios of Zinc and Tin oxides into single targets to create conductive targets in both planar and rotary geometries for DC sputtering. The study assesses the stoichiometric impact on target manufacturing and the subsequent thin film properties, comparing the electrical and optical properties of ZnO-based films with traditional TCOs like ITO. We also present a conductive rotary target designed for high power density, crucial for high-throughput industrial applications.

3:20pm MB2-2-WeA-5 Flexible FSMA Based Magnetoelectric Sensor, Davinder Kaur, Indian Institute of Technology Roorkee, India

The present study reports the fabrication of highly flexible, cost-effective, nano-structured magnetic field sensor comprising AlN/Ni-Mn-In ME heterostructure fabricated over magnetostrictive Ni foil. The magnetoelectric and magnetoelastic characteristics of the ME heterostructure based flexible magnetic sensor has been thoroughly investigated. The ultra-low magnetic field up to or less than ~1 µT has been easily detected from the fabricated sensor. Hence, the present lead-free ME heterostructure integrated over flexible substrate can enhance the multifunctionality in futuristic flexible magnetic field sensors for room temperature applications. Moreover, the surface acoustic wave (SAW) delay line-based piezo resonator was fabricated over highly flexible AlN/Ni-Mn-In/Kapton for flexible MEMS application. The fabricated device resonates at ~1.40 GHz. The effect of the external magnetic field on the resonance frequency (f$_r$) of the device has also been investigated and tunability (∆f$_r$/f$_r$) ~9% was observed. The device displays high sensitivity of ~0.94 Hz/mT at room temperature. The flexibility of the fabricated magnetic field sensors has been investigated in terms of the bending cycles and bending angle. The sensor characteristics remain unchanged up to ~ 2500 bending cycles. Hence, the device consisting ME heterostructure fabricated over flexible substrates shows its full potential towards the flexible and wearable electronics.

Keywords: Ferromagnetic shape memory alloys, flexible magnetic sensor, lead-free piezoelectric, magnetostrictive effect, surface acoustic waves (SAW), Bulk acoustic waves (BAW)

3:40pm MB2-2-WeA-6 Growth of Nanostuctured Molybdenum Disulfide (Moss) Thin Film for the Application of Electronic Materials, I. Giwa, K. Qian, F. Sanchez, E. Mawire, S. Dong, E. Smith, Q. Yuan, Zhigang Xiao, Alabama A&M University, USA

We report the fabrication of molybdenum disulfide (MoS$_2$) thin films—based electronic devices. Nanostuctured molybdenum disulfide (MoS$_2$) thin films are grown as the active semiconductor channel material for the fabrication of MoS$_2$-based field-effect transistors using plasma-enhanced atomic layer deposition (ALD). MoS$_2$-based electronic devices such as MoS$_2$ field-effect transistors, inverters, and ring-oscillators are fabricated with the ALD-grown MoS$_2$ film using the clean room-based micro- and nano-fabrication techniques. Hydrogen sulfide (H$_2$S) gas is used as the S source in the growth of molybdenum disulfide (MoS$_2$) while molybdenum (V) chloride (MoCl$_5$) powder is used as the Mo source. The MoS$_2$ film will be analyzed by the high-resolution tunnel electron micrograph (HRTEM), scanning electron micrograph (SEM), X-ray photoelectron spectroscopy (XPS) analysis and...
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Raman spectrum analysis. The fabricated MoS₂ device wafer will be annealed at high-temperatures (800 °C) and the electrical property of the MoS₂-based electronic devices will be measured before and after the high-temperature annealing and will be compared. The characterization results of the nanostructured molybdenum disulfide (MoS₂) thin films and the measurement results on the fabricated MoS₂-based electronic devices will be reported in the ICMCTF 2024 Conference.

Acknowledgements: The research is supported by National Science Foundation under Grant No. ECS-2105388.

4:00pm MB2-2-WeA-7 High Voltage on-Chip Micro Supercapacitor as a Miniaturized Energy Storage Device for Microelectronic Applications, Sheetal Issar, Indian Institute of Technology Roorkee, India; D. Jhajharia, Indian Institute of Technology Kanpur, India; R. Chandra, Indian Institute of Technology Roorkee, India

High voltage microsupercapacitors (MSCs) along with energy harvesters can be used to integrate miniaturized self-powered system in many microelectronic devices. On-chip MSCs are considered as one of the promising energy storage devices due to their high energy density, long cycle life, and fast charging-discharging rate. In this regard, transition metal nitrides (TMNs) based nanostructured are considered as an effective electrode material for fabrication of high performance on-chip MSCs due to their high electrical conductivity. We report fabrication of highly stable interdigitated micro patterns of titanium vanadium nitride (TiVN) and titanium chromium nitride (TiCrN) over a SiO₂-coated Si substrate by using single-step reactive DC magnetron sputtering technique. Generally, the low voltage window of on-chip MSCs is a bottleneck in designing miniature power source in microelectronic devices. One of the most technical challenges with the on-chip MSCs is to enhance cell voltage without compromising its tiny size. The electrochemical voltage window of the MSCs is greatly dependent on the electrolyte itself. In the present work, different electrolytes such as aqueous, water-in-salt, and ionic liquid incorporated polymer gel electrolyte are utilized to check the electrochemical performance of TMN-based MSCs. An exceptionally high voltage window of more than 3 V is achieved in TiVN and TiCrN-based MSCs with TEABF₄/ethylene carbonate/propylene carbonate ionic liquid entrapped in the polyvinylidene fluoride (PVDF) polymer gel electrolyte. The on-chip MSC exhibits an optimum capacitance of ~500 μF/cm² at a current density of 0.07 mA/cm² with an energy density of ~ 0.7 μWh.cm⁻² and a power density of 169.02 μW.cm⁻³. This study provides new opportunities to integrate nanocomposite-based microelectrodes directly for on-chip MSCs for utilization at high voltage miniaturized power sources.

4:20pm MB2-2-WeA-8 Few-layered Multi-transition Metal Dichalcogenide Alloy Absorber for High-performance Photodetector, T. Nguyen, J. Ting, National Cheng Kung University (NCKU), Taiwan

Low-dimensional materials including quantum dots, nanowires, and two-dimensional materials have attracted increasing research interest in the fields of electronics and optoelectronics. Photodetector is no exception as a spread of two-dimensional (2D) material in photodetector has attracted a great deal of attentions. Among them, 2D transition metal dichalcogenide (TMDC) offers unique semiconductor properties, including quantum spin Hall effect, valley polarization, and two-dimensional superconductivity.

We report the growth of few-layered multi-metallic TMDC alloys with salt-assistance on SiO₂/Si substrates with controllable composition using a chemical vapor deposition (CVD) technique. Composition control has been investigated by varying the concentration of individual precursors. Various analyses were carried out to understand the material properties, including structural, physical, chemical properties, and the performance of TMDCs in photodetectors.

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Tribology and Mechanics of Coatings and Surfaces
Room Town & Country B - Session MC3-1-WeA

Tribology of Coatings and Surfaces for Industrial Applications I

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany; Rainer Cremer, KCS Europe GmbH, Germany; Stephan Tremmel, University of Bayreuth, Germany

2:00pm MC3-1-WeA-1 Tribological Coatings to meet Future Requirements for Green Mobility, Steffen Hoppe, Tenecon Powertain, Product & Technology, Germany

The global transportation industry is taking on the challenge of decarbonizing propulsion with the goal of achieving climate-neutral mobility. Hydrogen-powered internal combustion engines (H-ICEs) are the mix of applicable and complementary technology solutions. This technology can drive decarbonization on a broad scale, especially in commercial truck, off-highway and industrial applications. Non-fossil fuels like ammonia, methanol or e-fuels are required to achieve net-zero CO₂ emissions in marine and aviation markets.

The introduction of non-fossil fuels has a significant impact on the tribology systems in ICEs. Due to the significant differences in physical and chemical properties of hydrogen, ammonia, and methanol compared to gasoline and diesel, the combustion strategies need to be adapted to these fuels. Advanced coating solutions are required for ICES components to address the impact on the tribological systems caused by higher combustion temperatures, oil dilution or deterioration, and water entrapment.

This paper will show how the critical tribological system of piston rings can be optimized by developing high performance coatings. Hydrogen free DLC coatings, advanced thermal spray coatings and new electrochemical coatings are applied to achieve robust tribological systems in decarbonized propulsion systems.

2:40pm MC3-1-WeA-3 Current-Induced Friction and Graphitization Effects in Amorphous and Tetrahedral Amorphous Carbon Coatings on M2 Steel: An Electro-Tribological Investigation, Amir Masoud Khodadadi Behtash, A. Alpos, University of Windsor, Canada

In electric vehicles, protecting bearings from shaft voltages and bearing currents is key to avoiding premature wear and failure. Diamond-like carbon (DLC) coatings, with their low friction and insulating properties, could extend bearing life and reliability. This study assesses how electrical current affects the frictional behaviour of M2 steel coated with non-hydrogenated diamond-like carbon (a-C) and tetrahedral amorphous carbon (ta-C), by comparing their coefficients of friction (COF) against an AISI 52100 steel counterface under varying currents but the same loading conditions using a ball-on-disk tribometer. The uncoated M2 steel exhibited COF values ranging from 0.55 to 0.62, suggesting frictional instability and a tendency towards oxidation with sliding under electrical currents (Figure 1). The a-C coatings maintained a stable coefficient of friction under 0.15 up to currents of 1200 mA. In contrast, the ta-C coatings showed variable COFs, starting at 0.20 and rising above 0.60, indicating less stability under electrical currents. Micro-Raman analyses revealed graphene formation within the wear tracks of a-C samples upon exposure to induced current (Figure 2a). This current-induced graphitization within the wear tracks correlates with the a-C coating’s low and stable COF. In contrast, ta-C coatings, with a higher sp³ content, underwent less graphitization and more oxidation (Figure 2b) at the steel interface when subjected to the same electrical current. The increase in D peak intensity within wear tracks of a-C samples at higher currents suggested a rise in defect density in graphene layers formed. The mechanisms underlying these observations, including the interplay between graphitization and electrical current, as well as their implications for electro-tribological systems, will be discussed in the presentation.

3:00pm MC3-1-WeA-4 Compositionally Graded MoS₂-WC Spray Coatings for Robust Tribological Protection in Low Viscosity Fuels, Euan Cairns, J. Decker, University of North Texas, USA; S. Dixit, Plasma Technology Inc., USA; S. Berkebile, Army Research Laboratory, USA; D. Berman, S. Aouadi, A. Voevodin, University of North Texas, Texas

Increased usage of low carbon emission fuels, such as ethanol and dodecane, are driving a critical need for advanced lubricious materials to extend the wear life of fuel pump components. Solid lubricants are traditionally employed in applications where liquid lubrication is insufficient if not impossible. We demonstrated that molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂) films spray-coated onto 52100 steel and WC-17Co...
surfaces decreased friction and wear during sliding in hydrocarbon fuels. Solid lubricant coatings were substantially more robust while sliding in non-polar dodecane fuel, where friction coefficients of less than 0.1 were maintained for thousands of sliding cycles. Meanwhile, in polar ethanol fuel, low friction was only kept for a few hundred cycles before sharp failure of the coatings, due to oxidation and removal of the lubricant from the wear track.

In this study, we propose to further enhance the wear resistance of crucial components in fuel pumps via designing compositionally graded Mo5–WC coatings. The microstructure and wear data were evaluated using scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). Analysis of worn surfaces was performed using optical profilometry and Raman spectroscopy to analyze the chemical evolution inside the wear track across multiple fuel chemistries. Insights gained from this study offer valuable information for the development of robust lubrication solutions in the realm of low carbon emission fuel applications.

3:20pm MC3-1-WeA-5 Tribological Behavior of DLC Coatings: Wear Map of Oil Lubricated Contacts in a Three-Pins-on-Disc Test Configuration, Julien Keraudy, N. Manninen, F. Rovere, Oerlikon Surface Solutions AG, Liechtenstein

Diamond-like carbon (DLC) coatings have emerged as a promising coating solution able to combine high wear resistance and low friction coefficient. In fact DLC coatings comprise a family of different carbon-based coatings which can show a broad range of properties based on the fraction of sp3/sp2 bonds and also on the amount of incorporated hydrogen or metal dopants.

In the present study different DLC coating variants were tested regarding their tribological performance. The coatings were tested in three pin-on-disc configuration under additive oil (ZDDP) lubricated conditions. Different pressure x velocity (PV) conditions were tested during endurance tests in order to identify the coatings performance over a broad range of PV conditions. The lubrication regimes were identified by Strubeck curve in order to determine the lubrication regimes for the different test parameters. The coatings were analyzed by scanning electron microscopy (SEM), profilometry and optical microscopy after the tribological tests, in order to evaluate the wear mechanisms. The coatings were characterized regarding their topography and morphology (by means of SEM analysis), roughness (by profilometry analysis) and hardness (by nanoindentation). The coatings chemical potentials, roughness and hardness are strongly correlated with the tribological performance.

3:40pm MC3-1-WeE-6 Tribological Behaviour of Cobalt-Based and Nickel-Based Systems Under Various Environmental Conditions for Gas Turbine Engines, Marie-Laurence Cliche, P. Stoyanov, Concordia University, Canada

Increase in capability, affordability, safety, and environmental compatibility are all challenges that can be associated to the advancement within the aerospace industry. Especially when it comes to the next generations of gas turbine engines which will be required to significantly reduce the overall CO2 emissions. To achieve this goal, the conditions in which materials are expected to operate will become harsher and thus, making the selection of materials for specific regions of the engines more challenging. Mechanical and tribological properties of materials dictate the lifetime of many contacting and moving mechanical assemblies that can be found in the engines, however, the degradation of these materials properties can lead to failure of the many components and severely damage the machinery. Metals and superalloys commonly used in the engines have been extensively characterized at high temperatures, but little attention has been given to their tribological behaviour at cryogenic and elevated (above 700°C) temperatures. Therefore, the objective of this study is to fully characterize and capture the tribological behaviour of commonly used nickel-based and cobalt-based superalloys and to evaluate how they behave when subjected to such extreme temperature ranges. In this study, the wear and friction behaviours of Ni-based and Co-based superalloys at cryogenic temperatures (-50°C & -80°C) and elevated temperature (800°C) were obtained using a ball-on-flat tribometer. The characterization of the unworn and worn surfaces was performed using confocal laser scanning microscopy (CLSM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Overall, this study will establish the wear and friction performance of commonly used Ni-based and Co-based superalloys in gas turbine engines and emphasis will be made on their interfacial behavior.

4:00pm MC3-1-WeA-7 Development and Process Optimization of Suspension Plasma Spray Coating to Enhance the Frictional Properties and Wear Resistance, Yong-Jin Kang, Y. Yoo, S. Lee, D. Kim, Korea Institute of Materials Science, Republic of Korea

Chromium oxide (Cr2O3) coating produced by the atmospheric plasma spray (APS) process is widely used in industrial fields such as anilox rolls, doctor blades in the paper-making industry, pump sleeves, and break discs that require resistance to sliding wear and corrosion. However, due to its low mechanical properties and high surface roughness and porosity, the development of alternative coating processes such as suspension plasma processes (SPS) is required. Accordingly, in this study, we developed a chromium dioxide coating with low surface roughness, high hardness, and excellent wear resistance through a suspension plasma spray (SPS) process. By optimizing the stand-off distance, feedstock powder size, and power during SPS process, dense Cr2O3 coating with a porosity less than 2% was achievable. Microstructures and mechanical properties of as coated samples were characterized by SEM, XRD, surface profiler. Then, tribological properties, such as friction coefficient and wear rate, were evaluated by ball-on-disc test. The wear resistance of Cr2O3 coatings via SPS and APS processes was compared with their intrinsic microstructure and mechanical properties.

4:20pm MC3-1-WeA-8 Excellent Mechanical, Tribological and Anticorrosive Properties of Nanocomposite Coating Based on Polyvinyl Alcohol/MXene/Tannic Acid Film, Dieter Rahmadiawan, National Cheng Kung University (NCKU), Taiwan, Indonesia & S. Chen Shi, National Cheng Kung University (NCKU), Taiwan

This study investigates the effects of incorporating tannic acid into a polyvinyl alcohol (PVA)/MXene film. The composite was characterized for its mechanical, corrosion resistance, and tribological properties. The addition of tannic acid was found to enhance the mechanical strength of the composite, attributed to its crosslinking capabilities and interactions with the MXene nanosheets. Corrosion resistance was significantly improved, as tannic acid acted as a corrosion inhibitor, forming a protective layer on the composite surface. Tribological tests revealed reduced wear rates and improved frictional behavior, indicating the effectiveness of tannic acid in enhancing the lubricating properties of the PVA/MXene system. The comprehensive analysis presented in this study underscores the potential of PVA/MXene/Tannic Acid composites for applications demanding superior mechanical performance, corrosion resistance, and tribological efficiency.

4:40pm MC3-1-WeA-9 Effects of Various Al/Cr Composition and Deposition Conditions on Surface Properties, Mechanical and Tribological Properties of AlCrN Coatings, SHINICHI TANIFUI, M. NAKAMURA, R. TAKEI, S. KIJIME, T. TAKAHASHI, Kobe Steel, Ltd., Japan

The environment in which tools and molds are used in production is becoming harder and harder year by year. Therefore, coatings applied by physical vapor deposition are required to have high hardness and oxidation resistance. In order to expand the lifetime of tools and dies, typical examples of coatings with such properties are AlTiN and AlCrN coatings. The oxidation resistance of coatings is attributed to the Al content of the coating, and it is known that the higher the Al content, the higher the oxidation resistance. On the other hand, the hardness of the coatings differs, with AlTiN and AlCrN coatings showing maximum hardness at 67 at% and 77 at% Al content, respectively. It is known that when the Al content in both coatings exceeds these levels, a decrease in hardness occurs due to the precipitation of soft AlN in the coating.

At last year's conference, KOBELECO introduced its new Cathodic arc evaporation system, AIP-iX. Using the new μ-Arc evaporation source installed in the system, KOBELECO reported on the surface properties of AlCrN coating with 75% Al content as observed by scanning electron microscopy, the coating hardness as measured by nanoindentation test, and the crystal structure of the coating by X-ray diffraction method. The results of the crystal structure of the coatings were also reported by the X-ray diffraction method. The results of the nanoindentation test and the crystal structure of the coating by X-ray diffraction are also reported. The surface smoothness of the coating is superior to that of the conventional cathodic arc deposition coating, and the cubic crystal structure is confirmed, indicating that a hard coating can be formed. On the other hand, one of the main characteristics of μ-Arc is that it has fewer surface macro-particles than conventional coatings, but the effect of the surface properties of the coating on the tribological properties of the coating has not yet been clarified. In order to meet the needs of industrial applications, it is important to clarify the relationship between tool and die performance and the properties of the coatings. In this report, we describe
the results of our studies of AlCrN coatings prepared under various compositions and deposition conditions, and the effects of these conditions on surface properties, mechanical and tribological properties, as well as the relationship of these coatings to tool and die performance.

5:00pm MC3-1-WeA-10 Effect of Multilayer Architecture on Mechanical Properties and Cutting Performance of AlTiBN/AlCrBN Coatings, Chungen Chang, Y. Chang, National Formosa University, Taiwan

Ti-6Al-4V alloy is a currently popular material known for its high fracture toughness and hardness, making it a preferred choice for industries like aerospace and automotive due to its excellent processing properties. However, during the machining of Ti-6Al-4V, substantial heat is generated due to its relatively low elastic modulus and thermal conductivity. This excess heat accelerates tool wear and can lead to tool failure. In recent years, AlTiN and AlCrN hard coatings have become widely used for cutting tools. Machining difficult-to-cut materials has become a trend, and to enhance the properties of the coatings for processing these materials, Appropriate amounts of Boron (B) elements can be added to improve hardness, toughness, thermal stability, and wear resistance of the AlTiN and AlCrN coatings. The addition of Boron (B) atoms promotes the formation of a nano-composite structure, which includes AlTiB and AlCrBN solid solutions, surrounded by an amorphous BN phase. In this study, the influence of AlTiBN/AlCrBN coatings with different multilayer architectures on the wear behavior and cutting performance of the carbide cutting tools was investigated in machining of Ti alloys. The multilayer thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of thin films. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM) equipped with energy-dispersive X-ray spectroscopy (EDS). A Rockwell indentation tester and a scratch tester were used to evaluate the adhesion strength between the coating and the substrate. The coating hardness and the elastic modulus were measured by nanoindentation. The design of multilayered AlTiBN/AlCrBN coatings is anticipated to inhibit the grain growth, and leads to grain refinement effect, which expected to increase the mechanical properties and cutting performance of coatings.

5:20pm MC3-1 WeA-11 Structural and Tribomechanical Properties of AlCrVON Thin Films with Varying O Contents Sputtered from Either AlCrVY or AlCrY and V Targets, W. Tillmann, Finn Ontrup, D. Aubry, Institute of Materials Engineering, TU Dortmund University, Germany; E. Schneider, M. Paulus, C. Sternemann, Fakultat Physik/Delta, TU Dortmund University, Germany; N. Lopez Dias, Institute of Materials Engineering, TU Dortmund University, Germany.

The incorporation of Y and V into AlCrN has previously proven effective in enhancing oxidation resistance and tribological properties at elevated temperatures. As this improvement stems from the oxide formation of these elements, depositing O-containing AlCrVYN presents a promising approach for directly synthesizing thin films with enhanced tribo-mechanical properties for high-temperature applications. Therefore, AlCrVYN with varying O contents were deposited using a hybrid dC/MS/HIPIMS process in two distinct approaches. In a reactive process, AlCrVYN was either sputtered from two AlCrVY targets or co-sputtered from AlCrY and V targets. For both configurations, the O flow rate was varied from 0 to 20 sccm. Sputtering from AlCrVY targets results in higher O contents from 1.4 to 31.3 at.-% compared to the other target setup which achieves up to 20.7 at.-%. High-resolution x-ray diffraction using synchrotron radiation reveals a cubic CrN phase for all thin films, independent of the O content and target configuration. Nanoindentation tests show that the hardness stays at a high level above 40 GPA for an O content of up to 6.5 at.-% for AlCrVYN sputtered from AlCrVY targets and up to 14.7 at.-% for those sputtered from AlCrY+V targets. However, for higher O concentrations the hardness for both AlCrVYN variants decreases. Due to a constant decrease in the elastic modulus with an increasing amount of O, a maximum in the H/E ratio is observed for the aforementioned O contents. Furthermore, the tribological properties were analyzed using a high-temperature tribometer. No significant reduction of the coefficient of friction is noted at room temperature and only a slight improvement is visible in the higher temperature range for all AlCrVYN thin films, except the ones with the maximum H/E ratio. Annealing the thin films deposited from two AlCrVY targets for 2 h at 500, 600 and 700 °C demonstrates a high oxidation resistance for all AlCrVON of at least 6.5 at.-% O, as no decrease in hardness, nor an increase in O content could be identified post-annealing. However, the thin films sputtered from AlCrVY+V targets perform different in this regard, as the hardness decreases for all thin films after annealing at 600 °C.

In summary, the AlCrV+V target configuration produces AlCrVYN with higher O contents, resulting in a significantly different oxidation resistance. Other than that, both configurations show similar trends, demonstrating the advantage of adding small amounts of O into AlCrVYN. Thus resulting in a maximum of the H/E ratio for explicit O contents, depending on the target configuration.

Coatings for Biomedical and Healthcare Applications Room Palm 3-4 - Session MD1-1-“WeA

Surface Coatings and Surface Modifications in Biological Environments I
Moderators: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, Phaedra Silva-Bermudez, Instituto Nacional de Rehabilitacion Luis Guillermo Ibarra Ibarra, Mexico

2:00pm MD1-1-WeA-1 Synergistic Antibacterial Activity and Ion Release of Ag-Cu and Ag-Cu-Mg Coatings, Serdar Sonay Ozbay, G. Rajmohan, Deakin University, Australia; A. Cobley, Coventry University, UK; J. Sharp, Deakin University, Australia; G. Azor, Coventry University, UK

Silver (Ag) and Copper (Cu) thin films have been widely studied as antibacterial coatings to functionalise textile surfaces to fight antibiotic-resistant bacteria and healthcare-acquired infections (HAI) in hospitals. The release of metallic ions is considered to be the main antibacterial mechanism for both metals. Therefore, maintaining a steady ion release from the metallic coatings is necessary to achieve a sustained antibacterial activity. Despite the high effectiveness of Ag ions as antibacterial agents, Ag coatings suffer from a limited antibacterial activity due to the decreasing Ag ionisation rate caused by surface passivation. In contrast, Cu coatings exhibit rapid but brief antibacterial action due to the fast release of Cu ions. Recently, studies on combined Ag-Cu systems have reported an enhanced Ag ionisation and a synergistic antibacterial activity between Ag and Cu. This study investigates how different compositions of Ag-Cu alloy thin film coatings can improve the limitations of pure metals to achieve a steady and long-term antibacterial efficacy. The Ag-Cu (Ag50Cu50–Ag80Cu20) alloys were deposited on PET textiles using magnetron sputtering technique. The growth process and microstructures of the thin films were characterised by XRD and TEM/EDS. Additionally, the galvanic relationship and antibacterial synergy between the Ag and Cu components in different alloys were investigated through the ion release studies and antibacterial tests. Finally, the effects of a more electrochemically active metal on the properties of Ag-Cu alloys were studied by co-sputtering Mg into Ag-Cu thin films. The results showed that both Ag50Cu50 and Ag50Cu50 alloys improved the plateauing of Ag ion release and provided a steady Cu ion release. Antibacterial efficacy of Ag-Cu thin films followed the order: Ag50Cu50 > Ag20Cu80 > Ag25Cu75 > Ag50Cu50 > Ag > Cu. Due to the sufficient release of both Ag and Cu ions in the Ag50Cu50 coating, this sample demonstrated superior antibacterial performance compared to both other alloys and pure metal coatings. Moreover, this coating maintained a >90% bacterial reduction rate after two antibacterial test cycles, outperforming the other coatings. The ion release studies of Ag-Cu-Mg ternary alloys showed a further reduction in both Cu and Ag ion release, with the effect of less noble Mg on the Cu ion release being more significant compared to that on the Ag ion release. Overall, our results suggest that Ag-Cu and Ag-Cu-Mg thin films are promising candidates for hospital textiles that require a steady and prolonged antibacterial activity.

2:20pm MD1-1 WeA-2 Iridium Oxide Based Electrodes for Bio-Interface Applications, Po-Chun Chen, National Taipei University of Technology, Taiwan

INVITED

Iridium oxide has attracted extensive attention due to its unique advantages including excellent chemical stability and sensitivity, impressive electrochemical catalytic activity, sufficient electric conductivity, and desirable biocompatibility. To date, iridium oxide has been widely explored in applications such as anodes for water electrolysis, electrochromic layers for smart windows, and pH sensors. In addition, iridium oxide is known for its superb charge storage capacity and long-term stability renders it a desirable candidate as a bio-interface electrode for implantable bio-medical
89-Zr can be produced by 89Y (p,n) 89Zr reaction. Fortunately, natural yttrium isotopic composition is 100 % 89Y, which makes the target production relatively cheap. A different method of Y target preparation has been adopted for Zr-89 production; for instance, many groups are using Y foils, while others are studying alternative methods such as pressing, sputtering, sedimentation and even electrodeposition from non-aqueous (ethanol) solutions [1-3].

Several works [2,4] reported utilisation of the yttrium sputtered targets for Zr-89 production. However, fewer details are available about the deposition system or parameters.

Our research group have been developing the yttrium deposition process for multiple targets manufacturing by DC magnetron sputtering technique, and the first results are published in [3].

The thick films are not a trivial task for the magnetron sputtering deposition. The stress evaluation in sputtering growth must be considered. In this work, we present the current development of the yttrium solid target manufacturing method by magnetron sputtering technique, implementing an enhanced protocol that allows the deposition of pure, thicker yttrium targets. As a result, the last deposition batch shows a significant increase in yttrium film thickness (up to 200 μm), maintaining the low residual stress necessary for successful irradiation under the proton beam. All irradiated targets demonstrated remarkable resilience under high power loads, exhibiting no signs of delamination or damage.

The irradiation of the solid targets with the following 89-Zr extraction shows a significant improvement in sputtered targets. The achieved saturation yield values are similar to the ones achieved by bulk or sintered targets [2].

Summarising, magnetron sputtering can provide an essential feature for solid target manufacturing; excellent adhesion between the deposition and substrate and tunable properties, such as thickness and density.

biocompatibility and poses challenges to improve its antibacterial ability through modification for inhibiting postoperative infection. In addition, PLA nonwoven is sensitive to most chemical methods for both functionalization and sterilization. To tackle these issues without impairing the PLA nonwoven, a tailored atmospheric pressure plasma (APP) system along with a hybrid precursor of acrylic acid and silver nitrate was designed and employed for surface functionalization. In this system, electrons and reactive species created during the APP process were utilized for reducing silver nanoparticles from the hybrid precursor. By performing APP polymerization and reduction simultaneously, a silver nanoparticle-embedded and carboxyl-rich polymerized film was prepared and deposited on the PLA nonwoven surface. This study presents a comprehensive analysis of the wettability, hydrophilicity stability, surface elemental composition, biocompatibility and antibacterial efficacy of the PLA nonwoven surface functionalized using the proposed APP method. Compared with conventional methods, this process is capable of immobilizing a higher percentage of carboxyl functional groups with improved efficiency on enhancing antibacterial properties.

Keywords: atmospheric pressure plasma, textile functionalization, biodegradable polymers, polyacrylic acid, scaffolds, acrylic acid, silver nitrate, antibacterial property

4:20pm MD1-1-WeA-8 Improvement of Corrosion Resistance of Biodegradable Mg-Ca Alloy by Atomic Layer Deposition Technique. Hsin-Chih Lin, P. Lin, H. Chen, K. Lin, National Taiwan University, Taiwan

Biodegradable Mg-Ca alloy has high application potential in the fields of cardiovascular stent, wound healing device and orthopedic implant. However, the degradation rate of Mg-Ca alloy is too fast to provide enough support for a long time, and it may also cause pH rise and excessive hydrogen production in vivo, which may lead to cell inflammation, vascular blockage, and other negative problems. Hence, how to precisely control the degradation rate and effectively reduce the corrosion rate is an important issue for Mg-Ca implants. Recently, we have constructive extensive studies on improving the corrosion resistance of Mg-Ca alloy by atomic layer deposition (ALD) technique. It is found that the atomic layer plasma treatment (ALPT) enhances the corrosion protection of the Zr2O film grown by thermal-driven ALD mode (TALD-Zr2O), further reducing the corrosion rate of Mg-Ca alloy. The ALPT effect significantly increases the crystallinity and reduces oxygen defects of the TALD-Zr2O film, effectively improving the corrosion resistance of the TALD-Zr2O film, and the maximum enhancement is observed by using 30s-ALPT time. The corrosion rate of Mg-Ca alloy is highly reduced by more than one order of magnitude, which is reflected in the reinforcement of diffusion suppression of TALD-Zr2O film processed by the ALPT treatment. ALPT technique is suggested as a potential and feasible method to prepare TALD-Zr2O films with high film quality and corrosion protection.

Plasma and Vapor Deposition Processes

Room Town & Country A - Session PP4-2-WeA

Deposition Technologies for Carbon-based Coatings II

Moderators: Ivan Kolev, IHI Hauzer Techno Coating B.V., Netherlands, Biplab Paul, PLATIT AG, Switzerland

2:00pm PP4-2-WeA-1 DLC-Coating Against the Backdrop of High Economic Requirements. Jens Emmerich, D. Tiedemann, Robert Bosch Manufacturing Solutions GmbH, Germany; V. Gupta, Robert Bosch Manufacturing Solutions GmbH, India; K. Boebel, Robert Bosch Manufacturing Solutions GmbH, Germany

INVITED

In the pursuit of economic viability, this study delves into the strategic utilization of Diamond-Like Carbon (DLC) coatings, emphasizing the distinctive advantages offered by diverse deposition sources. Microwave and cathodic arc deposition, magnetron sputtering as well as High-Power Impulse Magnetron Sputtering (HIPIMS) emerge as pivotal techniques, each contributing unique attributes to the economic landscape. Microwave and cathodic arc deposition showcase efficiency in scalability and uniformity, optimizing the cost-effectiveness of large-scale applications. Sputtering, on the other hand, proves adept at achieving precision and controlled film properties, catering to industries with specific coating requirements. The innovative approach of HIPIMS introduces enhanced adhesion and superior film density, paving the way for extended component lifespan and reduced maintenance costs. Beyond these, the infusion of artificial intelligence (AI) emerges as a pivotal factor in predicting coating parameters and thus orchestrating cost reduction and minimizing scrap rates. By leveraging AI algorithms, the deposition process is optimized with unprecedented precision, ensuring an ideal balance between coating thickness, quality, and resource utilization. This study delves into the economic benefits derived from the application of DLC coatings in combination with AI, shedding light on their potential to enhance durability, reduce maintenance costs, and contribute to overall operational efficiency. As industries strive to navigate the intricacies of a competitive economic environment, the integration of DLC coatings emerges as a strategic imperative for achieving both performance excellence and economic viability.

2:40pm PP4-2-WeA-3 Comparison of Performance Parameters of Carbon Coatings by Different PVD Methods. Martin Kope; J. Walther, B. Gebhardt, H. Proehl, VON ARDENNE GmbH, Germany

PVD based carbon coatings show superior electrochemical resistance enabling durable coatings for metallic bipolar plates in PEM fuel cells etc. High density and high conductivity (low interfacial contact resistance = ICR) of bipolar plates are essential, nevertheless only a cost-efficient coating method will have the chance for industrialization. Therefore, we only investigated PVD methods which allow scaling of the bipolar plate coating volume to MW and GW powers per year, which are electron-beam based PVD, as the method for highest productivity and deposition rate, and plasma based PVD which is high power magnetron sputtering and (pulsed) cathodic laser arc in our case. The electrical conductivity or ICR and corrosion performance of all those carbon coatings have been optimized to compete with gold coatings at fuel cell operation voltage. Anyway, the limits of the electrochemical corrosion performance of different carbon coatings at high electrochemical potentials occurring for split seconds on the cathode side of the bipolar plate during start/stop of a fuel cell can be crucial for the overall layer stack performance and durability. Depending on the deposition method and parameters, the properties of the carbon layer stack can highly differ from each other which leads to a different corrosion performance at such a high electrochemical potential.

3:00pm PP4-2-WeA-4 Carbon-Based Coatings with Tailorable Properties as a Function of sp3/sp2 Hybridization, Biplab Paul, G. Wahl; J. Kluson, H. Bolvardi, A. Lüskemann, PLATIT AG, Switzerland

Carbon-based coatings offer a variety of exceptional properties, including mechanical (hardness, elastic modulus, friction coefficient), physical (optical, electrical), chemical (chemical inertness), and biomedical (biocompatibility) properties. However, to exploit the entire range of functionalities from this class of coatings we need appropriate technologies to make the coatings preferentially engineered. For example, carbon-based coatings can be engineered to be graphite like or diamond like by preferentially tuning the ratio of sp3/sp2 hybridization in the coatings. The monolithic tetrahedrally-bonded coatings (ta-C), with 100% sp3 content, provide the highest hardness, while amorphous carbon (a-C) coatings with sp3/sp2 ~ 1 provide softer coatings with low coefficient of friction (COF), useful for many frictionless medical applications. PLATIT’s advanced coating units, integrating sputtering, arc and PECVD techniques, provide the unique scope to grow a plethora of diamond like coatings (DLC) with varying functionalities, categorized as DLC1 (metal doped a-C:H with sp3 > 50%, i.e., sp3/sp2< 1), DLC2 (Si doped a-C:H), and DLC3 (hydrogen free ta-C with sp3 > 50%, i.e., sp3/sp2< 1). The DLC1 coatings are grown by sputtering from metal targets (e.g. Ti, Cr, etc.) in acetylene atmosphere, offering the scratch proof aesthetic black coatings, useful for decorative and biomedical applications. The DLC2 coatings are grown by PECVD technique, offering the hard coatings (Hardness = 30-35 GPa, Lc2 > 30 N), useful for cutting tools and for various mechanical and electronic components. The DLC2 coatings being grown by PECVD technique, they offer the coating possibilities on difficult parts with complex geometries and miniaturized dimension (e.g., microtools). The DLC3 coatings are done by sputtering from carbon target at low temperature, providing hardness (H) > 40 GPa, and scratch resistance with Lc2 > 30 N, while COF < 0.2. With such high hardness and low COF values the DLC3 coatings offer the best coating solution for machining nonferrous materials. The physical properties of carbon-based coatings can be directly correlated to their color, which is defined by L*a*b* values. Figure 1 shows the L* values of carbon-based coatings as a function of hardness. The high L* values for DLC3 coatings indicate their higher transparency than other DLC coatings. This is attributed to the higher degree of sp3/hybridization in DLC3 coatings as compared to that of DLC1 and DLC2 coatings.
Negatively charged nitrogen vacancy centers (NV) in diamond have unique properties making them excellent candidates for nanoscale magnetic and electric field sensors, as quantum bits as well as other applications. As quantum sensors they promise comparable sensitivity at room temperature to commonly used magnetic field sensors that must be cooled to liquid helium temperature, for example. NV centers may occur as neutral NV or negatively charged NV, however, it is only NV that exhibits this magnetic sensitivity. With growing interest in the use of quantum sensor it is necessary to ensure predictable and reliable performance which requires uniform NV formation. However, the stability of NV centers is strongly influenced by the surface functionalization of diamond particles. Both nitridation and fluorination have been shown to help stabilize NV centers especially for shallow NV centers which provide greater sensitivity. Uniform functionalization of particles in batches is necessary for cost effective production. This has been investigated using an atmospheric pressure plasma system. Results of treatment in fluorine and nitrogen-based plasmas will be reviewed. Fluorescence spectroscopy was used as a means to determine the presence of NV and NV following treatment and the impact of the treatment will be discussed.

The advent of High-Power Impulse Magnetron Sputtering (HiPIMS) in the last two decades opened a new route for magnetron-sputtered coating. In HiPIMS, a large fraction of the sputtered atoms is ionized due to the several orders of magnitude higher plasma densities than in DCMS. Although HiPIMS has been successfully implemented for many metals, it is much less effective for DLC coatings deposition since C has significantly higher ionization energy and lower ionization cross-section than typical metals.

In previous works, the authors have shown that adding Ne to the plasma significantly improves the properties of DLC films deposited by Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS. Replacing half of the Ar process gas by Ne allowed for the deposition of denser films. In HiPIMS, the specific wear rate (SWR) of the DLC films decreased by close to 50 %, both in linearand reciprocating slidingagainst steel counterparts, being effective for DLC coatings deposition since C has significantly higher ionization energy and lower ionization cross-section than typical metals.

Quantitative evaluation of the sp² content in DLC films deposited by DOMS, to identify the relevant film formation mechanisms and to better understand process-properties relationships resulting from the addition of Ne to the plasma. DLC films were deposited by DOMS both in pure Ar and in mixed Ar + Ne plasmas. Quantitative evaluation of the sp² content in the films was performed by Electron Energy Loss Spectroscopy (EELS) and Near Edge X-ray Absorption Fine Structure (NEXAFS). Additionally, for comparison purposes, Raman spectroscopy was also used for qualitative assessments of the film's sp² content. Although hydrogen was not purposefully incorporated in the DLC films deposited in this work, the hydrogen content was measured by Elastic Recoil Detection Analysis (ERDA) in combination with Rutherford Backscattering Analysis (RBS). The surface morphology of the DLC films was characterized by Scanning Electron Microscopy (SEM) while their microstructure was investigated by High-Resolution Transmission Electron Microscopy (HRTEM).
Wednesday Afternoon, May 22, 2024

[2]. Yet, as further improvements are needed, implications of how the coating equipment field needs to develop will also be considered. Another perspective is the impact of performance of the total GHG emissions over the lifetime of the tool at the user, where its performance and stability determine the total contribution to the emission when manufacturing a component. Finally, the need for reuse and recycling of used tools is also considered, which also greatly affects their sustainability. In closing the need for holistic approaches will be emphasized, to avoid sub-optimizations, as it is our collective need and our collective improvements that will determine to what level we can mitigate climate change.

1. https://sciencebasedtargets.org/

2. Li, Xiao, Toward Energy-efficient Physical Vapor Deposition: Routes for Replacing Substrate Heating during Magnetron Sputtering by Employing Metal Ion Irradiation, Linköping University 2023, https://doi.org/10.3384/9789180752428

3:40pm TSS-Wea-6 Towards Responsible Surface Engineering, Marcus Hans, J. Schneider, RWTH Aachen University, Germany; A. Matthews, University of Manchester, UK; C. Mitterer, Montanuniversität Leoben, Austria

Surface engineering comprises technologies, which enable improved structural and functional surface properties. Plasma-assisted physical vapour deposition (PVD) covers a set of advanced plasma-assisted surface engineering technologies, increasingly employed to address global challenges, such as reduction of CO₂ emissions. Despite the smaller volume and mass of thin films and coatings compared to bulk materials as well as the relatively low synthesis temperatures of PVD compared to other surface engineering technologies, PVD processes are often resource-intensive. In this review we critically evaluate two important questions in this context:

1) How sustainable are PVD processes and materials?

2) Which pathways are needed for responsible surface engineering?

The consideration of energy and mass balances demonstrates that state-of-the-art PVD processes and materials are not necessarily sustainable. Responsible surface engineering comprises pathways to enhance the sustainability of processes as well as materials and involves a change in mindset of materials scientists and process engineers.

4:00pm TSS-Wea-7 Reprocessing High Performance Cutting Tools – Performance Plus with Dedicated Coating Solutions, Dominik Blüsch, C. Krieg, PLATIT AG, Switzerland; J. Kluson, PLATIT a.s., Czechia; H. Bolvardi, A. Lüdmann, PLATIT AG, Switzerland; B. Torp, PLATIT Inc., Switzerland

In the last decades, the research and development within surface engineering has focused mainly on the enhancement of surface properties by the design of multifunctional coatings and surfaces, while the sustainability of such processes and products was typically neglected. The approach of a circular economy for surface engineering requires innovative rethinking along the lines of reducing, reusing, repairing, and recycling. In this contribution we would like to introduce circular economy strategies for surface engineering as follows:

7. Sustainability with in-house PVD production: By integrating the coating process into the tool production plant, shipping between job coating centers and production places becomes superfluous, effectively reducing CO₂ production through optimized logistics. Furthermore, one major benefit of an vertically integrated coating center is having the PVD process including all aspects of the process chain on site. This permits functional coatings to be developed for specific applications, bringing us to the next point...

8. Extend usage by “Dedicated development”: Using flexible in-house PVD technology including pre- and post-treatment de-coating and washing, the life of the coated part is maximized. Each step in the process chain is optimized individually. The lifetime of the coated parts for each specific application can thereby be extended rather than applying the typical job-coating business strategy where “one size fits all”. The full potential of even the best PVD coatings cannot be exploited when making compromises in terms of coating type, coating thickness and plasma treatment.

9. Resource conservation by reprocessing to restore original production quality: Worn tools are refurbished several times by resharpening just prior to reaching end-of-life, effectively preventing scrap. One challenge of reprocessing (de-coating, resharpening, cutting edge preparation, washing, coating, post-polishing) is removal of the worn and often partially oxidized PVD coating without damaging the base material below. Leveraging know-how for each individual process step, we achieve the original manufacturing quality in tools to enable multiple service lives.

Using this threefold approach of vertical integration, dedicated development, and reprocessing, substantial improvement to the sustainability of PVD-coatings is achieved without necessitating any compromise on quality.
Protective and High-temperature Coatings
Room Town & Country C - Session MA5-1-ThM

Boron-containing Coatings

Moderators: Martin Dahlqvist, Linköping University, Sweden; Anna Hirle, TU Wien, Austria

9:00am MA5-1-ThM-4 W-Based Thin Film Metallic Glasses Doped with Ni, Zr and B for Industrial Applications, Antonin Kubicek, V. Sochora, SHM, s.r.o., Czechia; Z. Studeny, University of Defence, Czech Republic; P. Soucek, Masaryk University, Czechia; Z. Pokorny, University of Defence, Czech Republic; T. Schmidtaova, J. Zenisek, Masaryk University, Czechia

Thin film metallic glasses (TFMGs) have recently become the target of intensive research with a focus on potential applications in many sectors, where their properties can surpass their crystalline counterparts. However, their use in industry can be limited by their low hardness and Young modulus, which does not allow them to effectively withstand certain types of wear (e.g. abrasive).

As a material in the family of TFMGs, tungsten-based coatings stand out thanks to their relatively high hardness and Young modulus, and their high temperatures of glass transition and crystallization. In combination with low coefficients of friction and other outstanding properties, generally attributed to the metallic glasses, it makes them a promising candidate for potential industrial applications.

Therefore, W-Ni-B and W-Zr-B coatings were deposited using direct current magnetron sputtering. Several industrially relevant physical properties of these coatings were compared. Among others their response to Viickers indentation, surface roughness, mechanical properties, surface free energy and tribological performance in contact with industrially relevant types of materials such as Al2O3 ceramics and AISI 440C stainless steel.

9:20am MA5-1-ThM-5 Effect of Ti and Zr Contents on the Microstructure, Mechanical Properties, and Corrosion Resistance of W2ZrTiB Boride Thin Films, Wei-Xiang Fang, Ming Chi University of Technology, Taiwan; B. Lou, Chang Gung University, Taiwan; J. Lee, Ming Chi University of Technology, Taiwan

Transition metal borides (TMBs) are known for their high melting point, wear resistance, corrosion resistance, high-temperature resistance, and high hardness. In this study, the pure Ti, Zr, and W:B targets were connected with the high power impulse magnetron sputtering (HiPIMS) power and radio frequency power, respectively, to prepare five W2ZrTiB boride thin films with different Ti and Zr contents. The coatings were deposited on p-type Si (100), AISI 304, and AISI 420 stainless steel substrates. The cross-sectional morphologies and crystalline structures of thin films were investigated by field emission scanning electron microscopy (FE-SEM) and X-ray diffractometry. The transmission electron microscopy was also employed to study the microstructure and phase of each thin film. The hardness and elastic modulus of each film were further measured by a nanoindenter. A pin-on-disk tribometer was used to study the wear characteristics of these coatings. An electrochemical workstation to analyze the corrosion resistance of W2ZrTiB boride thin films. Effects of Ti and Zr contents on the microstructure, mechanical properties, and corrosion resistance of W2ZrTiB boride thin films will be explored in this work.

9:40am MA5-1-ThM-6 Influence of Spatial Heterogeneity on Mechanical Properties in Multilayered Coatings, Marek Gocnir, Montanuniversität Leoben, Austria

Excellent mechanical properties of hard coatings based on transition metal diborides are accompanied by typical problems of these ceramic materials – affinity to crack formation and weak plastic response to deformation. In this work we focused on preparation and investigation of the structure, mechanical properties and fracture toughness of hard coatings based on super-lattices (SL) and multilayers (ML) TiB2/TaB2 with different thicknesses of the bi-period λ in the interval of 4 to 40 nanometers, prepared by magnetron sputtering. In the work, series of analytical methods are used for the complex characterization of the coatings, and the results of the mechanical behavior are supported by the results of theoretical modelling based on density functional theory (DFT). The basic binary coatings differ in their structure and mechanical properties, where TiB2 is typically overstoichiometric, has a nanocomposite character and hardness (H) exceeds 40 GPa. In the case of TaB2, it is a understoichiometric coating with an amorphous structure and a lower hardness H ≈36 GPa. Their combination in the form of periodically repeating very thin layers lead to the typical behavior of nanostructured materials according to the Hall-Petch relationship when the hardness increases above 42 GPa at λ = 6 nm. Gradually increasing λ results in a subsequent decrease in H. This character of the change in mechanical behavior is hidden in the nanostructure. At a very fine modulation λ < 12 nm, local epitaxial growth occurs when lattice matching was observed at the interface of the layers. At the same time, the TiB2/TaB2 coatings had a crystalline character across the entire thickness, and the presence of the hexagonal TiB2 phase and TaB2 as well was identified in the individual layers. These layers showed higher resistance to deformation during hardness measurements and therefore higher hardness values were measured. At coarser modulation periods λ > 20 nm, the crystalline character of the TiB2 layer is preserved but the TaB2 layer again forms a disordered structure after growing a few nanometers. This softer TaB2 phase affects the overall hardness values which are lower. Nevertheless, hardness values above level of ≈33 GPa still classify these coatings as extremely hard. Fracture-mechanical behavior, i.e., resistance to crack propagation is dependent on the thickness of the bi-period when an increase in the value of the critical stress intensity factor K was observed by approximately 16% (Kc = 3.45 MPa m1/2) in the TiB2/TaB2 coating with λ = 8 nm compared to binary TiB2, where Kc = 2.974 MPa m1/2.

10:20am MA5-1-ThM-8 Self-Formation of Metallic Glasses Doped with Ni, Zr and B for Industrial Applications, Antonin Kubicek, V. Sochora, SHM, s.r.o., Czechia; Z. Studeny, University of Defence, Czech Republic; P. Soucek, Masaryk University, Czechia

Recently, we have demonstrated that dual-phase nanocomposite Zr-Cu-N coatings can be prepared by the one-step process of reactive magnetron sputter deposition. The nanocomposite structure of these coatings is based on a hard nitride phase represented by ZrN and a soft phase, which can be prepared either as metallic ductile Cu or as amorphous ZrCu alloy with metallic glass behavior, depending on the deposition conditions. In the present work, we focus on this research and investigate the possibility of preparing dual-phase nanocomposite coatings also within the ternary Zr-Cu-B system by non-reactive magnetron sputter deposition, focusing on the compositions corresponding to the stoichiometric ZrB2 and ZrCu phases. The Zr-Cu-B coatings were deposited in argon using four unbalanced targets, one Ti target, and one Cu target deposited with the ZrB2 and Zr targets were operated in dc regimes, while with the Cu target in a high-power impulse regime. All coatings were deposited onto rotating substrates with rf biasing at different substrate temperatures. The elemental composition of the coatings was varied so that the stoichiometry of both potential phases remained the same, but only the volume fraction was changed.

The obtained results show that the structure of Zr-Cu-B coatings deposited without external heating is amorphous for all compositions investigated. Increasing the substrate temperature promotes the crystallization of the coatings, leading to the formation of a dual-phase nanocomposite structure based on a nanocrystalline ZrB2 phase and an amorphous ZrCu phase. This effect becomes more pronounced as the volume fraction of the ZrCu phase increases. Mechanical properties such as hardness and stress are affected by the volume fractions of both phases and exhibit a dependence on the substrate temperature. The structural investigations are complemented by ab-initio simulations, which show very good agreement with experimental results.

10:40am MA5-1-ThM-9 High Rate Deposition of Ultrathick Boron Carbide Coatings for Inertial Confinement Fusion, J. B. Merlo, K. Kawasaki, J. Forien, S. Gonzalez, G. Taylor, S. Shin, L. Bayu Aji, S. Kucheyev, Lawrence Livermore National Laboratory, USA

Boron carbide has attractive properties for several applications, including fuel capsules for inertial confinement fusion (ICF). For ICF applications, boron carbide needs to be in the form of a hollow spherical shell, about 2 mm in diameter, with a wall thickness of about 100 microns. Sputter deposition of such non-crystalline boron carbide needs to be in the form of a hollow spherical shell, about 2 nm compared to binary TiB2, where Kc = 2.974 MPa m1/2.

Forien, S. Gonzalez, G. Taylor, S. Shin, L. Bayu Aji, S. Kucheyev, Lawrence Livermore National Laboratory, USA

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11:00am MA5-1-ThM-10 High-Rate Deposition of Ultrathick Boron Carbide Coatings for Inertial Confinement Fusion, J. B. Merlo, K. Kawasaki, J. Forien, S. Gonzalez, G. Taylor, S. Shin, L. Bayu Aji, S. Kucheyev, Lawrence Livermore National Laboratory, USA

Boron carbide has attractive properties for several applications, including fuel capsules for inertial confinement fusion (ICF). For ICF applications, boron carbide needs to be in the form of a hollow spherical shell, about 2 mm in diameter, with a wall thickness of about 100 microns. Sputter deposition of such non-planar ultrathick coatings with submicron density uniformity has many challenges. Remaining challenges include relatively low deposition rates, delamination and fracture due to residual stress, and the growth of nodular defects. Here, we systematically study effects of the deposition rate and substrate tilt on properties of amorphous boron.
carbide films deposited by planar magnetron sputtering on stationary substrates. Our focus is on optimizing the deposition rate and minimizing residual stress and the density of nodular defects. As a result of this systematic study, we demonstrate low-stress, ultrathick boron carbide films fabricated by magnetron sputtering with deposition rates approaching 10 microns per hour.

11:00am MAS-1-ThM-10 Ion Beam Assisted Pulsed Laser Deposition of Hexagonal Boron Nitride Thin Films, Venkata Ananth Kandadai, J. Petersen, B. Jasthi, J. South Dakota School of Mines and Technology, USA

In recent decades, there has been significant interest towards hexagonal boron nitride (hBN) films across diverse applications, including electronics, anti-corrosion coatings, tribology, and optoelectronics. Boron nitride films produced using physical vapor deposition are often reported for cracking and delamination. Moreover, synthesizing crystalline-quality hBN films requires higher deposition temperatures, chemical precursors, and catalytic metal substrates. Therefore, this study aims to produce crystalline and crack-free hBN films using ion beam-assisted deposition at low temperatures. hBN films are synthesized on silicon (100) substrates at 600°C using ion beam assisted pulsed laser deposition process. The microstructure, mechanical, and electrical properties of hBN thin films were investigated at different gas mixtures of Ar:N₂ (0-100% N₂) and varying ion beam energies (150-300 eV). hBN thin films were characterized using Raman spectroscopy, X-ray diffraction, and transmission electron microscopy. Films deposited with a higher N₂ content of ≥50% showed improved crystallinity of hBN films. Microstructural characterization revealed the formation of hBN nanograins for films deposited with ≥50% N₂, and the grain size increased with increased N₂ content. The electrical and mechanical properties of deposited films were influenced by the deposition parameters, such as the ratio of gas mixture and ion beam energies, and the properties were correlated to their microstructure. The overall results suggest that the ion bombardment leads to nanograin formation and improved crystallinity of hBN at lower temperatures.

11:20am MAS-1-ThM-11 Taking Advantage of Unique Lattice Sites – How to Find New Boron-Based Materials Through Large-Scale Stability Predictions, Martin Dahlqvist, A. Carlsson, J. Rosen, Linköping University, Sweden

Boron-based materials are highly desirable for their promising mechanical properties, rendering them ideal for various industrial applications. Previous experimental work has demonstrated that mixing two metals at a given ratio can result in preferential occupation of different lattice sites, leading to chemically ordered phases, e.g., W:CrB: and W:CrB₃. However, to experimentally identify new materials with improved properties, being simultaneously composed of abundant elements, is a challenging task. A useful tool for such mission is phase stability calculations which have proven to be useful for identifying stable and synthesizable candidates. In this work, we have searched for known binary metal borides which have two unique metal sites in their respective prototype structures, that may have potential for forming chemical order when mixing two metals, M° and M°°. The metal sites in these prototypes were then pair-wise decorated by combing 44 different elements resulting in over 20 000 ternary compounds. The thermodynamic phase stability of these compounds was assessed by evaluating the formation enthalpy with respect to competing phases. The thermodynamic phase stability of these compounds was assessed by evaluating the formation enthalpy with respect to competing phases.

References:
4. D. Llamosa et al., “The ultimate step towards a tailored engineering of core@shell and core@shell nanopolymers”, Nanoscale 6, 13483 (2014).

8:40am MB3-1-ThM-3 MGA Nanoparticle Thin Films for Enhanced Hydrogen Gas Sensing: Synthesis, Modeling, and Characterization, Stanislav Havír, T. Kozák, K. Šejdl, University of West Bohemia, Czechia; T. Košutová, Charles University, Czechia; B. Prifling, V. Schmidt, Ulm University, Germany; J. Čapek, University of West Bohemia, Czechia

Thin films formed by nanoparticles from various metal oxides (WO₃, CuO, PoO) were synthesized using a magnetron-based aggregation cluster source (MGA). The mixing ratios of the oxide particles were adjusted to achieve the best conductometric sensorial response toward hydrogen gas. (i) Single-material films were investigated utilizing electron microscopy, energy dispersive and photoemission spectroscopies and small-angle x-ray scattering (SEM, TEM, EDS, XPS, SAXS). (ii) Results of these analyses were used as an input for hard-sphere packing algorithm simulations generating models of synthesized mixed-materials films. (iii) Optimized finite element modeling was used to calculate the conductivity of modeled films. Various material parameters were adjusted to receive a quality estimation of mixed-materials behavior. (iv) Output of the simulation was used as a lead for synthesizing films with optimum ratios of materials to generate nanoheterojunction-rich materials. (v) Promising candidates were assembled as conductometric gas sensors and tested toward hydrogen gas. In the talk, the details of MGA system orchestration will be discussed. Special attention will also be paid to the simulation strategy and the process of simulation results verification.

See illustrative figures in the Supplemented file.


9:00am MB3-1-ThM-4 Enhanced Dimer Sputtering and Production of Nanoparticles by Pulsed Magnetron Discharge, Pavel Čapek, University of South Bohemia, Czechia; R. Hippner, University of Greifswald, Germany; M. Cada, Institute of Physics, Czech Academy of Sciences, Czechia; O. Kylän, Charles University, Czechia; Z. Hubicka, Institute of Physics, Czech Academy of Sciences, Czechia; V. Stronak, University of South Bohemia, Czechia

This study investigates the initial stage of nanoparticle formation in physical vapor deposition processes, emphasizing the role of atomic dimers as cluster nuclei. The process of metal nanoparticle formation and growth by gas aggregation starts with the release of free metal atoms and nuclei through magnetron sputtering followed by thermalizing collisions and by atom attachment and coagulation. By employment of energy-resolved mass
The research was financially supported by the Czech Science Foundation through the project GACR 21-05030K and by the Ministry of Education, Youth and Sports of the Czech Republic through the project “Solid state physics for the 21st century” CZ.02.1.01/0.0/0.0/16_019/0000760.

9:20am MB3-1-Thm-5 Plasma Polymer - Ag Nanocomposites: Is the Gas Aggregation Source of Nanoparticles an Appropriate Technique for Their Synthesis? Zdenek Krousa, T. Koutova, P. Pleškunov, Charles University, Prague, Czech Republic; B. Baloukas, L. Martinu, Polytechnique Montréal, Canada

Metamaterials or metasurfaces represent the emerging field of nanotechnologies focusing on pushing the limits of the standard optical coatings. One of the most promising types of metamaterials are plasmonic nanocomposites based on metallic nanoparticles. The usefulness of such materials was demonstrated for absorbers, plasmonic coloration, transparent electrodes and optical filtering. In this project, we investigate a classical type of plasmonic metamaterials – silver nanoparticles embedded in a plasma polymer matrix, prepared by simultaneous co-deposition of both organic and metallic components. The organic matrix is prepared by the recently developed Plasma Assisted Vapour Thermal Deposition (PAVTD). The PAVTD allows one to control the chemical composition and, as a result, the optical and mechanical properties of the matrix within a wide range. We investigate two different cases of synthesis of metallic nanoparticles. In the first case, which could be considered a more classical approach, the nanoparticles are formed by co-deposition of silver atoms by magnetron sputtering. The silver atoms form nanoparticles inside the polymeric matrix. The growth rate of the matrix limits the size of the growing inclusions. In the second case, the Gas Aggregation Source (GAS) was used to fabricate nanoparticles in the gas phase. Subsequently, pre-fabricated nanoparticles are landing on and being embedded into the growing matrix. Due to the different nanoparticle growth mechanisms, the optical properties of such nanocomposites are not equivalent even at similar filling factors. Finally, the applicability of the PAVTD – gas films is demonstrated by the fabrication of a nanocomposite-based Bragg’s reflector.

9:40am MB3-1-Thm-6 Fabrication of α-Fe2O3 Nanorod Arrays/Au Nanoparticles with an Enhanced Visible-Light Photocatalytic Activity, Yu-Han Hsu, K. Chang, Y. Chiu, National Cheng Kung University (NCKU), Taiwan

α-Fe2O3 is an attractive n-type semiconducting material in the visible-light photocatalytic application because of its characteristic of narrow energy band gap characteristics for absorbing the visible light. The optical property can be tailored through morphology control, elemental doping, or compositing with other materials. However, studies on the α-Fe2O3 nanorod arrays with the metallic nanoparticles directly through hydrothermal processes for the fabrication still lacking. In this study, well-aligned α-Fe2O3 nanorod arrays/Au nanoparticles were synthesized through a facile hydrothermal reaction and solution-based method. To optimize the morphology of Fe2O3 nanorod arrays for compositing with Au, hydrothermal parameters, including concentrations and types of precursor solutions, reaction time, and temperatures, were manipulated. And then, it was composed with different amounts and sizes of Au nanoparticles, finding an optimized condition for the visible-light photocatalytic application with the LSPR effect from nanogold. X-ray diffraction and scanning electron microscopy were employed to determine the phase and morphology of the resultant composite samples. In addition, the interfaces between the materials were observed from the transmission electron microscopy. UV-vis spectroscopy was utilized to measure the absorption and the energy band gaps of the materials, which were significant for building the energy band diagram of the system. The composites were further used in the visible-light photocatalytic application.

Keywords: α-Fe2O3 nanorod arrays, Au nanoparticles, hydrothermal reaction, LSPR, visible-light photocatalysis


The advancement of nanotechnology relies significantly on developing thin film metallic glasses (TFMGs), given their distinct attributes such as high strength and corrosion resistance at the atomic level. The exploration of new TFG systems holds the potential to revolutionize technology, enhancing performance and durability across applications in electronics, coatings, and medical devices. In this study, we employed a combinatorial approach to investigate the glass-forming ability of Zr-Ti-Al thin films synthesized through magnetron co-sputtering. Our findings demonstrate that controlled variations in chemical composition influence the amorphous or crystalline state of the layers, with an observed reduction in grain size with increasing the Al content. The SEM images illustrate notable modifications in surface and cross-sectional morphology. However, despite the glassy form, electrical property determinations reveal that TFMGs maintain consistent electrical characteristics with their ternary crystalline counterparts of Zr-Ti-Al films. Values ranging between approx. 100 and 200 µΩ·cm have been measured for either crystalline or amorphous films. Lastly, the thermal stability of Zr-Ti-Al TFMGs was assessed through TEM and Raman analyses following annealing processes. The crystallization starts at temperatures higher than 300 °C. Since the annealing has been performed in air, the formation of oxides (ZrO2 and TiO2) has been evidenced by Raman.

10:40am MB3-1-Thm-9 Study of Interfacial Reactions in Artificially Nanolayered Mg-Mo-N Thin Films, Baptiste Julien, National Renewable Energy Laboratory, USA

Ternary nitrides are an exciting class of materials for various applications such as hard coatings, LEDs, magnets, superconductors, or topological materials. Many of the most interesting nitride phases are predicted to be metastable. In bulk synthesis, reactions necessary occur at the interfaces, and so solid-state diffusion is required to drive complete nucleation. This leads to condition of high temperature and long-time reactions, which can bypass metastable phases.

Thin-film synthesis of ternary nitrides often leads to cation-disordered structure yet predicted unstable by thermodynamics calculation. Post-deposition thermal annealing can sometimes overcome energetic barriers and lead to nucleation of the layered targeted phase. However, the kinetic window is often narrow and requires high temperatures to trigger atomic diffusion. Therefore, nanolayered thin-film structures with designed diffusion lengths and interface densities offer an opportunity to overcome this situation.

To investigate the interfacial nucleation, we propose to reduce the atomic diffusion length (typically ~1µm in bulk synthesis) by fabricating multilayer nanolaminar structures of the binary precursors, as a model system. Post-deposition annealing, interlayer thickness, and the multilayer period modulation are studied as a mean to control the structural properties of the nitride thin films. In this study, we focus on the Mg-Mo-N system, in which MgMoN2 phase is predicted to be thermodynamically stable and exhibits a natural layered structure built up by alternating layers of edge-sharing MgN6 octahedra and MoN6 trigonal prisms. This makes it a good candidate for this work as in a thermodynamics point of view, the structure tends to naturally form a layered structure and should be more favorable to nucleate from a layered precursor.

The nanolayered films are fabricated by RF co-sputtering, using a computer-controlled sputtering chamber featuring programmable shutters in front of each sputter cathode, allowing us to control the modulation sequence during the deposition. One major challenge here is to minimize the interfacial roughness during the deposition, limiting the intermixing at the interfaces. Once co-calibration of deposition rate and composition is
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established for both binary phases, a set of multilayer films with different modulation period and composition are characterized by X-ray reflectivity and diffraction. The morphology and the composition of the interfaces are further characterized by electron microscopy.

11:00am MB3-1-ThM-10 Stainless-steel Nano-Pyramid Structure Coating to Enhance Oil/Water Separation, Helmi Son Hajj, National Taiwan University of Science and Technology, Indonesia; J. P. Chu, National Taiwan University of Science and Technology, Taiwan

The process of separating oil and water is crucial for modern human life. Oil waste can affect living environments and impact human health. Various industries require breakthroughs in this field, including the food, petrochemical, oil mining and semiconductor industries. The urgent need for oil waste treatment causes a growing focus on the research of oil effluent. An oil-water separation process's scalability, efficiency, and effectiveness are crucial factors in the successful purification of oily wastes. Therefore, this research proposed a highly scalable, low-cost production method for fabricating membranes with outstanding selectivity and permeability. The proposed membrane comprises mixed cellulose ester (MCE) with stainless steel (SS) nano-pyramid structure coating on its surface. The unique morphological characteristics of nano-pyramid stainless-steel coating exhibit superhydrophilic properties and superoleophobic underwater, which prevent oil adhesion and enable exceptional oil separation performance, achieving an impressive efficiency of up to 99% in the process of filtering oil with various solutions, reaching high recyclability up to 99% in four cycles, also having good stability performance at low until high temperature (60°C), and compatible with diverse environmental conditions from acidic (pH 1) to alkaline (pH 14) [1].

Keywords: Stainless-steel, Coating, MCE.

11:20am MB3-1-ThM-11 The Impact of Laser Annealing on Electrical Resistivity and Mechanical Properties in Highly(111)-Oriented Nanotwinned Ag Thin Films, Tsai-Shaun Kuo, C. Yang, F. Ouyang, National Tsing Hua University, Taiwan

Recently, with the trend of miniaturization in microelectronic devices, resistivity plays a crucial role in the performance of electronic devices. Isothermal furnace annealing is usually conducted to enable grain growth to possess lower resistivity on interconnects; however, furnace annealing is usually time-consuming. By approach of locally abnormal grain growth, the electrical resistivity could be much more improved and still remains good mechanical properties.

In this study, we proposed using laser annealing to facilitate the grain growth on the highly (111)-oriented nano-twinned Ag thin film. The laser pulse frequency was fixed at 100 Hz, the pulse width was fixed to 1 ms and the laser is incident from the side of the silicon substrate to heat the film in purpose to avoid high reflectivity of the silver thin film surface. The laser annealing experiments were conducted with low laser annealing power (8.54, 16.44, 19.08, 24.35 W) in long annealing time (3 and 5 minutes) or high laser annealing power (50, 60 W) win short annealing time (4-10 seconds). For temperature controlment, the thermal couple was used to measure the temperature in the central of substrate during the laser annealing process. Dual-beam focused-ion beam system (FIB) was used to observed the cross-sectional microstructure images of as-deposited and laser annealed silver films. And the surface orientation was analysed by electron backscatter diffraction (EBSD). X-ray Diffractometer (XRD) was introduced in detecting the preferred orientation. The surface microstructure was investigated by Scanning electron microscope (SEM). Finally, four-point probe was used to detect the resistivity and Nanoindentor (NIP) was used to study the hardness.

Exceptional abnormal grain growth of Ag films can be achieved at 210 °C in 3 min, being much faster and lower temperature than furnace annealing. The microstructural and property evolution during laser annealing and the corresponding mechanism were discussed in detail below.

11:40am MB3-1-ThM-12 Development of Porous Ceramic Scaffolds for the Fabrication of SLIPS Coatings, Maria Caruso, National Research Council of Italy; A. Corazzi, National Research Council of Italy; A. Ruffini, M. Raimondo, National Research Council of Italy

γ-AlOOH and γ-Al2O3 are important inorganic materials in industries in particular applications such as catalysis or as a support for catalytically active phase, adsorption and drug delivery. The properties and application of γ-AlOOH and γ-Al2O3 depend primarily on the morphology and specifically on their surface area and pore size distribution. Hierarchical flower-like structures, as porous scaffolds for the fabrication of superhydrophobic SLIP surfaces, have been synthesized using various routes such as hydrothermal, solothermal, sol-gel, and template-assisted methods. In particular, we present new methods for synthesizing γ-AlOOH nanostructures directly from pure aluminum, i.e. without the introduction of any other anions, via hydrothermal route. Hydrothermal synthesis involves the use of aqueous solutions at high temperatures and pressures, the properties and morphology depend on thermodynamics and chemical conditions. In this study, we have investigated the effects of varying reaction parameters, such as temperature, reaction time, pH level, and addition of urea, on the hydrothermal crystal growth of boehmite nanostructures directly from the aluminum alloy sample. In this study, SEM and AFM morphological characterization and XRD analyses clearly highlight the optimal pH value together with the key role of urea.

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Injection molded plastics are shown to be suitable for ta-C coating on industrial scale using laser-arc. Reinforced and non-reinforced parts of PA12 and PEEK have been coated and investigated. The promising coating variants were transferred to a gear system. In dry operation the ta-C coating increased the lifetime by a factor of five.

In addition, we will present an up-scaled laser-arc module allowing increase of productivity and reduction of coating cost.

9:00am MC3-2-ThM-4 Investigation of the Mechanical and Tribological Properties of TiBCN Thin Films, Cennet Yıldırım, Turkish Energy, Nuclear and Mineral Research Agency – Boron Research Institute / Istanbul Technical University, Turkey; Ö. Kısacık, H. Doğuran, C. Eseroğlu, Turkish Energy, Nuclear and Mineral Research Agency – Boron Research Institute, Türkiye, Turkey; E. Kapar, Hakkari University, Türkiye, Turkey. Recently, coatings with a nanocomposite structure have become increasingly significant compared to monolithic coatings, owing to their advantageous properties such as high hardness and wear resistance. Particularly, the impact of boron and carbon on coating hardness has led to a growing application of boron-rich and tribo-rich nanocomposite coatings. In the scope of this study, nanocomposite films with a TiBCN structure were produced on M2 HSS using titanium and B, C magnetron targets. To enhance adhesion on steel surfaces, Cr-CrN bond layers were deposited using the cathodic arc physical vapor deposition (CapPVD) technique, and films with different compositions were subsequently produced by varying the power of titanium and B, C targets. Cross-sections of the produced films were examined using electron microscopy, and surface morphologies, as well as film thicknesses, were determined. Phases formed were analyzed by XRD, Raman, and FTIR, and changes in bond structures and depth profiles were identified using XPS. The hardness of the produced films was measured using the nanoindentation method, and adhesion was examined through scratch tests. Wear behaviors against alumina balls were investigated at different temperatures ranging from room temperature to 600 °C. Wear volumes were determined using optical profilometry, and wear rates and friction coefficients were calculated. The formed tribo-films were characterized using XPS analysis. It was observed that the amount of boron and carbon incorporated into the films had an influence on hardness and wear behaviors.

9:20am MC3-2-ThM-5 Investigating the Influence of B, C, and N on the Tribo-Mechanical Properties of the Chemically Complex TiSiBCN Thin Film Using Design of Experiments, W. Tillmann, Julia Urbanczyk, A. Ebady, Institute of Materials Engineering, TU Dortmund University, Germany; A. Thewes, G. Bräuer, Institute for Surface Technology, TU Braunschweig, Germany; N. Lopes Dias, Institute of Materials Engineering, TU Dortmund University, Germany. TiSiBCN thin films show promising properties like high hardness and improved tribological behavior. Adjusting the chemical composition can tailor the properties of these thin films. To investigate this influence, usually one element is varied. However, the interplay and influence of especially the light elements B, C, and N on the tribo-mechanical properties of chemical complex TiSiBCN thin films remain unclear. Therefore, a Design of Experiment using a Central Composite Design (CCD) was employed to investigate the influences of these light elements on the tribo-mechanical properties of TiSiBCN thin films. TiSiBCN with varying chemical compositions were grown in a magnetron sputtering process by adjusting the cathode power of TiB2. The formation of tribo films adhered, homogeneous, without substrate exposure, and a high chemical composition. Therefore, it is imperative to ensure the machinability of the build sections and adhesion of the build materials. Hence, the machinability of the coatings using ultrasonic milling is investigated. The correlation of the demanding machining conditions through alloy modifications of the Co- and Ni-based alloys without impairing the wear protection potential and using the ultrasonic-assisted milling process is a joint project of BAM and ISAF at Clausthal University of Technology (Fosta P1550/IGF 21959 N).

10:20am MC3-2-ThM-8 An Alternative Thermal Route to Improve an Aluminum Alloy through a Deposition of NiP Coating, R. Davies, Pontificia Universidad Católica de Paraná, Brazil; M. Soares, Universidade Tecnológica Federal do Paraná, Brazil; F. Amorim, P. Soares, C. Netitzke, Ricardo Torres, Pontificia Universidad Católica do Parana, Brazil. This research aims to improve the main limitations of aluminum alloys: mechanical and wear resistance through the deposition of the nickel-phosphorus (NiP) coating. Due to the natural formation of a dense oxide layer on the aluminum surface, the NiP deposition process often becomes more costly. Furthermore, it is common for NiP coatings to undergo a postheat treatment to increase hardness due to crystallization and Ni3P precipitation and further increase adhesion through the interdiffusion layer with the substrate. Finding an adequate interdiffusion temperature is challenging, as aluminum significantly decreases its mechanical properties. It would probably soften or even melt if subjected to an interdiffusion temperature of around 400 °C. This work aimed to find a suitable process for depositing an autocatalytic nickel-phosphorus coating on AlCu4Ti aluminum alloy in an alternative thermal route using the aluminum typical aging temperature and time treatment to create an interdiffusion layer between NiP and aluminum substrate in a single step. The typical aging temperature of the alloy was investigated, i.e., 200 °C, as well as the minimum temperature for the beginning of Ni3P precipitation, i.e., 250 °C. The SEM and EDS analyses showed a NiP layer of about 40 μm, well adhered, homogeneous, without substrate exposure, and a high phosphorus content (≈ 10%) formed in the aluminum alloy surface. The
interdiffusion and aging treatment condition at 250°C/16h resulted in the highest hardness of both aluminum and NiP coating.

Coatings for Biomedical and Healthcare Applications
Room Palm 3-4 - Session MD1-2-ThM
Surface Coatings and Surface Modifications in Biological Environments II
Moderators: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, Phaedra Silva-Bermudez, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

8:40am MD1-2-ThM-3 The Biocompatibility of Thermal Sprayed Bioactive Glass Hydroxyapatite Composited Coatings, Pin-Jieh Chen, C. Wu, R. Chung, Y. Yang, National Taipe Institute of Technology, Taiwan
In recent years, with the trend of demographic changes and aging, the demand for medical care has continued to rise, and the demand for orthopedic medical devices has increased day by day. In order to maximize the benefits of biomedical composite materials. This experiment uses flame spraying (FS) to coat the surface of Ti-6Al-4V to study the effects of modified hydroxyapatite composite coatings prepared with different proportions of bioactive glass powder on bone healing in rats. The experiment will be divided into two parts for discussion. The first part is the microstructure observation, phase composition analysis, mechanical properties and bonding strength test of the modified hydroxyapatite composite coating. The acrylene flow rate will be 1.60 Nm³/h, the spray gun speed is 250 mm/s, the spraying distance is 125 mm, and the number of flame spray (FS) sprays is 2 times for animal experiments; the second part is the observation of bone healing situation on the modified hydroxyapatite composite coating. The coated round rods were implanted into the femurs of 6-week-old SD rats for 2 weeks and 4 weeks. Finally, microstructure and through-compression tests were conducted to test the implant bonding strength.

9:00am MD1-2-ThM-4 Mineralization Ability and Inflammatory Reaction of HFOB 1.19 and THP-1 Cells on the Surface of the Borided AISI 316 L Steel, Erick Japhet Hernandez-Ramirez, R. Perez Pasten Borja, Y. Marquez-Flores, N. Hernandez-Delgado, Instituto Politecnico Nacional, Mexico; L. Mejia-Caballero, Universidad Autonoma Metropolitana, Mexico; I. Campos-Silva, Instituto Politecnico Nacional, Mexico
Metal-based implants, including stainless steel, titanium-based alloys, and cobalt-based alloys, are the most commonly used materials in orthopaedic implants. They are favored for their cost-effectiveness, exceptional durability, and advantageous mechanical properties. Stainless steel, in particular, offers an economical alternative that can help reduce costs in public health services. However, its wear and corrosion behavior in body fluid environments can lead to various corrosion-related failures, exacerbated by the release of metal ions, such as chromium and nickel, or fretting debris from the steel.
To enhance the performance of stainless steel, a FeB layer developed through the boriding process has been applied to 316 L stainless steel. This boride layer generally improves wear and corrosion resistance on the stainless surface. In addition, cytotoxicity results indicate satisfactory properties with regard to the effects on the survival and proliferative activity of human fibroblasts, osteoblasts, and macrophage cells on the surface of the borided AISI 316 L steel.
The hFOB 1.19 (osteoblast cells) mineralization and the evaluation of nitric oxide formation in THP-1 (macrophage cells) on the surface of borided AISI 316 L steel were obtained in this study. The FeB layer on the stainless steel was developed using a novel method called the pulsed-DC powder pack boriding process at 900°C for 3600 s, with a 5 A current intensity and cyclic polarity changes of 10 s, resulting in a total boride layer thickness of 20 μm. The mineralization ability of hFOB 1.19 adhered to the borided surface during 1 – 28 days of exposure was analyzed with the alizarin red S assay, while the inflammatory reaction of THP-1 cells to borided AISI 316 L steel was estimated by the Griess reaction after 10 days of exposure. Both assays were also replicated in non-borided AISI 316 L steel.
Notably, for mineralization, the Gompertz and Michaelis-Menten models were used to describe the evolution of the calcium compounds and alkaline phosphatase over the borided and non-borided surfaces. Based on the mineralization results, it was evident that the FeB layer promoted osteoconductive and osteoinductive properties, rendering it a promising bioactive layer. Consequently, the THP-1 cells in contact with the borided surface exhibited a controlled inflammatory reaction, with NaNO₂ values measuring below 3μM.

9:20am MD1-2-ThM-5 Tribological Composite Coatings Prepared by Cold Spray, Sima Alidokht, Department of Mechanical and Mechatronics Engineering, Memorial University of Newfoundland, Canada
The cold spray process stands out as a cutting-edge coating technology within the thermal spray family. Its versatility spans from component repair to additive manufacturing. Initially, cold spray research predominantly focused on metallic materials within the first decade since its inception. Cold spray suitability is confined to materials exhibiting ductility at high strain rates. While metals remain primary in cold spray, recent research explores developing metal matrix composites, particularly for tribological purposes. This presentation touches upon a number of tribology fundamentals and principles underpinning the deposition of metal matrix composites via cold spray. It provides an overview of advancements in fabricating tribological coatings through this method. Strategies involving powder characteristics and process parameters optimization to enhance coating quality and retain ceramic or solid lubricant will be covered. Despite successful measures in controlling the retention, these changes might unintentionally impact the coatings’ tribological properties. The focus will be on the tribology aspects of composite coatings manufactured through cold spray. The presentation also covers structural, chemical, and mechanical changes in third bodies during sliding, offering insights into wear processes influencing cold-sprayed composite coating’s wear resistance and friction characteristics. Lastly, we will discuss potential future trajectories for metal matrix composites produced via cold spray and their suitability for tribological applications.

10:20am MD1-2-ThM-8 Bio-Tribocorrosion Performance of AISI 316 L Steel Enhanced by Pulsed-DC Powder-Pack Boriding, Alan Daniel Cantilla-Pacheco, TecnNM/Tecnologico de Estudios Superiores de Jocotlan, Mexico; I. Mejia-Caballero, Universidad Autonoma Metropolitana-Azcapotzalco, Mexico; A. Delgado-Brito, V. Castrejon-Sanchez, TecnNM/Tecnologico de Estudios Superiores de Jocotlan, Mexico; R. Perez Pasten-Borja, I. Campos-Silva, Instituto Politecnico Nacional, Mexico
Stainless steel, titanium and CoCrMo alloys are commonly employed in the fabrication of biomedical implants, particularly for artificial replacements like hip and knee joints, owing to their mechanical strength and corrosion resistance. Among these materials, AISI 316 L steel stands out for its corrosion resistance, biocompatibility, affordability, and nonmagnetic properties, making it a frequently utilized biomaterial. However, low hardness and poor tribological properties are the important disadvantages of AISI 316 L steel. In this sense, boriding process is known to increase the surface properties of AISI 316 L steel; the resulting boride layer has excellent wear resistance due to its high hardness, thermal and chemical stability, and adhesion to the substrate material.
This study presents novel insights into the bio-tribocorrosion resistance of borided AISI 316 L steel when immersed in calf serum. Initially, the boride layer (FeB layer) on the steel surface was formed through pulsed-DC powder pack boriding at 950°C for 0.5 h, using a 10 A of current intensity, and inverse polarity cycle changes every 10 s. Subsequently, a diffusion annealing process, at 1000°C during 3 h in an inert atmosphere, was conducted on the borided AISI 316 L steel to induce a microstructural change in the layer, resulting in the development of a monophasic Fe-B layer. In both experimental conditions, the bio-tribocorrosion experiments were performed following the procedure disclosed in the ASTM G119-09 standard; a ball-on-flat tribometer connected with a three-electrode chemical cell was used for this purpose. The experiments were also replicated in the AISI 316 L steel (reference material).
The results indicated a wear-corrosion regime for both borided AISI 316 L (FeB layer) and borided steel exposed to diffusion annealing (Fe-B), characterized by a material loss ratio of corrosion to wear (C/W) approximately 0.2. The regime was significantly influenced by the boride layer, enhancing the bio-tribocorrosion resistance on the material surface by approximately 2 times compared to the reference material. In contrast, the reference material exhibited a wear-dominated regime (C/W= 0.095) attributed to passive film removal and high contact pressure in the tribopair, resulting in an increased total material loss rate due to wear.
Titanium dioxide thin films have a multitude of different applications. While the amorphous TiO$_2$ has excellent optical properties and very good conductivity, the presence of defects leads to an increased recombination. For this reason, crystalline TiO$_2$ films are desired for photovoltaic applications as exemplified by plasmonic photon conversion devices for production of chemical molecules or oleophobic surface treatment by photofixation of SO$_2$ on anatase surfaces. In general, there is a great interest in deposition techniques that enable phase control of TiO$_2$ thin films with TiO$_2$ being the prominent example.

This contribution deals with reactive HiPIMS deposition of TiO$_2$ thin films. First, experiments with a relatively long target-substrate distance are presented. It is shown that in the absence of substrate heating, all deposited films are X-ray amorphous. Despite that, films prepared by an optimized HiPIMS process exhibit up to 3 times higher photocatalytic activity evaluated by photodegradation of stearic acid, as compared to reference pulsed DC films prepared using the same setup. High oxygen partial pressure is required to achieve the enhanced photocatalytic performance. Increased ion energy, however, has a detrimental effect on the photocactivity. The deposition conditions have also pronounced impact on the crystallization kinetics of the thin films as illustrated by in-situ GIWAXS studies. When the target-substrate distance is reduced, the crystallinity of the as-deposited films is greatly improved. Growth of anatase as well as rutile can be achieved by changing the total deposition pressure. Even here, the HiPIMS process facilitates crystallization of the films as compared to pulsed DC. The deposition, however, results in a pronounced unintentional heating of the substrate. The heat input to the substrate is characterized and results from alternative experiments are presented.

In summary, the HiPIMS deposited films clearly outperform the ones prepared by pulsed DC. Although the exact growth conditions are dependent on the deposition geometry and specifics of the deposition setup, some general trends can support the process development.
In sputtering deposition processes the atomic shadowing effect, originated from the preferential deposition of obliquely incident atoms on higher surface points of any substrate, drives the formation of open columnar anisotropic microstructures, with columns interspersed with voids or underdense regions. The effect increases the surface roughness as the film thickness increases and undermine their performance, also limiting the maximum achievable thickness of films. Energetic ion bombardment during film growth counteracts the atomic shadowing effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and triggering re-deposition processes. However, film surface bombardment with highly energetic particles forms higher density of defects, disrupting the crystalline structure of the films and adding compressive internal stress.

In a previous work was shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment. Thick chromium films were prepared by DOMS, with different levels of ionization to test and study the influence on the film growth conditions and respective coating properties, like structure and surface morphology. An electrostatic flat probe mounted at the substrate location was used to characterize the saturated current density of positive charges bombarding the substrate during film growth, evaluating the flux of positive ions bombarding the growing film. Film hardness decreases with increase of thickness, however, Young’s Modulus values remain close to Cr bulk value. The films have [110] preferential orientation depending on the bombarding conditions.

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11:00am PP2-1-ThM-10 Implementation of HiPIMS Technology in Different Industrial Sectors, IVAN FERNANDEZ, NANOENERGY SL, Spain

After 20 years of continuous development by several research groups and companies it is now clear that real industrial breakthroughs for the high-power impulse magnetron sputtering (HiPIMS) technology are happening. HiPIMS is a state-of-the-art tool for applying high demanding metal and ceramic coatings with superior properties for applications such as: metal fabrication process (machining, stamping, molding or other tools), functional decorative, trench filling in semiconductor industry, or tribological (H-free DLC coatings with reduced friction, high hardness and enhanced thermal stability). Despite the great perspective and the positive forecasts for HiPIMS-technology since its’ discovery in 1999, it has taken more than 15 years for the real industrial breakthrough to start. For example, the deposition rate of HiPIMS is still considered to be rather low compared with conventional magnetron sputtering and even more so when compared to cathodic arc-deposition. Another issue is the complexity of use due to the large number of adjustable process parameters. It is not only the HiPIMS power supply, which itself has more controllable parameters than any traditional power supply, what contributes to this great deposition technology. It is also the process regulation (monitoring), the magnetron system (magnetic configurations), the gas flow, the pumping speed, etc. Apart from the traditional use of HiPIMS which is being currently implemented by the industry, it has been recently demonstrated that the application of a positive voltage reversal pulse adjacent to the negative sputtering pulse (Bipolar HiPIMS) gives rise to the generation of high fluxes of energetic ions. This solution allows unprecedented benefits for the coating industry, such as the energetic deposition onto insulating or grounded substrates, improved coverage on 3D parts or components, or even substrate etching. Also, Dual Magnetron HiPIMS operation is implemented more often in combination with multiple magnetron sources for the large production of high-end decorative coatings. A few examples of implementation of HiPIMS technology in industrial systems as well as the experimental results obtained in different configurations will be presented in this talk.

11:20am PP2-1-ThM-11 Impact of Energetic Film-Forming Particles in Ion Beam Sputter Deposition of Epitaxial Ga2O3 Thin Films, Dmitriy Kalanov, Y. Unutulmazsoy, J. Gerlach, A. Lotnyk, J. Bauer, A. Anders, C. Bundesmann, Leibniz Institute of Surface Engineering (IOM), Germany

Ion beam sputter deposition (IBSD) is an energetic deposition technique, which provides intrinsic heating and kinetic assistance to the growing film by energetic particles arriving at the substrate surface, which affect various thin film properties such as density, microstructure, and forming phase. In IBSD, the kinetic energy distribution of film-forming particles on the thin film can be controlled by changing process parameters, including the sputtering geometry, the flux, and the energy of primary ions. This is especially important for the growth of epitaxial thin films since it is necessary to find the optimal energetic assistance while minimizing the damage to the crystal lattice.

In this study, reactive IBSD is used for deposition of epitaxial Ga2O3 thin films on Al2O3(0001) substrates. The influence of process parameters such as substrate temperature, kinetic ion energy, ion beam current, sputtering geometry, oxygen pressure, and deposition time on the properties of the epitaxial films is investigated. The kinetic energy distributions of ions in the film-forming flux are measured by using a combined mass and energy analyzer and the resulting films are characterized regarding growth rate, roughness, crystalline structure, and microstructure. The impact of energetic bombardment by film-forming particles on the thin film structure is analyzed, and a significant change in crystalline quality is observed above the threshold in the average energy of film-forming particles (around 40 eV for the sputtered Ga⁺ ions).

Topical Symposium on Sustainable Surface Engineering Room Town & Country D - Session TS4-1-ThM

Coatings and Surfaces for Thermoelectrical Energy Conversion and (Photo)electrocatalysis I

Moderators: Clio Azina, RWTH Aachen University, Germany, Carlos Tavares, University of Minho, Portugal

8:00am TS4-1-ThM-1 Inorganic Thermoelectric Films for Harvesting Waste Heat Near Room Temperature: Opportunities and Challenges, Rui Shu, Linkoping University, Sweden, USA

The abundance of untapped low-grade heat presents a significant opportunity for sustainable energy solutions. However, current recovery technologies often fall short due to their lack of cost-effectiveness. Effectively harnessing this waste heat holds the promise of fostering a more sustainable society. Notably, inorganic thermoelectric bulk materials have shown promise in capturing waste heat near room temperature, offering potential applications in energy harvesting and thermal cooling.

However, challenges persist, including limited thermoelectric performance when transitioning to thin films and hindered large-scale implementation due to the scarcity and costliness of elemental Te. Adapting high-performance inorganic bulk thermoelectric materials into consistent thin films remains a significant obstacle.

This presentation explores the opportunities and challenges associated with using inorganic thermoelectric films for waste heat recovery at room temperature. Recent research advancements focusing on materials like Mg₂Bi₃ and transition-metal-nitride-based thin films are highlighted. Notably, these materials circumvent the use of scarce and brittle tellurium, with Mg₂Bi₃-based substitutes showing promise as alternatives to commercially used Bi₂Te₃. Our study aims to pave the way for the practical utilization of highly efficient inorganic thermoelectric films in energy harvesting applications.

8:40am TS4-1-ThM-3 Retaining Crystallinity of as-deposited Thermoelectric Fe₃V₁₋ₓAlₓ-based Thin Films Grown from DCMS and HiPIMS, Ludwig Enzlbenger, TU Wien, Institute of Materials Science and Technology, Austria; S. Kolozsvari, Plansee SE, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Thermoelectric materials have gained much attention in recent years due to their ability to directly interconvert electrical and thermal energy via the Seebeck/Peltier effect. This can be used to convert waste heat back into usable electrical energy, making thermoelectrics very interesting materials in a world with increasing demand for renewable and efficient utilization of energy. The efficiency of this process is generally dependent on three parameters - the thermopower S, the electrical conductivity σ and the
thermal conductivity $\lambda$ - which are represented together in the dimensionless Figure of Merit ZT.

Among thermoelectrics, Heusler and half-Heusler materials have shown to be promising candidates, due to their high Seebeck coefficients at room temperature and their high electrical conductivity, while generally higher thermal conductivity is often a drawback in thermoelectric performance.

In 2019, Hinterleitner et al. managed to produce magnetron sputtered thin films of bcc-Fe$_3$V$_2$Al$_2$ with an exceptionally high Seebeck coefficient, Power Factor and Figure of Merit, but the samples needed to be heat-treated for one week to crystallize from their initially amorphous state.

In this work, we present Fe$_3$V$_2$Al-based full-Heusler thin films retaining their crystallinity during sputter deposition. By tuning deposition temperature, bias potential and pulse on-time we managed to fabricate films of Fe$_3$V$_2$Al in a W-type bcc-structure on silicon and austenite substrates. These films were analysed using XRD, EDX, electron microscopy and by measurement of transport data (resistivity, Seebeck coefficient). Thermal conductivity of the films was derived from measurements of thermorelectance and specific heat capacity.

9:00am TS4-1-THM-4 Thermoelectrical Investigations of TaC-Based Superlattice Protective Coatings, Barbara Schmid, S. Lin, T. Schöngruber, N. Koutný, TU Wien, Institute of Materials Science and Technology, Austria; S. Bühler-Paschen, TU Wien, Austria; L. Mitterhuber, Materials Center Leoben, Austria; D. Ingerle, TU Wien, Austria; S. Kolozsvari, Plansee SE, Germany; P. Mayerhofer, TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides (TMC) and nitrdes (TMN) feature high melting points up to 4000 °C and superior thermal stability and are therefore regarded as ultra high temperature ceramics (UHTC). Those materials are well-established in the realm of protective coatings. Superlattice architecture can impact a plethora of different material characteristics such as mechanical, chemical and electric properties. Inspired by preliminary DFT high-throughput screenings, we developed TiC/TaC and TiN/TaC superlattice coatings exhibiting bilayer periods between 2 and 50 nm via non-reactive DC magnetron sputtering. Those materials exhibit high hardness and fracture toughness and are therefore immuculacy choices as protective coatings. These superlattice materials also exhibit decent thermal stability and electrical conductivity which motivated us to calculate their thermoelectrical properties via DFT using BoltzTraP and VASP. The experimentally determined Seebeck coefficients exhibit a significant bilayer-period-dependence. By conducting Time Domain Thermorelectance investigations, we also derived their figure of merit (ZT) values.

9:20am TS4-1-ThM-5 Exploring the Potential and Challenges of Solution-Processed Inorganic Thermoelectric Materials, Maria Ibáñez, Institute of Science and Technology Austria (ISTA), Austria

INVITED

Over the past few years, there has been a significant surge in interest surrounding solution-based techniques due to their cost-effectiveness and scalability in the production of high-performance thermoelectric materials. This approach involves the synthesis of particles in a solution, followed by their purification and thermal processing to yield the desired dense polycrystalline material. In contrast to traditional methods, solution-based syntheses offer the ability to manipulate particle characteristics, including size, shape, crystal structure, composition, and surface chemistry, to an unprecedented degree. This fine-tuned control over powder properties opens up distinct opportunities for crafting thermoelectric materials with meticulously controlled microstructural attributes.

In this presentation, our primary focus will be on Ag$_2$Se, an important thermoelectric material for harnessing thermoelectricity at or near room temperature, an area where the selection of high-performance materials is currently limited. While Ag$_2$Se shows great promise, the main problems are the large discrepancy in the reported thermoelectric properties and difficulties in replicating its exceptional performance. These discrepancies often stem from the intricate control of defects within the material, such as vacancies, interstitial atoms, dislocations, grain boundaries, and precipitates.

We will show that our solution-based synthesis method enables precise defect control, especially avoiding fluctuations in stoichiometry. Additionally, we will illustrate how we can fine-tune microstructural defects, including strain, dislocations, and grain boundary density, leveraging the characteristic phase transition of Ag$_2$Se during the sintering process. Our results will highlight that besides stoichiometry, the microstructure is crucial for tuning Ag$_2$Se transport properties and how this control can be provided by our novel synthetic route. Furthermore, we will highlight the sustainability and scalability of our approach, where solvents can be recycled and energy consumption minimized, contributing to a more environmentally friendly production process.

10:20am TS4-1-ThM-8 3D Nanoscale Spatial Imaging of Doped ZnO and TiO$_2$ Transparent Thermoelectric Thin Films, J. Ribeiro, F. Correia, H. Faría, University of Minho, Portugal; A. Welle, T. Boll, Karlsruhe Institute of Technology (KIT), Germany; Carlos Jose Tavares, University of Minho, Portugal

Transparent thermoelectric materials are a promising technology for touchscreen displays and solar cell applications, rendering a sustainable powering of the device. In order to enhance the thermoelectric performance, the material must have a high Seebeck coefficient and high electrical conductivity. This work focuses on the impact of doping on ZnO and TiO$_2$-based thin films deposited by DC magnetron sputtering. The properties of the films depend strongly on the dopant type and concentration. On the one hand, it has been documented that Al and Ga doping can improve the electrical properties in ZnO, as can Nb doping in TiO$_2$. On the other hand, introducing heavier elements (such as Bi, Sb or Nb) into the metal-oxide matrix hinders phonon-mediated heat conduction, and consequently reduces the thermal conductivity, which is a promising approach. Atom Probe Tomography and Time-of-Flight Secondary Ion Mass Spectrometry are powerful tools to determine the composition and inherent homogeneity within the thin films, as well as to investigate the carbon and anion segregated in interfaces and grain boundaries. For the ZnO-based films, Al and Ga dopants are homogeneously distributed within the crystals, with the exception of Bi, which is not incorporated in the ZnO wurtzite cell and segregates at the grain boundaries and at the triple junctions. Thus, Bi contributes to grain boundary scattering of phonons and contributes less to the reduction of the thermal conductivity, in comparison to Ga-, Al-, and Sb-doping in ZnO. For the Sb-doped ZnO thin films, a larger Zn content was registered at the triple junctions of the grain boundary. As for the Nb-doped TiO$_2$ thin films, Nb is homogeneously distributed into the TiO$_2$ matrix and no grain boundaries are visible. However, the composition varies depending on the deposition conditions, where the Nb content inside the film changes depending on the oxygen content controlled through the reactive O$_2$ flow during the sputtering depositions.

10:40am TS4-1-ThM-9 Ni-B-based Polyalloy Electrocataylst Coatings Deposited by MSPVD for Efficient Oxygen Evolution Reaction, Kubilay Sahin, Institute for Clean Growth and Future Mobility, Coventry University, Department of Metallurgy, University of Mons (UMONS), UK; V. Vitry, Department of Metallurgy, University of Mons (UMONS), 23 Place du Parc, B-7000 Mons, Belgium; A. Coby, Institute for Clean Growth and Future Mobility, Coventry University, Priory St, Coventry, CV1 5BF, UK; J. Graves, G. Pourian Azar, Institute for Clean Growth and Future Mobility, Coventry University, UK

Molecular hydrogen has been considered as one of the best green energy sources due to its high energy density. Water splitting is a highly promising approach to generate molecular hydrogen without any damage to environmental health. However, electrocatalyst materials, which are generally expensive noble elements, are required to complete the reactions efficiently and sustainably. Due to their excellent features such as low cost, high abundance, high corrosion resistance and durability, catalytic activity, and good synergistic effect with other elements, Nickel-based electrocatalysts have been reported as one of the most valuable electrocatalysts for water splitting. Electrodeposition, hydrothermal deposition, and physical vapour deposition are some of the used techniques to synthesize Nickel-based electrocatalysts. Electroless nickel-boron plating is a remarkably beneficial technique to produce Ni-B coatings with outstanding features such as hardness, wear resistance, and corrosion resistance. In recent studies, Ni-B coatings have also demonstrated encouraging catalytic activity with remarkable stability. While Ni-B coatings have been extensively studied for various applications, there is not enough research on their catalytic applications. Furthermore, there is no existing literature regarding the deposition of Ni-B coatings utilising a technique other than electrodeposition or electroless plating. However, the Magnetron Sputtering Physical Vapour Deposition (MSPVD) technique has the capability of producing Ni-B coatings with porous and tunable structures together with easy alloyability to further improve the electrochemical performance.

The current study is designed to investigate the electrocatalytic performance of Ni-B-based polyalloy coatings produced by MSPVD.
Polyalloy coatings were co-deposited using a Ni-B and transition metal targets such as Fe, Co, and Mo. The coatings were deposited at different deposition parameters such as chamber pressure, substrate type and different chemical compositions. The electrocatalytic performance of the coatings was compared to see the effect of boron, alloying elements, morphology and crystal structure for the Oxygen Evolution Reaction. Superior features like low overpotentials, high stabilities, and high surface areas were obtained after the electrochemical analyses such as Linear sweep voltammetry, cyclic voltammetry, chronoanpeterometry and electrochemical impedance spectroscopy under alkaline conditions. The results showed promising efficiencies and stabilities for highly tunable, cost-effective Ni-B-based electrocatalyst coatings.

11:00am TS4-1-ThM-10 Role of Grain Boundaries in the Stress Corrosion Cracking of Nanoporous Gold Thin Films, Aparna Saksena, Max-Planck Institut für Eisenforschung GmbH, Germany; A. El-Zoka, Imperial College London, UK; A. Saxena, E. Hatipoglu, Max-Planck Institut für Eisenforschung GmbH, Germany; J. Schneider, RWTH Aachen University, Germany; B. Gault, Max-Planck Institut für Eisenforschung GmbH, Germany

For its potential as catalyst, nanoporous gold (NPG) prepared through dealloying of bulk alloys has been extensively investigated. NPG thin films can offer ease of handling and better tunability of the chemistry and microstructure of the nanoporous structure. They are however prone to intergranular cracking during dealloying, limiting their stability and potential applications. Here, we systematically investigate the grain boundaries in Au28Ag72 (± 2 at.%) thin films. We observe that a sample synthesized at 400 °C is 2.5 times less prone to cracking than one synthesized at RT. This correlates with a higher density of coincident site lattice (CSL) grain boundaries, especially coherent Σ3, increased, which appear resistant to cracking. Nanoscale compositional analysis of random high-angle grain boundaries reveals prominent Ag enrichment up to 77 at.%, whereas Σ3 coherent twin boundaries show a Au enrichment of up to 30 at.%. The misorientation and the chemistry of grain boundaries have a crucial role in their dealloying behavior, which controls the cracking. Our results provide a target for optimizing the longevity application of NPG thin films for possible applications.

11:20am TS4-1-ThM-11 Metal/Oxide Heterostructure as Hydrogen Evolution Reaction Electrocatalyst, Thí Y Phung Nguyen, National Cheng Kung University (NCKU), Taiwan; J. Ting, National Cheng Kung University (NCKU), Taiwan

In response to the growing demand for sustainable energy sources, there has been a concerted effort to develop efficient electrocatalysts for the hydrogen evolution reaction (HER). Previous researches indicate the need to improve consistent efficiency and stability at high current densities (> 500 mA/cm²) over 100 hours. In this study, we have investigated metal/oxide heterostructure HER electrocatalysts. The heterostructure is noble-metal free and synthesized using a hydrothermal method followed by thermal reduction for controlling the alloy/oxide ratio. Various characterization techniques, including scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and in-situ Raman spectroscopy are used to examine the obtained heterostructures. Furthermore, the electrochemical performance is evaluated using linear sweep voltammetry, electrochemical impedance spectroscopy, cyclic voltammetry, and electrochemical specific surface area analyses. We demonstrate highly efficient and stable heterostructure HER electrocatalyst. This work contributes to cost-effective and sustainable hydrogen production, with significant implications for renewable energy integration.

11:40am TS4-1-ThM-12 Copper-Based Porous Surfaces for Electrocatalytic CO₂ Reduction, Maria José Lima, University of Minho, Portugal; J. Castro, S. Carvalho, University of Coimbra, Portugal

The United Nations (UN) has identified carbon dioxide (CO₂) as a greenhouse gas (GHG) that is present in the atmosphere as an environmental issue in Goal 13 for climate action.

Decreased CO₂ emissions and participation in a circular economy are crucial to achieving these goals. To include CO₂ in a circular economy, capture and electroreduction of CO₂ into long-chain hydrocarbons or alcohols (C2+) can be the solution. From a material perspective, copper-based catalysts are active and selective cathodes capable of producing hydrocarbons, increasing the Faradaic efficiency of the CO₂RR to C2+ molecules.

Enhancing electrochemical active sites can be an additional strategy to improve CO₂RR. Different strategies can produce porous electrodes, thus increasing the electrochemical active surface area (ESCA) and the CO₂-
Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM3-1-ThA

Accelerated Thin Film Development: High-throughput Synthesis, Automated Characterization, and Data Analysis I
Moderators: Davi Marcelo Febbia, NREL, USA, Sebastian Siol, Empa, Switzerland, Andriy Zakutayev, NREL, USA

1:40pm CM3-1-ThA-1 Collaborative Intelligence in Thin Film Research for Clean Energy Technologies, Shijing Sun, University of Washington, USA

Addressing global environmental challenges, particularly in the realm of energy storage and conversion, necessitates innovative approaches. In this context, artificial intelligence (AI) has emerged as a transformative tool, catalyzing the discovery of new materials. However, the practical application of computational models in laboratory settings presents distinct challenges. This talk will explore the evolving role of AI in scientific research, focusing on its capacity to enhance rather than replace human expertise. This synergy paves the way for advanced collaborative efforts in the development and analysis of thin films.

Drawing from my experience as both an experimentalist and a materials data scientist in academic and industrial settings, I will showcase data-driven approaches that accelerate the formulation of precursors for solution-processed thin films. Additionally, I will delve into how AI-assisted image characterization can effectively detect imperfections and establish crucial structure-property correlations. These advancements are particularly significant in the pursuit of clean energy solutions, demonstrating the integral role of AI in accelerating scientific innovation in thin film technology.


Amorphous thin films are employed in many applications and offer unique characteristics, which are not observed in their crystalline counterparts.

We present the discovery and design of amorphous Y-W-N ceramic thin films. We performed an exploratory synthesis and high-throughput characterization of Y,W,N thin films. The compositions are performed using combinatorial, reactive radio-frequency magnetron co-sputtering of Y and W targets in Ar/N2 atmosphere, resulting in materials libraries with orthogonal composition and deposition temperature gradients. This allows for a rapid screening of the synthesis phase space. A composition window within 0.1<x<0.85 is covered, whereas the substrate temperature (T) is varied from 80°C up to 600°C. High-throughput screening of the composition and structure of the libraries by means of XRF and XRD reveals a wide composition range of 0.25<x<0.6 where thin films grow with an amorphous structure without precipitation. Moreover, the amorphous structure shows remarkable temperature stability of up to 600°C. Optical properties mapping using an automated high-throughput UV–vis photo-spectroscopy system suggests a band gap of >2.5 eV and confirms the 1s; S. Siol, ≤2.5 eV and confirms the 1s; S. Bette, NREL, USA, on of these experimental findings are corroborated by theoretical calculations for a wide composition range of 0.2<x<0.85.

To comprehend the application potential of these latter films by means of high-resolution TEM reveals a homogeneous amorphous structure of the films with no signs of elemental segregations or crystallization. To comprehend the application potential of these materials, a comprehensive study of a wide range of functional and physical properties is performed including a set of optical and dielectric constants, diffusion barrier performance, oxidation resistance, and thermal stability. Experimental findings are corroborated by theoretical calculations for a better understanding of a complex relationship between the elemental composition of amorphous Y,W,N thin films and their physical and functional properties.

2:40pm CM3-1-ThA-3 Deposition of Highly Crystalline AlScN Films Using Synchronized HiPIMS – From Combinatorial Screening to Piezoelectric Devices, Jyotish Patidar, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; S. Bette, aixACCT Systems GmbH, Germany; O. Pshyk, K. Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; R. Kessels, aixACCT Systems GmbH, Germany; S. Siol, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Piezoelectric thin films are crucial for many technologies, in particular for RF components for telecommunication. Wurtzite Aluminum Nitride (w-AlN) is one of the most widely used material for these types of applications. Recently, Aluminium Scandium Nitride (AlScN), is becoming more popular due to its increased piezoelectric coefficient. Highly crystalline and textured thin films are essential for high-performing piezoelectric devices. In our prior work, we demonstrated that metal-ion synchronized HiPIMS (MIS-HiPIMS) with moderate substrate bias potentials can offer key advantages in the deposition of these materials.[1] Here we explore how these concepts can be applied to AlScN films.

In AlScN films, high Sc concentrations enhance the piezoelectric response by softening of the phonon modes. However, high Sc content can also lead to structural frustration and precipitation of cubic ScN (c-ScN). Investigating the Sc non-equilibrium solubility and structural evolution upon scandium alloying is experimentally involved and thus rarely discussed. In our work, we employ a combinatorial approach for an accelerated estimation of the solubility limits and optimization of film’s properties, for varying synthesis environmental. We investigated different synthesis routes by hybrid co-sputtering of Al/Sc in a reactive environment through a combination of direct current magnetron sputtering (DCMS) and HiPIMS processes, along with different biasing strategies.

The combinatorial screening reveals a striking correlation between the ion kinetic energy and non-equilibrium Sc solubility. In addition, certain deposition modes prove to be more resilient against structural frustration than others. Particularly, a reduction of misaligned grains is observed with the application of a negative substrate bias potential. Based on the results from the screening, uniform Al0.5Sc0.5N thin films were deposited on Ti/Pt contacts, for each synthesis strategy. Detailed characterization of these films show that based on the chosen synthesis modes, the stress state can be tailored from -1.5 to 1.5 GPa. On the other hand, measurements of the piezoelectric coefficient d33 show a performance comparable to the current state-of-the-art.

The results of this study showcase how high-throughput experiments can facilitate the development of complex sputter processes while also highlighting the potential of synchronized HiPIMS processes for the deposition of piezoelectric thin films and other defect-sensitive materials.

Protective and High-temperature Coatings
Room Town & Country C - Session MA5-2-ThA

Boron-containing Coatings II
Moderators: Martin Dahlqvist, Linköping University, Sweden, Anna Hirle, TU Wien, Austria

1:20pm MAS-2-ThA-1 Tuning Oxidation Resistance and Mechanical Properties of Diborides by Transition Metal Alloying Deposited by Combination of Magnetron Sputtering and Cathodic ARC Evaporation, Daniel Karpinski, P. Karvanci, C. Krieg, PLATIT AG, Switzerland; H. Joost, H. Frank, Gesellschaft für Fertigungstechnik und Entwicklung Schmalkalden e.V., Germany; A. Lütkemann, PLATIT AG, Switzerland

Titanium diboride is currently the most widespread boride coating used in industry. Its most common application is machining non-ferrous metals, due to its outstanding properties such as high hardness 40–50 GPa, high elastic modulus ≥ 500 GPa, high chemical inertness, high melting point above 3000°C, and low propensity for sticking to soft metals. The main drawbacks of diborides are their generally low oxidation resistance (between 600-700°C for TiB2) and brittleness. As productivity demands from customers rise, the cutting speed and feed rate of the tool increase as well, resulting in elevated temperatures at the contact point between the workpiece and the tool. Therefore, there is a strong incentive to increase the oxidation resistance and/or reduce the coefficient of friction of the coating. This study investigates the effect of alloying diboride materials with transition metals, altering the boron-to-metal coating stoichiometry (x = B/Me), mechanical properties, tribological properties, and oxidation resistance of the coating. A Plätti Pi411 coating machine equipped with LAC5 technology was used to synthesize the coatings. This technology enables magnetron sputtering to be performed from a central cylindrical cathode (SCiL®) while simultaneously running a cathodic arc evaporation process from cylindrical cathodes located in the chamber door (LARC®). For this study, the metal boride (MeB2) coatings were deposited by concurrent magnetron sputtering of a MeB2 target and cathodic arc evaporation of a Me target (Me = Ti, TiS, Cr and Zr) to tune the coating stoichiometry and composition. Nanoindentation tests revealed that this alloying strategy can decrease the B-to-Me ratio from 2.0 to 1.5, resulting in a hardness drop from about 45 GPa to 35-40 GPa. Isothermal annealing tests conducted in air at 600°C for 1 hour showed that decreasing the B-to-Me ratio of the coating effectively doubles the oxidation resistance of the coating. In addition, it was found that the use of ternary boron alloys leads to an even more pronounced increase in oxidation resistance, up to threefold.


Transition metal diboride films are characterized by high mechanical hardness, wear resistance and chemical stability at elevated temperatures. Combination of these advanced properties makes them applicable as protective coatings for alloy-machining tools. Typical nanocomposite structure of these films, consisting of hexagonal P6/mm/m columns grains surrounded by boron tissue phase, leads to high hardness above 37 GPa [1]. However, formation of the boron tissue phase is not convenient in terms of brittle fracture and oxidation resistance, which are the main drawbacks of
Thursday Afternoon, May 23, 2024

diboride films. Therefore, one of the ways to improve the properties is to reduce the boron to metal ratio and aim for understoichiometric films [2]. Here, it is important to understand, how the boron deficiency will be accommodated by the films’ structure, because it can significantly affect the mechanical properties [3]. In this work, we study the effect of boron understoichiometry on structure in case of ternary $V_1xMoB_2$ films prepared by magnetron sputtering and ex-situ annealed up to 1200°C. We present results of detailed structural analysis by high-resolution transition electron microscopy, which revealed interesting structural features, including several types of planar defects and coexistence of coherently linked orthorhombic and hexagonal phase accompanied by chemical decomposition.


This work was supported by the Slovak Research and Development Agency (Grant No. APVV-21-0042), Scientific Grant Agency (Grant No. VEGA 1/0296/22), European Space Agency (ESA Contract No. ESA AO/1-10586/21/NL/SC), and Operational Program Integrated Infrastructure (Project No. ITMS 313011AUH4).

2:40pm MAS-2-Tha-5 Constitution, Microstructure and Properties of Magnetron Sputtered CrBx-TiBx and CrBx-ZrBx Thin Films, V. Ott, Karlruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany; H. Riedel, T. Wojciech, Vienna University of Technology, Austria; S. Ulrich, Karlische Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany; Michael Stueber, Karlische Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal diboride thin films can provide interesting properties profiles related to wear, oxidation and corrosion resistance, preferably at higher temperature and thermomechanical loads. To achieve such properties, intense efforts have recently been undertaken with regard to the microstructural design of diborides. These include for example different alloying strategies, incorporation of Si, formation of core-shell structures, defect engineering and advanced hybrid PVD processes for optimized thin film growth. However, the database on phase formation, microstructure and properties for PVD thin films in some material systems of interest is still surprisingly limited in comparison to transition metal nitrides and carbides. This study aims to contribute such information on DC magnetron sputtered thin films in the binary systems CrBx-TiBx and CrBx-ZrBx systems, a combinatorial approach for thin film deposition was followed, using segmented ceramic targets. The composition, phase and microstructure formation, characterized by EPMA, XRD and TEM methods, are systematically described for a broad compositional window in both systems. Selected mechanical properties, such as indentation hardness and modulus, as well as elastic and plastic deformation energies in micro indentation, are discussed versus the thin films’ constitution and microstructure. Special focus is laid on the potential formation and impact of solid solution structured diboride thin films in the two quasi-binary systems that exhibit significantly different phase diagrams in thermodynamic equilibrium.

3:00pm MAS-2-Tha-6 Fracture Characteristics of Si Containing Ternary and Quaternary Transition Metal Diborides, Anna Hirl, A. Bahr, O. Beck, R. Hahn, Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; S. Kolozsvári, P. Poliček, Plansee Composite Materials GmbH, Germany; O. Hulond, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; H. Riedel, Institute of Materials Science and Technology, TU Wien, Austria

Alloying with silicon or Si-based phases is an efficient approach to improve the oxidation resistance of transition metal diborides (TMBs). It is well established for bulk ceramics [1,2] but was also recently verified for thin film TMBs such as CrBx, FeBx, or TiBx [3,4]. Adding these strong oxide formers to diborides results in highly dense and protective SiO2-based scales, whereas the amount of Si required differs between ternaries (pure Si addition) and quaternaries (alloying via disilicides), respectively. In more detail, alloying of TaSi2 and MoSi2 into TiBx thin films not only reduces the amount of Si needed to provide excellent oxidation resistance but also minorly influences the mechanical properties. For quaternary TiB3 based coatings, hardness values of 36 GPa (TaSi2) and 27 GPa (MoSi2) compared to around 38 GPa of the binary system have been achieved. Interestingly, for ternary Ti-Si-Bx films the mechanical properties vary in a wide range, ceasing 20 GPa while exhibiting similar oxidation stabilities. All these coatings crystallized in the α-AlB2 structure type with a preferred 0001 orientation being decisive for highest hardness.

Meanwhile the oxidation behavior and mechanical properties have been thoroughly described for ternary and quaternary TMBs so far [3,4] the fracture characteristics of these coating materials are rather unexplored. Based on a recent study [4] the fracture toughness (KIC) of binary TiB2x is known to be highly dependent on the amount of phase present at the grain boundaries.
Coatings for Biomedical and Healthcare Applications
Room Palm 3-4 - Session MD2-ThA

Medical Devices: Bio-Tribo-Corrosion, Diagnostics, 3D Printing

Moderators: Steve Bull, Newcastle University, UK, Hamdy Ibrahim, University of Tennessee at Chattanooga, USA

1:40pm MD2-ThA-2 Corrosion Risk Analysis of CoCrMo alloy as a Function of Microstructure: Biomedical Applications, Maansi Thapa, University of Illinois at Chicago, USA; Y. Sun, B. Keaty, M. Mathew, C. Takoudis, M. Daly, D. Ozevin, University of Illinois - Chicago, USA

CoCrMo alloys are widely used in orthopedic implants and various biomedical applications, exhibit excellent corrosion resistance and mechanical properties. However, it has raised concerns about inferior corrosion behavior and subsequent side effects due to metal ion release. While the electrochemical nature of this alloy is well studied, the microstructure’s effect needs further research. The objective of this study is to evaluate corrosion behavior of CoCrMo alloys in two microstructures: unbounded (transverse) and bonded (longitudinal).

Six CoCrMo disks (11x7mm) were prepared and polished following metallurgical protocol for a surface finish of <50 nm. The unbounded CoCrMo rod was cut perpendicular to the axis, while the bonded CoCrMo rod was cut parallel to the axis. The electrolyte used was bovine calf serum (30 g/L proteins) with a pH of 7.6 to simulate the joint environment. The electrochemical test followed ASTM G61 standard using a three-electrode system: the sample as the working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a graphite rod as the counter electrode. The typical protocol involved: open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and cyclic polarization curve. Using Tafel estimation, the corrosion potential (Ecorr) and corrosion current (Icorr) were determined. EIS data was utilized to generate Bode and Nyquist plots and construct an equivalent electric circuit to determine polarization resistance (Rp) and double layer capacitance (Cd). The corroded surfaces were characterized by white light microscopy, SEM, and EBSD.

Our study showed that the CoCrMo specimens with unbounded microstructures exhibited increased corrosion resistance (Ecorr: -0.678 V vs SCE, Icorr: 1.85E-06 A/cm²) compared to bonded microstructures (Ecorr: -0.736 V vs SCE, Icorr: 5.05E-06 A/cm²). The EIS data supported this observation, revealing higher Rp and lower capacitance. SEM observations revealed larger pits in the bonded microstructure compared to unbounded. Previously, Jacob et al. reported superior fretting-corrosion behavior of unbounded microstructures and potential risk of bonded microstructures under an infected environment.

The bonded microstructure, with increased grain boundary exposure, heightens the risk of intergranular and galvanic corrosion. Further exploration is needed to understand microstructural mechanisms and develop strategies to inhibit increased corrosion risk. Our investigation emphasizes the vital role of material composition and configuration in microstructural and corrosion behavior.

nanocarbon coatings and electrodes directly on polymers. Unlike different transfer techniques of CVD-grown nanocarbons, or printing methods from inks, this talk will focus on a bottom-up approach for directly growing different types of graphenic nanocarbons on aromatic polymers by laser irradiation. The speaker will present an approach that leverages this direct-write process, often referred to as laser-induced graphene (LIG), for creating spatially-varying morphologies and chemical compositions of LIG electrodes, by leveraging gradients of laser fluence. Three distinct morphologies are identified, and process control map is generated for maximizing the electrical conductivity of these porous graphene for biomedical devices. Moreover, this talk will introduce a method for controlling heteroatom doping of LIG based on controlling the molecular structure of the polymer being lased, i.e. by introducing sulfur- and fluorine- containing backbones. We demonstrate superhydrophobic and parahydrophobic surface properties for the fluorine-doped LIG patterns. We also show antibacterial properties of LIG coated surgical devices. Finally, a demonstration of these functional doped LIG electrodes as electrochemical biosensors will be presented for the detection of the neurotransmitter dopamine with nanomolar sensitivity.

3:20pm MD2-Tha-7 Microfluidic Device for the Isolation, Detection, and Purification of Exosomes Based on Metallic Nanostructure Arrays, Alfredo Krisna Altama, Y. Hsiao, C. Chen, National Taiwan University of Science and Technology, Taiwan; R. Halli, National Taiwan University of Science and Technology, Indonesia; P. Yu, Ming Chi University of Technology, Taiwan; P. Wu, J. Chu, National Taiwan University of Science and Technology, Taiwan.

Due to their low cost, rapid processing, and ability to analyze even minuscule sample volumes, microwell platforms are widely used in disease detection and specimen separation. In this study, metallic nanostructure arrays (MeNTAs) with tube-like features are embedded into microfluidic devices for immunoaffinity-based detection and efficient exosome isolation. MeNTA candidates were evaluated based on their ability to mechanically withstand the stress during microfluidic operations, X-ray diffraction, zeta potential, and electrostatic interactions. The Zr50Cu20Al15Ni5 thin film metallic glass (Zr-TFG) exhibited superior mechanical properties and a negative zeta potential compared to other materials. (e.g., Cu, Bronze, Ag, 7075Al, Ti64, 718Ni, 55316, Cu-TFG, W-TFG, and Al-TFGM). The resultant microfluidic device featured Zr-based MeNTAs with an interdigital electrode in a microchannel. In testing with derived exosomes (liquid biopsy of 500 μL), the device achieved a 95.3% exosome recovery rate within 1 hour while resisting nonspecific binding to HeLa-derived exosomes (recovery rate < 0.1%). The device facilitated the isolation of 1 x 10^8 exosome particles per mL for electrochemical impedance spectroscopy detection and allowed efficient release of captured exosomes via cyclic voltammetry operations. The proposed Zr-MeNTA microfluidic device holds significant potential for the isolation, detection, and purification of exosomes in liquid biopsy samples for cancer diagnosis, as mentioned by Hsiao et al. (2023).

4:00pm MD2-Tha-9 Mass-Production of Ultra-Sensitive 2d Electronic Biosensors via Roll-to-Roll Sputtering and Laser Patternning, Ben Robertson, M. Muratore, University of Dayton, USA; N. Glavin, Air Force Research Laboratory, USA; C. Muratore, University of Dayton, USA.

Materials with high surface-volume ratios demonstrate exquisite sensitivity and detection limits in diverse molecular sensing applications. Integration of nanowires, nanotubes, and two-dimensional (2D) semiconductors into sensing devices, however, presents challenges inhibiting product development. For example, thousands of trials are required to obtain US government approval for point-of-care diagnostics, yet producing a suitable number of 2D devices via conventional synthesis and fabrication techniques to meet this testing requirement is not currently feasible. To realize commercial applications of 2D transducers in ubiquitous low-cost diagnostic devices, new synthesis and fabrication approaches were developed. Processes for high-rate (>10^4 per day) mass-production of low-cost two-dimensional electronic medical diagnostic devices with limits of detection rivaling PCR (<10 fg/mL) with response times of <2 minutes will be presented. Rapid and inexpensive sensor chip fabrication relies upon sputter deposition, laser patterning, and laser annealing processes in a roll-to-roll physical vapor deposition system. Moreover, naturally abundant and recyclable materials were selected for use in these scalable processes for reduced waste stream impact in anticipation of large numbers of devices are consumed daily. An automated high-speed Raman spectroscopy system was developed for quality control of mass-produced materials during fabrication. Fundamental studies employing this system to measure point defect densities in 2D semiconducting transducer materials will be shown to correlate synthesis and fabrication process parameters, 2D material structures, and diagnostic device performance.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP2-2-ThA

2:00pm PP2-2-ThA-3 Metal-Ion Synchronized HiPIMS of AIN and AlScN for Piezoelectric Applications, J. Patdar, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; Bette, aixACCT systems GmbH, Aachen, Germany; P. Pschyk, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; R. Kessels, aixACCT systems GmbH, Aachen, Germany; Sebastian Sioi, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland.

Invited talk on ionized physical vapor deposition (PVD) techniques, such as High Power Impulse Magnetron Sputtering (HiPIMS), offer unique opportunities to control the microstructure of thin film materials by accelerating ions onto the growing film using substrate-bias potentials. At moderate acceleration potentials, the increase in ad-attracting mobility often leads to improved crystalline quality and texture. This, in turn, enables the deposition of high-quality thin films at low deposition temperatures. However, gas-ion incorporation can limit the feasibility of such synthesis approaches for defect-sensitive materials. In recent years, HiPIMS processes with a synchronized pulsed substrate bias have been developed with the goal to selectively manipulate the energy and angular distribution of the film-forming species, particularly the metal ions. These processes hold remarkable potential to significantly reduce the defect concentration and stress in HiPIMS-deposited films, potentially unlocking a host of new applications for the technique.

In this presentation, I will showcase our latest work on the development of reactive metal-ion synchronized HiPIMS processes for the growth of piezoelectric AIN and AlScN thin films. It will be shown how highly textured, c-axis oriented AIN and AlScN films can be grown using reactive metal-ion synchronized HiPIMS. Here, even unconventionally moderate substrate bias potentials of up to only -30 V already lead to significant improvements in the films’ properties. Most strikingly, the application of a substrate bias facilitates the deposition at oblique deposition angles and on structured substrates, while also significantly reducing the fraction of undesirable misoriented grains. A detailed characterization of the piezoelectric coefficients of the materials show values comparable to the current state-of-the-art. In addition, for AlScN in particular, the phase formation and stress state can be tailored by applying different biasing schemes and combinations of different sputter modes (i.e., HiPIMS or DCMS, or hybrid). Importantly, it will be shown that the applicability of these types of processes can be significantly extended, even on insulating substrate materials.

The goal of this presentation is to demonstrate the tremendous potential of synchronized HiPIMS processes for the deposition of defect-sensitive materials, especially in applications where tailoring microstructure and texture of the thin film materials is important.

2:40pm PP2-2-Tha-5 Plasma Dynamics of Individual HiPIMS Pulses Investigated by High-Frame-Rate Camera, Matijaz Panjan, Jozef Stefan Institute, Slovenia.

Plasma of high-power impulse magnetron sputtering (HiPIMS) discharges is not azimuthally homogeneous instead it is concentrated in dense angular regions called spikes [1]. These regions are oriented in periodic or quasi-periodic patterns, typically have triangular shape and rotate with velocities of several km/s. Spikes are also present in other types of magnetron discharges. They have been observed in DC magnetron sputtering [2] and RF magnetron sputtering discharges [3].

In this work, we studied the dynamics of HiPIMS plasma with microsecond time resolution using a high-frame-rate camera. The individual pulses were investigated for different Ar pressures (0.25-2 Pa) and peak currents (10-400 A). The experiments show three distinct stages in the plasma dynamics and self-organization with the kinetic energy and momentum transfer processes. The pulse onset and up to currents of 25-50 A the dynamics is similar to one observed in DCMS discharges. Spikes rotate in the +E×B direction with velocities from 4 km/s to 15 km/s and exhibit elongated triangular shape. The growth rate in discharge current strongly influences the spike velocity – spikes rotate faster for higher growth rates. This DCMS-like stage is followed by a chaotic
plasma reorganization with the formation of irregular patterns and complex spike propagation. As current increases above approximately 50 A, plasma starts to form regular patterns with triangular spike shape. During this stage, spikes rotate in the E-B direction with velocities from 6 km/s to 9 km/s. The spike velocity depends on the pressure but is practically independent of the discharge current. Spikes rotate faster at lower pressures than at higher pressures. Remarkably similar plasma evolution is observed for pulses with comparable discharge current waveforms.


3:00pm 4:00pm
PP2-2-THA-5 PowerFlex 500CG: A New HiPIMS Machine for Microtools Coating, Gerardo Corletto, VIA BENACO 88, Italy A new PVD platform for the deposition of ultra-smooth hard coatings on microtools is introduced: the PowerFlex 500CG. This PVD machine is based on HiPIMS technology and allows the reliable deposition of multiple industrial coatings (TiSiN-based, AlCrN-based or sputter taC) for demanding applications such as high precision machining of hardened steel (HRC60), TiAlV or Al-alloys. The current cutting applications require coatings with extremely high smoothness, durability, and thermal resistance as well as tailored stress and toughness. The performance of the PowerFlex 500CG machine will be described in this paper, including its new etching protocol allowing in-situ microtool edge preparation or a stable reactive sputtering process to improve deposition rate. Finally, a comparison with the industrial benchmark coatings for high precision machining is presented.

3:20pm 4:20pm
PP2-2-THA-7 Toward Decoupling the Effects of Kinetic and Potential Ion Energies: Ion Flux Dependence Structural Properties of Thin (V,Al)N Films Deposited by Pulsed Filtered Cathodic Arc, Yeliz Unutulmazsoy, D. Kalanov, X. Oh, Leibniz Institute of Surface Engineering (IOM), Germany; S. Karimi Aghda, Institution for Surface Engineering (IOM), Germany; J. Fischer, Imperial College of Science, Technology and Medicine, UK; Arutun P. Eliaisanian, Leibniz Institute of Surface Engineering, Germany. Multiply charged ions formed in pulsed filtered cathodic arc process carry significant kinetic and potential energy which contributes to the formation of dense, adherent and macroparticle-free thin films. While the impact of kinetic ion energy on thin film formation during energetic processes such as cathodic arc deposition is well explored, the effects of ion potential energy are less known. We aimed to decouple the contribution of ion kinetic and potential energy regarding the structural effects on the forming thin films. To reach this goal, different arc source configurations are utilized in the filtered cathodic arc experiment including biasing the plasma in relation to the grounded substrate and applying an external magnetic field at the source. Charge-state-resolved energy distribution functions of ions measured at the substrate positions revealed the differences in plasma properties between the arc source configurations, and applying external magnetic field is found to be the primary tool to increase the ratio of multiply charged ions. Thin films of metastable cubic (V,Al)N films are deposited using different electrical configurations and characterized in detail. The resulting thin films demonstrate the possibility to deposit crystalline films without substrate heating due to “atomic scale heating” stemming from the high flux of multiply charged ions, namely the ions carry significant kinetic and potential energy, in the case of an external magnetic field. However, additional complexity added by the high flux needs further research to distinguish the sole effects of ion flux and ion potential energy on the structure of a forming thin film.

4:30pm PowerFlex 500CG: A New HiPIMS Machine for Microtools Coating, Gerardo Corletto, MIS, Brenning, M. Raadu, J. Fischer, Leibniz Institute of Surface Engineering (IOM), Germany; S. Karimi Aghda, University of Iceland; J. Fischer, Linkoping University, Sweden; N. Breenning, M. Raadu, KTH Royal Institute of Technology, Sweden; D. Lundin, Linkoping University, Sweden; J. Gudmundsson, University of Iceland. The ionization region model (IRM) is applied to explore working gas rarefaction in high power impulse magnetron sputtering operated with graphite, aluminum, copper, titanium, zirconium, and tungsten targets. The various contributions to working gas rarefaction including electron impact ionization, kick-out by the sputtered species, and diffusion, are evaluated and compared for the different target materials, and over a range of discharge current densities. For all cases the working gas rarefaction is found to be significant, and to be caused by several processes. Their relative importance varies between different target materials. In the case of a graphite target, electron impact ionization (by both primary and secondary electrons) is the dominating contributor to the working gas rarefaction, with 65 – 69% contribution, while the sputter wind kick-out, has almost negligible influence. In the case of a copper and tungsten targets, the kick-out dominates. The main factor determining the relative contribution of the kick-out by the sputtered species to working gas rarefaction appears to be a multiplication of the mass of the target atom, the cohesive energy, which determines the most probable velocity with which the sputtered particles leave the target, and the self-sputter yield.

4:40pm 5:00pm
PP2-2-THA-11 Synthesis and Characterization TiAl2TaBN Coatings Obtained by High-power Impulse Magnetron Sputtering, J. Gonzalez Avila, L. Gonzalez Lozano, O. Piombo Tulcan, Jhan Iairo Olaya Florez, Departamento de Ingeniería Mecánica y Mecatrónica, Universidad Nacional de Colombia. TiAl2TaBN coatings were obtained by High-Power Impulse Magnetron Sputtering and deposited on superalloys and Ti alloy substrates. The effect of working pressure and bias voltage on hardness, corrosion and wear resistance was investigated and correlated with the microstructure of the samples. The microstructure, morphology and chemical composition of the coatings were analyzed by X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy. The sample porosity and corrosion resistance were studied by electrochemical methods. The mechanical properties were evaluated by means of nanoindentation, and the tribological properties was studied with pin-on-disk technique. The pulse power and current peak have been affected by working pressure which modified significantly the films properties. The relationship between growth conditions, microstructure, wear and corrosion resistance is presented and discussed in this work. Finally, the effect of substrate-coating system and the deposition parameters are highlighted in order to further enhance HiPIMS coatings properties.

4:40pm 5:40pm
PP2-2-THA-10 Tough Plasmonic Titanium Nitride Films Deposited by High Power Impulse Magnetron Sputtering, F. Muir, Sheffield Hallam University, UK; R. Bower, P. Petrov, Imperial College of Science, Technology and Medicine, UK. TiN is one of the most plasmonically active and environmentally robust materials with photocatalytic function. However thin films suffer from high optical losses due to a high uptake of C and O impurities at grain boundaries. Densification of the microstructure through High Power Impulse Magnetron Sputtering (HiPIMS) deposition improves the optical properties, however the influence of plasma chemistry is not known. This study utilises constant-current HiPIMS as a technology to achieve high pulse-to-pulse reproducibility and overall operational stability in the discharge in a wide operating window. Time-resolved optical emission spectroscopy reveals a gas-rich ignition phase with duration of 30 μs which develops into a metal-rich phase where the metal component is continuously pumped over 70 μs while the plasma density remains constant. A steady metal-dominated state is reached for pulse durations above 100 μs. Films deposited during the ignition stage were markedly different than those deposited when the discharge develops into the “pumping” and “steady state” regimes, for a constant peak and average power. Differences are observed in the crystallographic texture shifting from a strong (111) to a stronger (200) component confirmed by XRD pole figures, and Hν/Ei,2 ratio (toughness) increasing dramatically from 0.2 to 0.3 GPa for a nano-hardness increase from Hν = 33 to 34 GPa. The changes are correlated with the grain morphology observed by AFM. All films were deposited without heating or substrate bias and exhibited excellent plasmonic properties with a single wavelength of electric permittivity near zero and low optical losses represented by the imaginary component of the electric permittivity as determined from modelling of ellipsometry data. The antimicrobial properties of the films will be discussed.

4:40pm 5:40pm
PP2-2-THA-11 Synthesis and Characterization TiAl2TaBN Coatings Obtained by High-power Impulse Magnetron Sputtering, J. Gonzalez Avila, L. Gonzalez Lozano, O. Piombo Tulcan, Jhan Iairo Olaya Florez, Departamento de Ingeniería Mecánica y Mecatrónica, Universidad Nacional de Colombia. TiAl2TaBN coatings were obtained by High-Power Impulse Magnetron Sputtering and deposited on superalloys and Ti alloy substrates. The effect of working pressure and bias voltage on hardness, corrosion and wear resistance was investigated and correlated with the microstructure of the samples. The microstructure, morphology and chemical composition of the coatings were analyzed by X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy. The sample porosity and corrosion resistance were studied by electrochemical methods. The mechanical properties were evaluated by means of nanoindentation, and the tribological properties was studied with pin-on-disk technique. The pulse power and current peak have been affected by working pressure which modified significantly the films properties. The relationship between growth conditions, microstructure, wear and corrosion resistance is presented and discussed in this work. Finally, the effect of substrate-coating system and the deposition parameters are highlighted in order to further enhance HiPIMS coatings properties.
Topical Symposium on Sustainable Surface Engineering
Room Town & Country D - Session TS4-2-ThA
Coatings and Surfaces for Thermoelectric Energy Conversion and (Photo)electrocatalysis II

Modерators: Clio Azina, RWTH Aachen University, Germany, Carlos Tavares, University of Minho, Portugal

Thursday Afternoon, May 23, 2024

1:40pm TS4-2-ThA-2 Multifunctional Materials for Emerging Technologies, Federico Rosel, University of Trieste, Italy

This presentation focuses on structure property/relationships in advanced materials, emphasizing multifunctional systems that exhibit multiple functionalities. Such systems are then used as building blocks for the fabrication of various emerging technologies. In particular, nanstructured materials synthesized via the bottom-up approach present an opportunity for future generation low cost manufacturing of devices. [1] We focus in particular on recent developments in solar technologies that aim to address the energy challenge, including third generation photovoltaics, solar hydrogen production, luminescent solar concentrators and other optoelectronic devices. [2-40]

References

2:20pm TS4-2-ThA-4 Enhanced Photoelectrochemical Water Splitting on ZnCoOx Electrodes in Chloroplasts Driven by Spin Injection, Chien-Yu Lin, Yu Su, National Cheng Kung University (NCKU), Taiwan

This work demonstrated the photoelectrochemical water splitting efficiency of spin-structured ZnCoOx on carbon paper substrate as photoelectrode and also coating on chloroplasts. ZnCoOx is p-type transition metal oxide semiconductor and could be synthesized by hydrothermal method and different annealing temperature, showing nanoparticles in morphology. Furthermore, we extracted the chloroplasts from chlorella to make it coat on ZnCoOx electrodes as protection layer, which also could be boosting the photosynthesis reaction when the water splitting process goes on. We observed the applied bias photon-to-current efficiency (ABPE) by changing spin quantum states, and the chloroplasts photoelectrochemical water splitting cell shows a splendid efficiency of hydrogen production. Accordingly, the device can be successfully applied on energy storage and solar applications, suggesting the great potential of the applications in electronic, catalysis, and solar applications.

2:40pm TS4-2-ThA-5 Piezoelectricity-Assisted Photocatalyst of BiOBr-Based Composites on a Flexible Substrate, Thi Ngoc Huan Nguyen, K. Chang, National Cheng Kung University (NCKU), Taiwan

A novel 3D network of BiOBr flakes was grown on carbon fiber (CF) substrates through a straightforward chemical deposition process. The BiOBr-based composites served as catalysts for photodegradation and as photoelectrodes for photoelectrochemical cells. The p-n junction formation was determined by Mott–Schottky measurements and was also confirmed through high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. The piezoelectric properties of BiOBr were verified using piezoresponse force microscopy. The photoelectrochemical performance of samples was assessed through various techniques, including linear sweep voltammetry, chronoamperometry

[https://www.sciencedirect.com/topics/chemistry/chronoamperometry], amperometry and cyclic voltammetry. Under simultaneous illumination and mechanical pressure, the Ag2O/BiOBr composite demonstrated a photocurrent of approximately 20.0 mA cm−2 at 1.23V, showcasing a remarkable enhancement over 4 and 20 times compared to individual BiOBr and Ag2O, respectively. The maximum applied bias photon to current efficiency values of Ag2O/BiOBr composite with external stress was approximately 2.7 % at 0.9V. Additionally, a glucose sensor based on Ag2O/BiOBr composite exhibited a high sensitivity of 400 µA cm−2 mm−1, within a detection glucose range of 0.1–12 mM. The Ag2O/BiOBr-based photoelectrodes showed excellent stability and repeatability in glucose detection. Furthermore, the CuS/BiOBr composite displayed outstanding performance in TC degradation. The effectiveness of the BiOBr composites was attributed to the p-n junction formation, piezoelectric potentials, substantial active surface area and advantageous band positions.

3:00pm TS4-2-ThA-6 Hydrothermal Synthesis of (Ba,Sr)TiO3/AgBr Films and Their Application for the Visible-light Piezo-photocatalysis, Yen-Lun Chiu, K. Chang, S. Han, National Cheng Kung University (NCKU), Taiwan

Perovskite-nanostructured films are attractive because of their excellent characteristics. Different kinds of properties can be obtained, e.g., dielectric properties, piezoelectricity, and thermoelectricity, from different materials. With the hydrothermal fabrication, the perovskite materials can be synthesized in a facile way with lower power consumption. However, studies on this topic directly through hydrothermal processes for the fabrication of perovskite-nanostructured films are still lacking. In this study, well-aligned (Ba,Sr)TiO3 nanorod arrays composites with p-AgBr were synthesized through the hydrothermal method and coated on visible light piezoelectric photocatalytic application. The hydrothermal parameters, including concentrations of precursor solutions, reaction time, temperatures, different types of ion species, and the surfactants used for the reaction, were manipulated. X-ray diffraction and transmission electron microscopy were employed to determine the phase and microstructure of the resultant samples. The amplitude of the piezoresponse (δι) was measured through a piezoresponse force microscope for the materials. The photoelectrochemical activity of the samples was also studied for related applications. An energy band diagram was constructed to elucidate a potential mechanism for the remarkable activity.

Keywords: perovskite-nanostructured films, hydrothermal, (Ba,Sr)TiO3 nanorod arrays, p-AgBr, piezo-photocatalysis

3:20pm TS4-2-ThA-7 Advances in Piezo-Photothermal Effect Enhanced Photocatalytic Activities of Heterostructure Composites, Van Ty Tran, D. Chen, National Cheng Kung University (NCKU), Taiwan

This study focuses on developing heterostructure energy converters to enhance the efficiency of piezoelectric and photothermal-assisted photocatalytic processes for pollutant degradation and photocatalytic water splitting. The Ag2O/BiFeO3 and CuS/MoS2 composites were fabricated through a hydrothermal method. The morphologies and microstructures of the samples are analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy. The composites exhibit a low band gap, indicating their capacity to absorb light in the Vis-NIR range. The conductive type of the samples and p-n junction formation is determined through Mott Schottky (M-S) measurements. The formation of a p-n junction facilitates the separation of electron-hole pairs, thereby improving the efficiency of the photocatalyst. Additionally, the induced piezoelectric potential in the piezoelectric material promotes photocatalytic activity by reducing the recombination of photogenerated charges. Under irradiation, the generated heat further supplies kinetic energy to photogenerated carriers, enhancing reaction rates in photocatalytic processes. The piezoelectric composite demonstrates the ability to produce O2, •OH, and h+ through photocatalysis, effectively degrading pollutants like tetracycline (TC) and Rhodamine B (Rb B) through oxidation. The degradation efficiency of the TC solution was further increased to 95% for CuS/MoS2 composite in 30 min, which was higher than that of individual components. Moreover, The Ag2O/BiFeO3 heterostructure exhibited excellent photocatalytic degradation of Rhodamine B and TC, and photocatalytic water splitting activity.

4:00pm TS4-2-ThA-9 Photoelectrochemical Properties of Chlorophyll Coating on CuO Photocatalyst by Mediating Charge Transfer Characteristic, Yu-Teng Wu, Y. Su, National Cheng Kung University (NCKU), Taiwan

Metal oxide semiconductors have impressive applications in the field of photo electrochemistry. This study utilizes electrochemical deposition to generate nano-thin films of cuprous oxide, applying them in green energy sources. During the photoelectrochemical (PEC) process, cuprous oxide

[https://www.sciencedirect.com/topics/chemistry/chronoamperometry]
faces issues of instability and insufficient durability due to photo-induced corrosion in aqueous solutions. To address this, the natural photosensitizing material chlorophyll is adhered to enhance charge transfer efficiency and provide a better surface electric field distribution. Additionally, the chlorophyll layer effectively isolates the aqueous solution from direct contact with cuprous oxide, enhancing sample stability. Detailed research results, including atomic force microscopy (AFM) and electrostatic force microscopy (EFM) surface electric field analyses, along with electrochemical methods, confirm that Chlorophyll/Cu2O exhibits superior stability and durability, enhancing the overall value of this PEC cell.

4:20pm TS4-2-ThA-10 Ligand Modified Bimetallic Metal-Organic Frameworks Electro catalysts for Urea Oxidation Reaction, Hui Chuan Chen, National Cheng Kung University (NCKU), Taiwan; T. Nguyen, National Cheng Kung University (NCKU), Taiwan, Viet Nam; J. Ting, National Cheng Kung University (NCKU), Taiwan

In the quest for energy efficiency, electrocatalytic urea oxidation reaction (UOR) is a promising alternative to oxygen evolution reaction (OER) due to the favorable thermodynamics, meanwhile, it is also an environmentally friendly strategy.

In this regard, metal-organic framework (MOF) materials have the advantages of high specific surface area, high porosity, structural adjustability, etc., providing abundant metal active sites to achieve high efficiency electrocatalytic performance. However, due to the poor conductivity of MOF, the charge transfer ability is limited. In order to improve the shortcoming, ligand having redox activity is introduced. This ligand can not only adjust the synergistic effect of metal clusters and organic ligands to increase the charge transfer ability, but also can be an additional adsorption sites to promote the adsorption/desorption ability of intermediates. In this study, we report ligand modified bimetallic MOF synthesized via a low temperature hydrothermal method, this optimized bimetallic MOFs exhibits an outstanding UOR performance with high catalytic activity, low resistance and excellent electrochemical stability.

Keywords: MOFs, urea oxidation reaction (UOR), electrocatalyst
Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Golden State Ballroom - Session CM-ThP

Thursday Afternoon, May 23, 2024

**CM-ThP-1 Localized Surface Plasmon Resonance of Silver Nanoparticle Thin Films on Moissanite: Simulation, Fabrication, and Characterization**, Tsung-Jen Wu, S. Song, W. Chen, National Taiwan University, Taiwan; W. Lin, National Taiwan University of Science and Technology, Taiwan; M. Phan, National Taiwan University, Taiwan; S. Tseng, National Synchrotron Radiation Research Center, Taiwan

**Abstract**

The fabrication and characterization of silver nanoparticle (Ag NPs) thin films on a moissanite (silicon carbide) substrate and their inherent localized surface plasmon resonance (LSPR) properties were investigated in this study. The preliminary phase of this investigation employed Finite-Difference Time-Domain (FDTD) simulations to anticipate the LSPR effects and the resultant hue of the films. The size of the silver nanoparticles was maintained within a range of 10-25 nm, producing a greenish yellow hue attributed to the LSPR effect.

Two methods were harnessed to produce these size-specific Ag NP films. The first approach involved a dual-target co-sputtering technique utilizing silver and silicon dioxide. It prompted the spontaneous formation of Ag NPs, leading to a visible coloration due to the LSPR effect. The other method involved a single-target sputtering of silver, followed by an annealing process to foster the emergence of Ag NPs, yielding a characteristic color induced by the LSPR effect.

**CM-ThP-2 Greybox-Models to Describe the Wear Behavior of Coated Cutting Tools**, K. Bobzin, C. Kalscheuer, Nina Stachowski, Surface Engineering Institute (IOT) - RWTH Aachen University, Germany

The real application behavior of coated carbide tools can neither be satisfactorily measured, nor described within existing models with the current state of research. The wear development, beginning tool failure as well as the remaining tool life cannot be accurately identified or predicted. This inhibits the knowledge-based qualification of coated tools for more efficient cutting processes. In the current state of research, the tribological system of machining must be evaluated and repeatedly analyzed for every small change in the cutting condition. This is despite the fact that both involved disciplines of production and material engineering have already detailed whitebox models. However, not all available data from both disciplines can be integrated into these models. The main objective is therefore to combine the existing whitebox models with new data driven blackbox models in greybox models. These new greybox models are used to determine the temporal changes of the tools in use, which cannot be described in purely deterministic terms, right up to the end of their service life. Further developments in machining, material and coating technology enable the evolution of new methods for analyzing and simulating the wear behavior of coated cutting tools. This includes the investigation of time- and temperature-dependent coating properties such as indentation modulus, indentation hardness, thermal diffusivity and surface roughness with increasing cutting time. Such changes have not been considered in simulation models up to now. However, by taking such data into account, the description of the wear behavior can be probably significantly more accurate. Another key factor within the SPP 2402 is the data storage as well as the comparison of measurement methods. This enables a better estimation of quality within all participating consocial projects. The final greybox models allow the description of the time-dependent changes in the material properties and the stress collective during machining.

**CM-ThP-3 Flow Curve Determination of TiAlSiN Coatings Using Nanoinindentation and Iterative FEM Simulations**, K. Bobzin, Christian Kalscheuer, X. Liu, Surface Engineering Institute - RWTH Aachen University, Germany

Physical vapor deposition (PVD) coatings are extensively employed to improve the service life of tools under high thermomechanical load in forming processes. The wear resistance of coatings is highly related to their mechanical properties, especially elastic and plastic properties that can be delineated by the flow curve. Consequently, the accurate determination of the flow curve holds paramount significance in the coating development process. While the elastic modulus can be easily measured using nanoindentation, other flow curve parameters are difficult to determine. The current analytical Juliano approach for determining the yield stress lacks precision and becomes challenging to use when the Juliano signal is not obvious, particularly evident in the investigated TiAlSiN coatings that exhibit minimal plastic behavior. Therefore, an easier and more precise flow curve determination method is required. In this study, flow curves of TiAlSiN coatings are determined combining nanoindentation and iterative finite element simulations (FEM). Initially, nanoindentation using a spherical indenter is performed accompanied by the measurement of time-load and time-displacement curves. Then the nanoindentation is simulated time-dissolved using FEM based on the load at each time step directly derived from the time-load curve. The flow curve parameters in FEM including the Young’s Modulus E, yield stress $\sigma_y$, strain hardening coefficient $B$ and strain hardening exponent n are iteratively adjusted by comparing the experimental and simulated time-displacement curves until a good match between two curves. Consequently, the flow curve can be obtained from the FEM model with the best match. The simulated time-displacement curves with physically reasonable flow curve parameters have a good agreement to the experimental time-displacement curves of various TiAlSiN coatings. The method uses FEM simulations to determine all flow curve parameters without measuring the Young’s Modulus using nanoindentation and determining the yield stress using the Juliano approach.

**CM-ThP-4 Material Property Distributions of Sputter-Deposited Thin Films on a Two-Dimensional Diagram with Incident Particle Energy and Substrate Temperature**, Ichiro Ikeda, K. Kuroshima, Osaka Vacuum, Ltd., Japan; Y. Gotoh, Department of Electronic Science and Engineering, Kyoto University, Japan; M. Iguchi, S. Sugimoto, Osaka Vacuum, Ltd., Japan

Recently, we have confirmed that Anders’ structure zone model (SZD)[1] is applicable to the case of conventional magnetron sputtering[2-3]. The SZD shows the difference of the film structure on a two dimensional diagram with the normalized incident particle energy and normalized substrate temperature. Based on the fact that the properties of the films depend upon the film structure, we assumed that the distribution of mechanical or electrical property is also well expressed on this two-dimensional diagram. We named the diagram the material property diagram (MPD)[4].

In this study, we attempted to make MPDs of electrical conductivity and optical reflectancedistribution of Ti films. Titanium thin films were deposited under various deposition conditions. The deposition conditions were translated to the particle energy incident on a film surface using the computer simulation[2-3] to identify the deposition condition on MPD. From the accumulated data, we drew contour lines for each film property. As a result, it was confirmed that contour lines for electrical conductivity were arranged in parallel to ZONE border on SZD. The electrical conductivity is well explained by the SZD, reflecting the fact that film structure. On the other hand, the contour lines for the optical reflectance were not arranged in parallel to the ZONE border of the SZD. The optical reflectance has relationship different from the film structure. The film property will be well expressed on the MPD, and the diagram differs depending on the material and property itself. About the film property distribution, we confirmed little difference between equipments.

We made the simulation program calculating the sputtering condition from the requested film property value (ex. the conductivity) using the MPD on the assumption that the MPD does not depend on the sputtering condition and the equipment. We may be able to take out the experience, the intuition or the test sputtering by the use of this program.

**References**


Successful heteroepitaxial film growth enables the integration of heterogeneous films despite lattice mismatches. Exceptional heteroepitaxial films alleviate lattice mismatch stress and diminish material defect density, resulting in smoother surfaces and reduced deposition time for subsequent thin-film epitaxial growth. This study introduces a materials genome approach to predict heterostructures. Employing this novel method, we explore new thin-film heterostructures on flexible muscovite mica substrates. As flexible electronic devices rapidly advance, traditional epitaxial substrates are being supplanted by flexible alternatives, yielding substantial economic benefits. While polymers are commonly used for such devices, they suffer from poor thermal stability, low solvent resistance, and a low thermal expansion coefficient. Layered muscovite mica materials have emerged as a promising solution. Muscovite mica, with its two-dimensional layered structure, can be easily divided into flakes, offering mechanical flexibility, optical transparency, and high thermal stability. We have successfully developed a novel artificial intelligence-generated heterostructure for studying the GaN(001)/Muscovite(001) heterostructure. Our findings reveal that the GaN thin film, characterized by the gene T1, epitaxially grows on muscovite substrate models characterized by gene arrangements S1 and S3. The heterojunction demonstrates the potential to form 12 Ga-O bonds, with a calculated lowest interface energy of $\sim$1.21 eV/$\AA^2$.


For the in-line absolute thickness analysis of FeZn layers on galvanized steel we developed a Rietveld [1] based, full-pattern fitting method that fits a general layered structural model to a measured XRD Scan. The fitted model then delivers both the absolute layer thicknesses as well as the chemical composition of the layers and other key information like unit cell sizes, size/strain, and texture related information for all phases of the model. The method is implemented in the Malvern Panalytical software package HighScore Plus [2] V5.2.

The layer thickness modelling is based on the variable and increasing absorption of x-rays in the layers with different chemistry and thickness. Basically, by integrating over all beam paths, we accumulate the reduction in intensity of the total beam. Each layer adds a new absorption term with its own linear absorption coefficient. The method is theoretically correct, still in practice we need to know the packing factor and density of each layer. To solve that, we introduced an instrument dependent (alignment, tube aging etc) calibration factor for each layer. These calibration factors are determined from a dedicated data set, where many samples are characterized using multiple methods like SEM, wet analysis etc. In this presentation we show some data and analysis of about one year of continuous online analysis. The initial fit model comprises:

- Initial/expected thickness values, for all the phases
- Calibration factors for all phases determined based on analyzed knowns
- Intensity calibration factor to counteract tube aging
- Atomic phase models, typically taken from structural databases

Output after fit:

- Absolute thickness for all as layer marked phases
- Known model parameters, like unit cells, size/strain information, texture index and more
- Quality of fit indicators, Chi-Square, $R_{wq}$ etc.

CM-ThP-7 Transfer Learning in Characterization of Nanoindentation Induced Acoustic Signatures, Jurgis Daugela, Johs Hopkins University, USA; M. Daugela, A. Daugelo, Nanometronix LLC, USA

A passive monitoring of acoustic waves during nanoindentation has been attracting the attention of material scientists since the inception of nanomechanical test instruments. The conventional acoustic wave signal treatment via RMS or integrated energy values proved that quantitative acoustic wave properties correlate well with the local contact materials' phenomena such as yield point initiation for W(100) [1, 2], Sapphire [3], phase transformations on SMA, and differentiating of thin film fracture modes. A nanofatigue phenomenon can be observed on thin films by monitoring the resulting multiphase nanoindentation loading-unloading curves and post test imaging helps in identifying materials' phenomena [4]. However, the true potential of the acoustic characterization method is unleashed in a synergy of joint time-frequency domain signal decomposition and machine learning [5].

The Transfer Learning is a subclass of machine learning which utilizes existing Deep Learning Neural Networks [5]. In this work, a Transfer Learning based signal classification of nanoindentation induced passive and active acoustic events is explored. Both passive and active acoustic monitoring can be conducted during nanoindentation with the integrated ultrasonic tip. The proposed Transfer Learning technique yields a reliable classification of acoustic signatures on submicron thick coatings during nanoindentation.

References:


CM-ThP-8 In-Situ Characterization of the Crystallization Kinetics of Sputtered TiO$_2$ Thin Films, Daniel Felix Fernandez, Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden; J. Hernández, Madrid Institute for Advanced Studies in Nanoscience (IMDEA Nanoscience), Ciudad Universitaria de Cantoblanco, C/ Faraday 9, 28049 Madrid, Spain; J. Martinez, ALBA Synchrotron, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallés, Barcelona, Spain; T. Kubart, Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden, Spain

Crystalline TiO$_2$ thin films are attractive owing to their photocatalytic, electronic, and optical properties. Anatase is the lower-temperature metastable phase of this material system and is the desired phase in many applications. While the phase formation can be controlled by both the deposition and post-deposition annealing temperatures, it is often desirable to reduce the overall thermal budget. For the large majority of cases, the employed temperatures for the crystallization of such films are considerably high, making it incompatible with heat-sensitive substrates.

In this study, the crystallization kinetics of TiO$_2$ thin films during post-deposition annealing is investigated. These were grown by reactive magnetron sputtering at different temperatures and the kinetics assessed by in-situ Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS), with synchrotron radiation. The films were heated for 2 hours and, using an adapted Avrami model for phase change kinetics, the crystallization times were compared for three annealing temperatures: 225, 250 and 300°C. The growth conditions achieved in pulsed-DC (pdcMS) and High Power Impulse Magnetron Sputtering (HiPIMS) were investigated. For both techniques, the influence of the mode of reactive operation, the ionization of the sputtered flux and the deposition temperatures were studied.

All studied films were X-ray amorphous in their as-deposited state. However, the deposition conditions have a significant impact on the transformation kinetics. The results show that the deposition temperature is the single most influential parameter. While the reactive mode of operation also affected the transformation dynamics, HiPIMS was found to facilitate the crystallization compared to pdcMS films, and generally promoted faster formation of the anatase phase. Additionally, from the GIWAXS experiments, a set of optimal growth conditions are identified for ex-situ post-deposition annealing. The optimized conditions were investigated for a 2 hour period at 250°C. In all cases, anatase was achieved. Depending on the growth conditions, specific anatase planes were favored, as seen in GIXRD measurements.
Surface Engineering - Applied Research and Industrial Applications
Room Golden State Ballroom - Session IA-ThP
Surface Engineering - Applied Research and Industrial Applications (Symposium IA) Poster Session

IA-ThP-1 Application and Practice of Surface Aluminization Treatment in Zinc Pot Equipment of Hot Dip Galvanizing Production Line, Lu wang, BAOSTEEL, China

hot dip galvanizing is a process of coating the surface of a steel strip with a zinc layer to prevent corrosion. This process is widely used in industries such as automobiles, home appliances, and construction. During the hot dip galvanizing process, various components on the galvanizing line are immersed in the high-temperature molten zinc liquid in the zinc pot, which has a certain degree of corrosiveness and can cause corrosion to components such as sink rolls, stabilizing rolls, zinc pumps, and snout. In the continuous hot dip galvanizing process of strip steel, due to the corrosiveness of the high-temperature molten zinc liquid in the zinc pot, the service life of some components in the galvanizing equipment is concise, with an average service life of only 12-15 days. This seriously restricts the production efficiency of continuous hot dip galvanizing, increases economic costs, and also affects product quality. Parts in direct contact with high-temperature molten zinc on the galvanizing line are required to resist zinc corrosion and thermal shock.

The use of thermal spraying technology for surface coating treatment of components in zinc pots can have a certain anti-corrosion effect, but it cannot be widely used due to its high cost. This article introduces an aluminizing technology that involves placing components in a molten aluminum pot for hot dip aluminum pot, and then diffusing at a temperature of 800-950 °C to transform all the aluminum plating layers on the hot-dip aluminum surface into aluminum iron compound layers, forming a diffusion type aluminizing layer. This thin film can effectively prevent the corrosion of zinc solution on components and also inhibit the formation of zinc dross on the surface of components. Through experiments, we found that after muffle furnace annealing, a uniform and dense Al2O3 film is formed on the surface of aluminized stainless steel. Aluminum oxide has unique properties that metal and organic polymer materials do not have. Aluminum oxide films have excellent wear resistance, corrosion resistance, heat resistance, high-temperature oxidation resistance, insulation, and other properties. The Al2O3 film isolates the steel substrate from the zinc liquid, preventing mutual diffusion and reaction between Fe and Zn atoms. The Al2O3 film serves as an isolation layer, which can prevent corrosion of the steel substrate by zinc liquid. The cost of this surface aluminizing treatment is much lower than that of thermal spraying, which not only prolongs the service life of the components but also significantly reduces maintenance costs.

IA-ThP-2 Effect of Phase Separation in the Anticorrosion Performance of AlCrFeNi High-Entropy Alloy, Chih-Chen Lee, I. Tasl, National Yang-Ming Chiao Tung University, Taiwan; H. Chen, Michigan State University, Taiwan; C. Chen, National United University, Taiwan; S. Chen, National Yang-Ming Chiao Tung University, Taiwan

Due to reaching net-zero emissions, offshore wind power is one of the methods to get clean energy. To improve the anti-corrosion performance of wind turbine towers, researchers are always seeking the candidates to enhance or replace the stainless steel 316 base material. In our study, we found that AlCrFeNi HEA exhibited a better anticorrosion performance than SS 316 in both the salt spray and acid immersion test. Especially, its corrosion resistance could be significantly improved by controlling the phase ratio. Gas-atomized HEAs can retain the ideal high-entropy state owing to the sluggish effect and rapid cooling process. The as-atomized AlCrFeNi powders presented a superior resistance to acid solutions, but weakened after experiencing high temperature environment. Through careful investigations, it was found that Al and Ni elements have the lowest mixing enthalpy, promoting the preferential formation of AlNi phase from the uniformly distributed matrix. As a result, ordered AlNi and FeCr phases are formed within the BCC structure. It has a chemical composition closely matching the designated component ratios, composed of a BCC/2 phase composed of AlNi and a BCC/A2 phase composed of FeCr. From the acid immersion test, we found that the rich AlNi phases were preferentially corroded, decreasing corrosion resistance. Furthermore, argon gas was commonly used to atomize the melt and has a lower specific heat capacity, which allows sufficient time for melted droplets to form spherical shapes with better flowability due to cohesive forces. The AlCrFeNi HEA powder produced by gas atomization exhibits a good anti-corrosion performance because it maintains the initial high randomness phase and prevents the segregation of elements. It also shows a spherical shape and excellent flowability, making it suitable for coating applications in harsh environment.

Keywords: High-entropy alloys, Gas atomization, AlCrFeNi, Annealing, Phase transition, anti-corrosion performance

IA-ThP-3 The Behavior of Surface-Activated Fine Particles with Variation of Acoustic Field, Hyo-Soо Lee, Gaetbeol-ro 156, Republic of Korea; K. Kim, T. Choi, Sejong University, Republic of Korea; J. Lee, Kongju National University, Republic of Korea

In recent times, the presence of nano-particles in media such as air and water has become a major concern due to environmental pollution. Traditional methods like physical filtering or electromagnetic charging have not been sufficient to solve this problem. To address this issue, a new technology has been investigated which involves the use of acoustic fields to move, collide, and agglomerate the nanoparticles present in the media. The acoustic fields were created using frequencies ranging from 20Hz to 20kHz and sound pressures ranging from 0 to 100dB. The density of the media was varied with specific acoustic fields, and the agglomeration of nanoparticles was observed. This new approach has shown promise in reducing the levels of nanoparticles in polluted media. It is worth noting that the technology's effectiveness in agglomerating nanoparticles depends on various factors such as the size and shape of the particles, the density of the media, and the specific acoustic fields used. Therefore, further research is needed to determine the optimal conditions for different types of nanoparticles.

IA-ThP-4 Protective Layer Formation of Magnesium Fluoride Resistant to Fluorine Plasma on AI Alloys, younseon wang, j. nam, Y. Kim, H. Choi, Samsung Electronics, Republic of Korea

Recently, chemical vapor deposition (CVD) processes for a semiconductor manufacturing require a high temperature condition to improve mechanical properties of the deposited thin films. After the deposition steps, the clean process is required to remove by-products in the processing chamber with NF3 plasma. Considering the efficiency in the use of the processing chamber, the temperature in the clean process also keeps as high as that in the deposition steps. However, the fluorination of the aluminum components in the chamber is accelerated at a higher temperature via NF3 clean process. A showerhead, one of important parts to control the processing condition, is covered with the AlFx, resulting in several changes in the hole sizes, the surface emissivity, the radio frequency impedance, and the gas flow under the processing condition. As repeating CVD and NF3 clean processes, it is difficult to maintain the same characteristics of the deposited film. Not only the change in the chamber condition, but the fluorination of the particles also causes the contamination issues in devices. Herein, we developed the surface treatment for the formation of a protective layer on Al-Mg alloys from fluorine radicals at high temperature. We investigated the fluorinated layers on four Al alloys with different chemical elements via the NF3 clean process at 520 °C. It was found that the impurity of Mg dissolved in Al alloys was segregated up to the surface, and then formed the MgF2 layer as the protective layer. The Al alloys with especially higher content of Mg element showed the dense and uniform MgF2 layers which efficiently suppress further fluorination of the underlying Al alloys. The characteristics of magnesium fluoride were analyzed by XPS, XRD, TEM, and EDS. Therefore, we suggest the MgF2 layer on Al alloys as a promising protective material to maintain the surface condition of the Al parts in plasma processing chambers under harsher F plasma condition for next-generation devices.

IA-ThP-5 Bismuth Thin Film Electrodes, B. Fantana-Uribé, V. Ugolde-Saldivar, A. Hernández-Gordillo, A. Vazquez, Universidad Nacional Autónoma de Mexico; Sandra E. Rodil, Universidad Nacional Autonoma de Mexico

Bismuth film electrodes (BiFE) for trace metal detection using electroanalytical techniques have been researched since 2000, after the demonstration that the BiFE could substitute mercury drop or mercury film electrodes, leading to a safer and eco-friendly solution. However, after more than 20 years of research, the BiFEs are not yet available for commercial use. In this work, bismuth-based thin films produced by magnetron sputtering have been tested for detecting trace metals and organic molecules of interest. Moreover, the stability of the Bismuth-based
electrodes in different non-aqueous solutions has been studied, aiming to use the electrodes for the electro synthesis of organic molecules. Pure bismuth, bismuth-tin, and bismuth-indium films were deposited on both smooth and rough glass substrates. These were used as the working electrodes in a three-electrode electrochemical cell, where different electroanalytical techniques were used to detect metal ions or organic molecules of interest, such as acetaldehyde. The same electrodes were also tested for the electro synthesis of organic molecules, which constitutes a sustainable method to produce high-value chemicals without using catalysts.

The results are summarized to present the potential use of bismuth-based electrodes produced by a physical vapor deposition technique for detecting cadmium, zinc, acetaldehyde, and insulin. The Bi-In electrode was tested to drive the cathodic reduction of benzophenone using Cyrene™/EEOH (1:1) as a green solvent mixture. Interestingly, the Bi-In electrode yielded a 56% of the pinacol compound. Such reaction can be used to prepare alcohols and diols from the electrochemical reduction of carbonyl compounds, such as aldehydes and ketones.

**IA-ThP-6 Fabrication of TiO₂ Nanotube/SiNW Arrays Structure at Different Synthesis Parameters for Solar Cell Application, Al-Huei Chiov, Z. Lin, National Formosa University, Taiwan**

Titanium dioxide is renowned for its non-toxicity, high chemical stability, and excellent photocatalytic activity, making it widely applicable in areas such as photocatalysis, photodegradation, and solar energy-related applications. Various methods, including hydrothermal synthesis, sol-gel techniques, and anodization, can be employed to obtain titanium dioxide nanostructures. Among these methods, anodization is favored by many researchers for its simplicity, cost-effectiveness, and ease of observation.

This study utilizes the anodization method to prepare a novel hybrid silicon nanowire array structure and explores its feasibility for application in solar cells. The research primarily focuses on the preparation of titanium dioxide nanotube structures, comparing the results of nanoscale structures with non-nanoscale structures in solar energy measurements.

Currently, most anodization methods used for preparing titanium dioxide nanotubes utilize platinum metal as the cathode, despite its better stability, it is expensive. The anode is typically made of pure titanium foil or sheet. In this study, a novel structure is proposed, involving the deposition of a seed layer on the anode silicon nanowire array, and using a pure titanium plate as the cathode for anodization. The study investigates structural changes under different experimental parameters.

The research employs a trial-and-error approach to sequentially adjust parameters such as electrolyte water content, current, voltage, and film thickness to confirm the conditions for subsequent anodization. An magnetron sputtering machine is used to deposit titanium on the silicon nanowire array, and finally, anodization is employed to prepare a divergent structure of titanium dioxide nanotubes.

SEM observations indicate that with appropriate water content, current, voltage, and film thickness, a complete pore morphology can be obtained. Raman analysis reveals TiO₂ lattice peaks under different growth times, confirming the prepared TiO₂ has a rutile structure. Additionally, UV-Vis analysis shows that when the substrate is non-nanoscale, the reflectance is approximately 80%, but when the substrate is a silicon nanowire, the reflectance decreases with increasing TiO₂ thickness. In terms of electrical properties and solar energy analysis, the TiO₂ nanotube/Si structure demonstrates a conductivity of 8.856 × 10⁻⁵ S/cm and a photovoltaic conversion efficiency of 2.31 × 10⁻², while the TiO₂ nanotube/SiNW Arrays Structure exhibits a similar conductivity of 8.856 × 10⁻⁵ S/cm and a higher photovoltaic conversion efficiency of 5.46 × 10⁻¹.

**Protective and High-temperature Coatings**

**Room Golden State Ballroom - Session MA-ThP**

**Protective and High-temperature Coatings (Symposium MA) Poster Session**

**MA-ThP-1 Predictive Modeling and Experimental Validation of Phase Formation in High-Entropy Alloys Thin Films, Salah-eddine Benazzoug, J. Ghanbaja, S. Migot, J. Pierson, V. Milichko, Institut Jean Lamour - Université de Lorraine, France**

High-entropy alloys (HEAs) introduce a new class of materials that challenge existing theories on phase stability due to their complex, multi-element composition. Initially theorized to gain stability from the significant entropy associated with mixing five or more elements, these alloys have garnered interest for their potential applications. However, the scientific community has yet to develop a robust model that can predict with certainty which element mixtures will form a single-phase alloy. In this investigation, we try some predictive model grounded in thermodynamics to forecast the phase behavior of high-entropy alloys (HEAs). By computationally analyzing the enthalpies of binary compounds, the model identifies combinations of elements likely to form single-phase alloys. This method has successfully pinpointed all previously known single-phase HEAs and excluded compositions that result in multiple phases. Moreover, we have experimentally validated numerous new single-phase alloy compositions proposed by our model.

Subsequently, this work employed X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) to characterize the structural and microstructural properties of the films, specifically the Cantor alloy (Cr₅MnFeCoNi) with additional elements like Pt, Cu, Ti, Zr, Al, and Ag. We found that the Cr₅MnFeCoNi base alloy, along with its Pt and Cu variants, retained a homogeneous FCC crystalline structure. In contrast, the Al-modified films underwent a phase transformation from FCC to a mixed FCC+HCP structure and eventually to a singular BCC phase. The Ti and Zr variants exhibited amorphous structures at certain concentrations, whereas the Ag-doped films presented a multiphase structure with silver precipitates embedded in the Cantor alloy matrix.

Our findings show that some alloys consistent alignment between the predicted phases through thermal analysis criteria and the actual observed phases, even when the synthesis conditions are far from equilibrium. This consistency suggests a significant role of underlying thermodynamic factors in determining the phase stability of HEAs thin films.

**MA-ThP-2 Study of ALD Nano-Oxide Films on Corrosion Protection of Al-SiC Composites, H. Chen, Hsin-Chih Lin, Y. Chen, P. Lin, K. Lin, National Taiwan University, Taiwan; J. Lin, Huang Chieh Metal Composite Material Technology Company, Taiwan**

In recent years, aluminum matrix composites (AMCs) have attracted attention due to their promising properties. However, the presence of ceramic particles in the aluminum matrix renders AMCs a high corrosion rate and makes it challenging to use traditional corrosion protection methods. In this study, atomic layer deposition (ALD) techniques are used to deposit HfO₂, ZrO₂, TiO₂, and Al₂O₃ thin films on AMC reinforced with 20 vol.% SiC particles. Our results indicate that the presence of micro-cracks between the Al matrix and SiC particles leads to severe micro-crack-induced corrosion in Al-SiC composites. The ALD-deposited films effectively enhance the corrosion resistance of these composites by mitigating this micro-crack-induced corrosion. Among these four atomic-layer deposited films, HfO₂ film exhibits the most effective reduction of corrosion current density of Al-SiC composites in a 3.5wt% NaCl solution from 1.27 × 10⁻³ A/cm² to 5.89 × 10⁻⁴ A/cm². The electrochemical impedance spectroscopy (EIS) investigation shows that HfO₂ deposited on Al-SiC composites has the largest Rₚ value of 2.0 × 10⁶Ω. The HfO₂ film on Al-SiC composites also exhibits effective inhibition of pitting corrosion, remaining at grade 10 even after 96 hours of salt-spray test.

**MA-ThP-3 Optimizing Temperature Stability in Non-Reactively Sputtered (Hf,Ta,Ti,V,Zr)B₂C-N Coatings by Design of the Non-Metal Sublattice, Andreas Kretschmer, A. Kirnbauer, TU Wien, Institute of Materials Science and Technology, Austria; R. Frost, D. Primetzhofer, Uppsala University, Sweden; H. Rojacz, E. Badisch, ACZT Research GmbH, Austria; M. Hans, J. Schneider, RWTH Aachen, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria**

In the past, we have studied the (Hf,Ta,Ti,V,Zr)B₂C-N coatings by design of the non-metal sublattice. To investigate the impact of C in this system, we have deposited new coatings with a Ti:N target, on which we placed diboride and/or carbide pieces of the materials Hf, Ta, V, and Zr. We have varied the composition by using either only borides, only carbides, or different mixtures of the two material types to make 5 coatings containing either N and B, N and C, or all three. The B concentration varies between 2 and 5 at%. X-ray diffraction (XRD) shows that when the substrate is non-nanoscale, the reflectance is approximately 80%, but when the substrate is a silicon nanowire, the reflectance decreases with increasing TiO₂ thickness. In terms of electrical properties and solar energy analysis, the TiO₂ nanotube/Si structure demonstrates a conductivity of 8.856 × 10⁻⁵ S/cm and a photovoltaic conversion efficiency of 2.31 × 10⁻², while the TiO₂ nanotube/SiNW Arrays Structure exhibits a similar conductivity of 8.856 × 10⁻⁵ S/cm and a higher photovoltaic conversion efficiency of 5.46 × 10⁻¹.
coatings, with especially fine grains in the B-richer coatings. Electron diffraction confirms that no secondary phases are present. We annealed the coatings in a vacuum furnace at 1000, 1200, and 1400 °C for 10 min, followed by XRD and nanoindentation. The coatings stay stable up to 1200 °C and start decomposing at 1400 °C. The as-deposited hardness of all coatings lies between 36 and 38 GPa, and is maintained after annealing at 1000 °C. After annealing at 1200 °C, the coatings containing only C or only B both soften to ~34 GPa, while the coatings with both C and B do not lose any hardness at this temperature. Only after annealing at 1400 °C does the hardness of all coatings drop below 30 GPa. The exceptional thermal stability of the solid solution was confirmed by atom probe tomography, which shows no onset of decomposition despite the high B content even after annealing at 1200 °C. Only after the 1400 °C annealing, a TiB phase is formed.

The structural and mechanical properties of the coatings were characterized by a broad variety of methods, such as scanning electron microscopy, X-ray diffraction analysis, and nanoindentation. The chemical composition was determined by inductively coupled plasma optical emission spectrometry and elastic recoil detection analysis. To verify the suggested enhancement on the brittle behavior of Ti,Mo-B coatings, and depict a major challenge. Alloying of Mo leads to an increase in Ti content and a decrease in B content for both DCMS and HiPIMS deposited coatings. In contrast, the Mo content is significantly lowered while using HiPIMS. All coatings exhibit a structured (SG191) Ti,Mo-B coatings. An increased hardness for both binary and ternary thin films, with a maximum value of 45 ± 1 GPa (TiMo) and a minimum 28 ± 0.8 GPa (~6 at.% Mo) can be obtained by using HiPIMS. Overall, this study highlights the influence of Mo additions on the structure-mechanical properties of TiMo, using different growth techniques.

In the present study, the accompanying experiments to the theoretical investigations have been conducted. Three different target compositions were used for the non-reactive growth of ternary Ti-Mo-B coatings. TiB,MoB 95/5 mol%, TiB,MoB 80/20 mol%, and TiB,MoB 80/20 mol%. The binary TiB, system was deposited with a TiC/C 99/1 wt.% target. In addition, direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HiPIMS), were employed in order to investigate the influence of different deposition techniques – hence ionization degrees.

MA-ThP-4 Unravelling Diffusion Processes and Morphology Changes of Ternary and Quaternary Diborides During High-Temperature Oxidation, Sophie Richter, A. Bahr, T. Glechner, T. Wojcik, Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; S. Kolozsvari, P. Polcik, Plansee Composite Materials GmbH, Germany; O. Hunold, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; D. Primetzhofer, Department of Physics and Astronomy, Uppsala University, Sweden; P. Feller, Department of Materials Science and Engineering, FAU Erlangen, Germany; H. Riedl, Institute of Materials Science and Technology, TU Wien, Austria.

Transition metal diborides (TMBs) are currently in the focus of diverse academic and industrial research studies, as they obtain a unique mix of properties. Here, especially their mechanical strength, chemical inertness, but also electrical conductivity is in focus [1]. However, the oxidation resistance is a weak point in binary TMBs and strongly limits a broad application. Therefore, to improve the oxidation resistance of transition metal diborides (TMBs) at high temperatures (T > 1000 °C), alloying approaches using silicon (Si) as a strong oxide-forming element have been successfully established [2,3]. However, both ternary (TM-Si-B) and quaternary (e.g., TM-Mo-Si-B) by alloying TMBs with Mo, we have shown pore formation due to phase transitions and diffusion processes during oxidation above 1100 °C. Over extended periods of time (t > 1000 h), these pores significantly weaken the protective function of these coatings and depict a major challenge. In this study, physical vapor deposited ternary and quaternary transition metal diborides are investigated to study the influence of different alloying elements on the pore formation. In more detail, the influence of additional elements such as Mo or Ta based on diliscide alloying to TMBs is in focus. High-resolution techniques such as transmission electron microscopy (TEM), elastic recoil detection analysis (ERDA), Rutherford backscattering spectrometry (RBS), and atom probe tomography (APT) are used to gain insights on the prevailing phase transformations, diffusion processes and hence pore formation. These results are correlated with mechanical analysis to assess the tolerance with respect to porosity.

MA-ThP-6 Investigation of Microstructure and Mechanical Properties of TiCrAlNiCu High Entropy Alloy Nitride Nanocomposite Coatings Deposited by DC Magnetron Sputtering, J. Shin, G. Kang, H. Park, S. Hong, T. Choi, Sejong University, Republic of Korea; J. Lee, Kongju National University, Republic of Korea; H. Lee, Korea Institute of Industrial Technology, Republic of Korea; Ki Buem Kim, Sejong University, Republic of Korea.

In this study, to overcome the limitation of brittleness, TiCrAlNiCu composition was developed to improve fracture toughness of transition metal nitride coatings. Based on Ti, Cr, and Al, known for as transition metal elements with negative bonding enthalpy with nitrogen(Nitride-forming elements), Ti, Cr, and Al, which have positive bonding enthalpy with nitrogen(Non-nitride-forming elements) were added to the composition to form a high hard phase of TiC, TiAlN, and AlN. The nanostructured composition was deposited using an alloy powder target and a mixed powder target, to find out the difference in microstructure and mechanical properties of nitride coatings according to the type of target powder.

In this study, reactive DC magnetron sputtering, one of the physical vapor deposition processes, was selected as deposition equipment, and substrate temperature and nitrogen partial pressure were used as process variables. Transmission-electron-microscope (TEM) and X-ray diffractometer (XRD) were used to analyze the crystal structure and phase of the coatings. TEM and Field-emission-scanning-electron-microscope (FE-SEM) were used to analyze the nanostructure and thickness. Energy dispersive x-ray spectroscopy (EDS) was used to analyze the chemical composition of the coatings, and X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical bonding state of the coatings. A nano-indentation test was used to measure the mechanical properties of the coatings.
Titanium diboride is widely known as a superhard material achieving an indentation hardness of 40 GPa and beyond. Coatings of TiB₂, produced by DC magnetron sputtering (DCS) and subsequently investigated by TEM, XRD and nanoindentation. Their fracture toughness values increase from 3.72 ± 14 GPa and their residual compressive stresses vary between 2 and 3 GPa. Their fracture toughness values – derived from cube corner indentation experiments – increase from 3.72 ± 0.46 to 5.15 ± 0.22 MPa√m with increasing substrate temperature. To gain information about the thermal stability of the coatings, they were vacuum annealed up to 1050 °C and subsequently investigated by TEM, XRD and nanoindentation.

Reactive deposition of such AlN coatings is studied in-depth, showing that especially for sputtering the resulting microstructure and consequently properties (next to deposition rate) hugely depend on the N₂ to partial pressure used. Alternatively, such nitrides can also be prepared non-reactively using nitride compound targets. Here, we use powder metallurgically prepared AlN compound targets to prepare coatings with pulsed DC magnetron sputtering with a 3° target and a 6° target.

The primary investigations focused on how the mechanical properties such as hardness and indentation modulus depend on various deposition conditions, such as sputtering power density, pulse frequency, substrate temperature, substrate-to-target distance and target-to-substrate distance. Additionally, several experiments were conducted by adding H₂ to Ar to study the effect of a reducing agent during the ion-etching of the substrate as well as during the deposition of the AlN film. To counteract understoichiometry, we added sometimes N₂ as well.

Detailed investigations by X-ray diffraction reveal that all coatings were single-phase hcp-structured, with various amounts of an amorphous phase and/or a metallic Al, depending on the deposition conditions. The highest hardness obtained for such films is 26.9 GPa. With the addition of H₂ to the working gas Ar, the discharge became more stable even for high power densities, allowing for a deposition rate of up to 1 µm/h.

MA-Thp-7 Impact of the B/Ti-ratio on Microstructure, Mechanical Properties, and Thermal Stability of DCMS and HIPIMS TiB₂ Thin Films, Ludwig Enzlbberger, TU Wien, Institute of Materials Science and Technology, Austria; M. Podaşnik, TU Wien, Austria; S. Kolozsvari, Plansee SE, Germany; A. Limbeck, TU Wien, Austria; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria


MA-Thp-9 Non-Reactive Magnetron Sputtering of AlN Coatings, Balint Hajos, A. Foki, T. Wojcik, TU Wien, Institute of Materials Science and Technology, Austria; D. Primetzhofer, Uppsala University, Angstrom Laboratory, Sweden; S. Kolozsvari, Plansee SE, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria


Superlattice structures offer a unique playground for simultaneous hardness and fracture toughness enhancements by tuning the layer thickness and volume ratio of the layer constituting materials. The superlattice effect has been widely studied within the cubic transition metal nitrides but nearly unexplored for hexagonal transition metal diborides (TMB). Here we focus on the nanolayered WBₓ/AlBₓ system, where already one of the chosen materials, AlBₓ, is nearly unreported despite its great potential for increasing the typically low oxidation resistance of TMB.

Aiming to combine exceptional mechanical properties and oxidation resistance, we develop WBₓ/AlBₓ superlattice thin films with different modulation periods (λ, 3-30 nm) and thickness ratios (η, WBₓ/AlBₓ=1, 2, 3). All superlattices reveal single-phase AlBₓ-type structure. With the template effect of the WBₓ layers, the AlBₓ layers are supported for their crystallization as single phase AlBₓ-type layers, even for deposition parameters which would otherwise result in a dual phase constitution of Al and AlBₓ. TEM investigations of selected samples reveal clearly coherent interfaces between WBₓ and AlBₓ layers. Nanindentation studies show that these WBₓ/AlBₓ superlattice films facilitate the superlattice effect for hardness, which we rationalize with the shear modulus mismatch and oxidation period. Among the WBₓ/AlBₓ superlattices studied here, the one with λ of 3 nm and η of 2 shows the highest hardness (33.1 GPa), compared to the 26.6 GPa calculated from rule of mixing. Isothermal oxidation experiments demonstrate significantly improved oxidation resistance of WBₓ/AlBₓ superlattices compared with WBₓ monolithic thin film.

MA-Thp-11 Effect of Preplaced Graphene and Graphite Films on Stellite 6 Metallurgical Coatings, J. Sippel, PG-MEC/ Universidade Federal do Paraná, Brazil; W. de Oliveira, Universidade Estadual de Ponta Grossa, Brazil; J. Ribeiro da Cruz Alves, Instituto Senai de Inovação – Sistema de manufatura e Processamento a laser, Brazil; Ana Sofia C. M. d’Oliveira, Universidade Federal do Paraná, Brazil

Protective coatings are a key player on a sustainable development of equipment with a longer and better service life. This goal motivates the search for better coatings by offering the opportunity to put together new materials and efficient processing techniques. Carbon-based compounds are materials widely studied for their unique properties which are distinct from others engineering materials due to a variety of atomic arrangement.
These materials exhibit excellent mechanical, thermal and tribological properties. An approach to use these materials is tailoring a metal matrix composite focusing on improved performance through the he distribution of carbon compounds in the matrix. This study is part of an ongoing project on the development of carbon-base compounds metallic matrix hardfacing coatings by Plasma Transferred Arc (PTA). PTA process is a hardfacing process that uses feedstock in the powder form that melts in a plasma arc column allowing for the customization of coatings. Although some reports coatings reinforced with carbon compounds materials were produced by powder metallurgy before deposition by PTA. This work assesses the impact of pre-deposited layers of graphene and graphite on Co based (Stellite 6) coatings processed by PTA, particularly at the interface with the substrate. Deposition was carried out on AISI 304L stainless steel, with and without predeposited films of graphite and graphene, with a surface Sq roughness of 1.4 μm for better anchoring of the preplaced micro/nanoparticles of graphite and graphene, respectively. The geometry at the cross section of single beads showed the dilution of coatings with modifying particles being higher than pure that of Stellite 6 coating. EDS analysis showed an increased presence of iron in the coating, explained by increased dilution. EBSD characterization revealed a larger heat affected zone in the substrate of graphene-modified coating, exhibiting smaller grains due to recrystallization, comparing with others processed coatings, suggesting that this material increases thermal transfer from the plasma arc to the substrate. The Vickers microhardness shows graphite improves hardness and graphene reduces it. Nanoscraping testing on the coatings near the fusion line revealed lower wear rate in the graphene-modified coating when compared to the Co-based coatings with and without graphite. The contributions of this research include: (1) advances on identifying viable techniques for processing graphite and graphene enriched coatings, (2) understanding the influence of graphene and graphite in Stellite 6 hardfacing coatings.

MA-Thp-12 Modified High Hardness Steel Coating for Biomass Combustion Boilers, Alina Agiero Bruna, Ctra. Ajalvir km 4, Spain; M. Gutierrez, S. Rodriguez, Instituto Nacional de Técnica Aeroespacial (INTA), Spain Biomass is a renewable, CO₂ neutral source of energy. However, the efficiency of biomass combustion plants is not as high as that currently obtained with fossil fuels. Biomass plants currently operate at a maximum temperature of 550 °C in order to reduce corrosion caused by the very aggressive species present in biomass combustion. In the European project BELENUS, new materials and coatings are being evaluated, aiming to increase the operating temperature to 600 °C and consequently the plant efficiency. Among the different coatings that are being studied, a high hardness steel modified with Al, applied by HVOF thermal spray has shown a very promising performance in the laboratory when exposed to a model biomass environment including KCl deposits, for 8000 h. Moreover, the coating has also been tested in pilot plants burning eucalyptus and wheat straw at 600° C for 2000 h and the results indicate high resistance to corrosion. Microstructure analysis of the tested samples by SEM, EDS and XRD, was performed in order to study the coating evolution in these environments as well as the protection and degradation mechanisms.

MA-Thp-13 Effect of Austenite Stability on Pack Aluminizing of Stainless Steels, Bryant Hernandez, C. Sullivan, L. Rodriguez, V. Ravi, California State Polytechnic University, Pomona, USA Austenitic stainless steels are extensively used in a range of engineering applications. When high temperatures are involved, oxidation is an issue that may affect service life. In certain use conditions, phenomena such as molten salt attack may also be relevant. Under these operating conditions, it would be advisable to modify the surface of stainless steel components for ensuring reliability and additional life. In this study, the surfaces of stainless steels were aluminized using the halide-activated pack cementation process. The particular focus of this study was to investigate the relationship between the stability of austenitic stainless steels and aluminide coating characteristics, e.g., thickness and morphology. Aluminizing of SS 304 and SS 330 resulted in mass gains per unit area. An inverse relationship between the austenite stability of these stainless steels and the respective aluminide coating thicknesses was obtained. Other stainless steels being studied include SS304L, SS301, and SS302B. It is notable that these alloys have lower austenite stabilities than SS 304 and SS 330. The results of these studies will be discussed and placed in context with respect to previous studies from this group and others. The results of these studies will provide valuable insights for industrial applications where the surfaces of austenitic stainless steels need to be protected against high temperature degradation.

MA-Thp-14 Co-Deposition of Chromium and Silicon on Nickel, and Iron-Based Alloys, Catherine Sullivan, B. Hernandez, L. Rodriguez, A. Coronado, V. Ravi, California State Polytechnic University, Pomona, USA Halide activated pack cementation is a surface modification process in which, typically, a single element is deposited onto the surface of an alloy and subsequently incorporated into the substrate through diffusion. For some applications, it would be desirable to co-deposit more than one element simultaneously onto the substrate surface. During service life, this co-deposition surface would offer improved resistance to degradation in high temperature environments. The current study focuses on chromium-silicon codeposition process studies via halide activated pack cementation. Coatings containing chromium are expected to improve the corrosion resistance of the alloy, while the presence of silicon should improve the erosion resistance, thereby providing a dual benefit when co-deposited. The results of the co-deposition process for pure nickel and selected ferrous alloys will be presented and discussed. The discussion will incorporate coating characterization including phase analysis using x-ray diffraction, microstructural characterization using optical and scanning electron microscopy, and elemental analysis using energy dispersive spectrometry.

Functional Thin Films and Surfaces Room Golden State Ballroom - Session MB-Thp

Functional Thin Films and Surfaces (Symposium MB) Poster Session

MB-Thp-1 Effective Ways to Enhance the Performance of n-MoS₂/p-CuO Heterojunction Based Self-Powered Photodetectors, Davinder Kaur, Indian Institute of Technology Roorkee, India The present study investigated two effective routes to improve the response time and the detection range for the n-MoS₂/p-CuO heterojunction (a conventional p-n heterojunction). In the first rectification, an insulating aluminum nitride (AlN) layer was inserted in between the molybdenum disulfide (MoS₂) and cupric Oxide (CuO) layer, which eventually converted the conventional p-n heterojunction to Semiconductor-Insulator-Semiconductor (SIS) with a superior carrier tunneling mechanism. Interestingly, the fabricated heterostructure exhibits self-powered and broad-range photoresponse. The response time (rise time and fall time) of the fabricated n-MoS₂/p-CuO heterojunction decreases from 93.35 ms and 102.68 ms to 11.31 ms and 12.73 ms with the insertion of ultrathin insulating AlN Layer. The higher responsivity and ultrafast photoresponse in n-MoS₂/AiN/p-CuO (SIS) heterojunction can be ascribed to the carrier tunneling mechanism through the ultrathin-insulating AlN layer. Moreover, the detection range can be enhanced up to the UV region by adding a layer of MoS₂ quantum dots (QDs) on the surface of the MoS₂ layer in the fabricated heterostructure. The fabricated n-MoS₂, QDs/n-MoS₂/AiN/p-CuO heterostructure shows photoresponse in a broad range from UV to NIR radiations. The obtained results demonstrate the n-MoS₂/AiN/p-CuO (SIS) heterojunction with the addition of MoS₂ QDs shows excellent potential for next-generation ultrafast optoelectronics applications.

KEYWORDS: MoS₂, CuO, Quantum Dots, Photodetectors, Heterojunction, broad-range, and ultrafast.

MB-Thp-2 Porous Metal/Metal-Oxide Nanostructured Coatings Produced Using Gas Aggregation Sources of Nanoparticles as Recyclable SERS-Active Platforms, A. Hanková, D. Novák, N. Khomiakova, E. Kočišová, M. Procházka, Ondřej Kylián, Charles University, Prague, Czech Republic Due to their low cost, chemical and thermal stability, and unique electronic, optical or bioresponsive properties, metal-oxides (MeO) have become almost irreplaceable materials in an impressive range of modern technologies, such as (photo)catalysis, sensing, detection, or energy harvesting. In many cases, the functional properties of MeO may be enhanced by their nanostructuring that increases the specific surface and facilitates physicochemical phenomena like adsorption and diffusion of chemical species. One possibility of producing these materials relies on the deposition of highly porous transition metal (e.g. Ti, V, Nb, W) nanoparticle films by magnetron-based gas aggregation sources followed by the subsequent annealing of such formed nanoparticle films that assures their controllable oxidation and crystallization. The aim of this study is to demonstrate that further improvement of the functional properties of MeO nanoparticle-based films may be achieved if they are decorated with sputter-deposited noble metal nanostructures. In this way, different
functionality intrinsic to metal-oxide and metal components may be successfully combined or enhanced. As shown in this study, such metal/MeO nanomaterials are highly interesting as novel platforms for surface-enhanced Raman spectroscopy (SERS), in which the noble metals act as highly SERS-active component, while the transition MeO due to its photocatalytic characteristics provides the possibility of highly effective recycling of the platforms after cleaning them with UV light irradiation.

This work was supported by the grant GACR 21-05030K from the Grant Agency of the Czech Republic.

MB-Thp-3 Exploring the Magnetoelectric Functionality in PMN-PT/FSMA Multiferroic Heterostructure for Flexible MEMS Applications, Diksha Arora, D. Kaur, Indian Institute of Technology Roorkee, India

Flexible microelectromechanical systems (MEMS) are poised to scaffold technological innovations in the domains of wearable sensors, implantable health monitoring systems and touchless human-machine interactivity. In this study, a cost-effective and flexible magnetoelectric heterostructure comprising thin films of 0.67Pb(Mg1/3Nb2/3)O3-0.33PbTiO3 (PMN-PT) and ferromagnetic shape memory alloy (Ni2/3Mn1/3Fe2/3O4 (FSMA)) over flexible stainless steel and Ni substrates has been reported. The growth of the tetragonal structured pure perovskite phase of PMN-PT thin film without any pyrochlore impurity is confirmed by the dominant (002) orientation in the XRD pattern. The magnetoelectric coupling characteristics of the flexible PMN-PT/FSMA multiferroic heterostructure have been explored for magnetic sensor and nonvolatile memory applications. The influence of phase fraction, anisotropy and poling on magnetoelectric coefficients has been thoroughly studied to obtain the optimum magnetoelectric coupling.

A notable magnetoelectric coupling coefficient of ~4.1 Vcm⁻¹Ω⁻¹ at 250 Oe of He, has been obtained, making it promising for room-temperature magnetic field sensors. These results have been explained by an analytical model based on strain-mediated magnetoelectric coupling between interfacially coupled PMN-PT and FSMA layers of the multiferroic heterostructure. The electric field-controlled switching of magnetoelectric coefficient observed in PMN-PT/FSMA heterostructure is beneficial for high-density nonvolatile memory devices. The flexible ME heterostructure displays excellent mechanical endurance up to 2000 bending cycles. The remarkable response of such flexible magnetoelectric heterostructures at room temperature makes them promising for flexible magnetic field sensors, nonvolatile memory, spintronics and multifunctional device applications.

MB-Thp-4 A Carbon Nanotubes-Based Microwave Resonator for Ammonia Gas Sensing, Hsuan-Ling Kao, Y. Tsai, Chang Gung University, Taiwan

Carbon nanotubes (CNTs) have been used as gas-sensing material owing to their high specific surface areas and structural porosities that enable rapid responses and high sensitivity at room temperature. Fully inkjet printing technology promotes the green process using by digital controlled pattern in required location to offer fast, material saving, low cost, high substrate selectivity, and low annealing temperature. In this work, inkjet-printed CNT films can be conferred with the appropriate resistance for embedding into transparent terahertz-permanganic coupling between droplet spacing (DS) and layer number. CNTs films as sensing layers and silver films as conductive layers to realize gas sensors using fully inkjet printing technology. Gas sensors, including resistive and microwave resonator sensors, were inkjet-printed on CLTE-MW to measure their response in the presence of ammonia. Gas responses of CNT films with regular electrode and interdigital electrode patterns were compared by resistive-type gas sensors. CNTs with the IDE pattern can provide large contact areas between the silver film and CNTs for the provision of more effective conductive sensors. CNTs with the IDE pattern can provide large contact areas between the silver film and CNTs for the provision of more effective conductive sensors.


Across a wide range of application areas, understanding the chemistry and structure of surfaces and interfaces is crucial. In the last fifty years, X-ray photoelectron spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry, and advanced instrumental developments have led to a new dimension in understanding of the requirements for both academia and industry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry, but the limit on spatial resolution for XPS can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using just XPS.

Other experimental techniques which are unable to match the surface selectivity of XPS are able to provide complementary information to extend the data from XPS. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This can be a perfect complement to XPS analysis, so long as the same points of interest can be identified. Molecular spectroscopy, such as FTIR or Raman, can also provide complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures using the wide range of spectral libraries available for those techniques.

In this poster, we will describe how a correlative approach using both surface analysis instrumentation and scanning electron microscopy can be used to characterize 2D nanomaterials. Samples of MoS2 grown on Si substrates have been investigated using XPS, Raman and SEM to determine their composition and structure. To facilitate co-alignment of the analysis positions when moving between the instruments, special sample carriers and software alignment routines have been developed.

MB-Thp-6 CsPbI3-Based Perovskite Thin Film Using All Vacuum Deposition Process, HYO SIK CHANG, M. Jeong, J. Park, Chungnam National University, Republic of Korea

We deposited CsPbI3 films using a co-evaporation method, and optimized the film thickness and heat treatment. UV-vis and PL analysis confirmed the presence of a peak at 710nm wavelength, indicating the absorption and emission properties of the a-phase CsPbI3. In this study, a cost-deposition for CsPbI3 perovskite film. The use of vacuum co-deposition for CsPbI3 deposition allows for excellent uniformity and thickness control, leading to optimized film thickness. To make inorganic CsPbI3 perovskite solar cell, the phase change must be lowered and a low phase change temperature of less than 200 °C is required. We have developed low phase change temperature CsPbI3 with additive deposition. In this study, we manufactured a perovskite solar cell by combining the co-deposited CsPbI3 perovskite with an inorganic charge transport layer using atomic layer deposition (ALD). ALD NiOx and SnO2 films used as a hole transport layer and electron transport layer (ETL). The aim is to apply vacuum co-deposition of FAPbI3 and CsPbI3 to tandem perovskite-Si solar cell applications.

MB-Thp-7 Synthesis and Characterization of AlCrTiZrSiW High Entropy Alloy Coating by High-Power-Impulse Magnetron Sputtering, C. Chung, Ming Chi University of Technology, Taiwan; J. Tang, Lunghua University of Science and Technology, Taiwan; Bo-Ruel Lu, J. Tsao, M. Lin, Ming Chi University of Technology, Taiwan; F. Yang, National Taiwan University of Science and Technology, Taiwan

High-entropy alloy coating feature high hardness, excellent thermal stability, and corrosion resistance. They have been considered as promising candidates for next-generation surface coating material because of their advantageous properties. In recent years, the popular high power-impulse magnetron sputtering technology has attracted considerable attention due to the ability to produce coatings with excellent properties. It is preferable to replace high entropy alloy target with a sputtering method involving the use of more target(single element metal target) simultaneously, which can greatly reduce the process cost. In this study, AlCrTiZrSiW high-entropy alloy coating deposited on the various substrates (SKH-9 high-speed steel, SUS304 stainless steel, Si wafer) by HIPIMS technology. To obtain the Non- equiatomic high-entropy alloy coatings was adjusted by varying the output power of Al and CrSi target (2r
MB-Thp-8 Increasing the Sensitivity of ZnO Piezoelectric Pressure Sensor by Vanadium Doping. Heng-Chi Chu, S. Brahama, J. Huang, National Cheng Kung University (NCKU), Taiwan

ZnO is a common semiconductor material recently, due to its piezoelectric property, it can be used to fabricate the piezoelectric devices such as pressure sensor for monitoring the human health. Beside, doping vanadium(V) into ZnO can boost up the device performance because of increasing the piezoelectric coefficient and the p-type carrier concentration. In our research, we will prepare the thin film V doped ZnO piezoelectric pressure sensor by RF magnetron sputtering system with different working power. After deposition, we will annealing the sample at Ar atmosphere. XRD, SEM & EDS were observed the structure, surface morphology and doping concentration. XPS results show the V⁺⁺⁺ amount will reduce with higher doping concentration, and these trends were similar with the piezoelectric coefficient. The optical measurement will analysis by UV-vis, UPS, PLE & RAMAN, these suggest the defect properties and energy level. When we enhance the doping concentration, the intrinsic defect will decrease, however, the lattice arrangement becomes disordered because the zinc sites were replaced by the vanadium. Finally, the sensor current sensitivity will discus by the I-V curve. When the V concentration is about 0.24 at%, piezoelectric coefficient and carrier concentration can reach the balance, promoting the device’s sensitivity significantly.

MB-Thp-9 Location-Dependent Super-amphiphobic Nano-Structured Films Deposited by Tubular Microwave Plasma. Ta-Chin Wei, Y. Shen, Chung Yuan Christian University, Taiwan

Super-hydrophobic and oleophobic surfaces have attracted much interest for both fundamental research and practical applications. In this study, Teflon-like fluorocarbon films with different nano-structures were deposited on various substrates by microwave-generated CH2HF4/CF4 plasma. The reactor was a tubular quartz tube with diameter of 5 cm and length of 80 cm. The substrates were placed in 20 different locations along the gas flow direction in upstream region, discharge region, and afterglow region. It was found that the surface morphology of the deposited film was very location dependent. The fluorocarbon films deposited in upstream and afterglow region consisted of nano-particulate structure with F/C atomic ratio of about 2.0, namely the Teflon-like structure. However, the fluorocarbon film was rough and thick with a low F/C atomic ratio when substrate was located in the discharge region. Interestingly, Teflon-like fluorocarbon films with vertical nano-wall structure could be deposited only on substrates located in the end of upstream region and in the beginning of the afterglow region. It was also found that water contact angle on the Teflon-like nanowall or nano-particulated film was above 160° and the CH212 contact angle was above 140°. Moreover, by using the same operating parameters, we successfully deposited transparent super-amphiphobic fluorocarbon nanowall film onto various substrates such as glass, copper, polycarbonate, and etc. Moreover, we found that Teflon-like films with nano-wall structure could also be deposited onto various porous substrates. Finally, from the time evolution of the deposited film, the growth mechanism of nano-wall structure film was realized.

MB-Thp-10 Enhancing Oxygen Evolution Reaction Performance with Sputter-Deposited High Entropy Alloy Thin Film Electrocataysts. Siuang-Yun Li, T. Nguyen, Y. Su, Y. Shen, C. Liu, J. Ruan, K. Chang, J. Ting, National Cheng Kung University, Taiwan

Thin film catalyst, giving a different morphology, provides a significant advantage over catalyst particles for gas evolution reaction. Taking the advantage of sputter deposition, we hereby report high entropy alloy (HEA) thin film electrocatalyst for oxygen evolution reaction (OER). We investigate the catalyst characteristics not only in its as-deposited state but also during and after the OER. For comparison, unary, binary, ternary, and quaternary thin film catalysts were prepared and characterized. The surface electronic structure modification due the addition of a metal is studied experimentally and theoretically using density function theory calculation. We demonstrate that sputtered FeNiMoCrAl HEA thin film exhibits OER performance superior to all the reported HEA catalysts with robust electrocatalytic activity having a low overpotential of 220 mV at 10 mA cm⁻², and excellent electrochemical stability at different constant current densities of 10 and 100 mA cm⁻² for 50 h. Furthermore, we have investigated the microstructure transformation during the OER, which is important for the understanding of the OER mechanism provided by HEA electrocatalyst. Such finding would contribute to future catalyst design.

MB-Thp-11 Transition Metal Nitride Anti-Reflective Coatings. Barbara Schmid, B. Hajas, N. Koutno, TU Wien, Institute of Materials Science and Technology, Austria; J. Błaschke, TU Wien, Austria; P. Polčik, Plansee SE, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Anti-reflective (AR) coatings are of high importance for our everyday lives in the field of optics, for example in visual aids and photography equipment. Lesser known, those coatings are also essential in the realm of photovoltaics, like solar cells, because they are able to reduce the reflectivity of the material surface. There is a plethora of different design approaches to this topic. Within our work, we want to change the optical properties of hard TiC/TaC superlattice protective coatings without sacrificing superior mechanical properties. Using DC magnetron sputtering, we create nano-scale transition metal nitride-based (AlN and ZnN) thin films exhibiting different material characteristics. We investigate the influence of deposition parameters and film thickness on the optical properties of our materials system. Apart from structural and morphological investigations and the determination and comparison of mechanical properties of our material systems, we conduct optical investigations using differential reflectance spectroscopy (DRS).

MB-Thp-12 Enabling Robust Chemical State Analysis of Sn-Based Perovskites via Auger Parameter Analysis in XPS. Alexander Wieczorek, S. Siol, Empa – Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Sn-based perovskites exhibit compelling properties such as reduced toxicity and lowered band gaps over those purely based on Pb. As a result, they are of increasing interest for photovoltaic applications in single-junction and all-perovskite tandem applications. For high performances, control of the oxidation state and interfacial chemistry is paramount, which can be determined using X-ray photoelectron spectroscopy (XPS). However, the minor chemistry related shifts of the Sn core level emission complicate the analysis, especially for semiconducting materials. Here, surface band-bending as well as differences in the work function can be particularly pronounced.

In this presentation, we demonstrate that studies based on the modified Auger parameter α' provide a robust method to resolve different chemical states in Sn-based perovskites. Using a set of reference samples, we identified a high sensitivity to the halide, resulting in a shift of up to Δα' = 2 eV between ASnI3 and ASnBr3-type polycrystalline perovskite thin-films. Observed dependencies of α' on the Sn oxidation state and local chemistry provide a framework that enables reliable tracking of degradation as well as X-site composition for Sn-based perovskites and related compounds. Recently, we successfully applied this framework on Sn-based perovskite nanocrystals to ensure the absence of Sn(W) impurities upon optimized synthesis procedures.

The higher robustness and sensitivity of such studies not only enables more in-depth surface analysis of Sn-based perovskites than previously performed, but also increases reproducibility across laboratories. Due to the vast data analysis, this method is ideal for high-throughput studies that are increasingly being adopted in the development of new semiconducting materials.

References


Thursday Afternoon, May 23, 2024

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11:00 AM
MB-Thp-13 Pvd Deposition of Tin Based Antimultipacting Thin Films for Applications in Particle Accelerators, Yanis Pisi, CNRS, Université Paris-Sud, France

The multipactor phenomenon is a critical issue that can occur in particle accelerators. To improve the performance of components used in particle accelerators, we have chosen to develop a materials approach with innovative coatings.

The SEY is the ratio of the number of secondary electrons to the number of incident electrons (primary electrons). To avoid the multipactor effect, the ratio must be less than 1. Currently, most materials have an SEY greater than 1 [1]. The investigated coatings based on nitride or carbide titanium because the SEY ratio is intrinsically low [2,3]. My work consists of elaborating based TiN (TiONx), TiN, TiN(Cx) thin films and study their properties. Another approach concerns the investigation of thin layers consisting of alternating layers of NbN and TiN. The preferred deposition method is PVD (Physical Vapor Deposition) by cathodic pulservation. We will present the results obtained as a function of coating nature: (i) firstly, the physical properties (such as electrical properties by 4-point measurements) and chemical characterizations (such as the layer composition determined by XPS analysis); (ii) the values of secondary electron emission yields at the fully conditioned state (see table, the surface was conditioned by electron bombardment). In this work, we study the SEY without the effects of roughness, which is known to significantly influence the SEY.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Layer</th>
<th>Substrat</th>
<th>Roughness (nm)</th>
<th>SEY</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work TiNC Si</td>
<td>0.5</td>
<td>1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work Multilayer NbN/TiN Si</td>
<td>1</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[1] TiNC Si</td>
<td>High</td>
<td>0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[2] TiZrVC Si</td>
<td>High</td>
<td>0.93</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table: SEY values of different thin films obtained PVD

REFERENCES


Nickel oxide (NiOx) thin films were deposited by r.f. magnetron sputtering on n-type silicon and corning glass substrates. The deposition conditions were 60 W of power during 6 minutes, a pressure of 5 mTorr and different substrate temperatures in the range of 250-200 °C. The partial pressure between O/Ar was varied between 0 and 4 %. Prior to deposition, the substrates were cleaned in an ultrasonic bath with acetone, isopropyl alcohol and deionized water for 5 min each and dried with high-purity nitrogen after each step. Besides, the target was pre-sputtered for 15 min. MOS capacitors were fabricated by deposition of gold and aluminum as top and back contacts using thermal evaporation. The thickness and optical constants of the films were obtained by spectrscopic ellipsometry. Measurements of current-voltage (I-V) and capacitance-voltage (C-V) dependences were carried out to study the effect of temperature and oxygen partial pressure on the electrical properties of the NiO thin films. The obtained results indicate that it is possible to obtained high quality films at low r.f. power that are viable for applications in electronic devices.

MB-Thp-15 Characterization of Tin Oxide deposited by ALD for EUV Photoresist Applications. Songwoo Lee, T. Choi, Sejong University, Republic of Korea; I. Choi, J. Park, J. Yang, TES Co., Ltd, Republic of Korea

At present, metal oxide photoresists are being explored as alternatives to chemically amplified resists. The metal oxide film may take the form of a photosensitive metalorganic oxide film, such as an organonit oxide. The deposition process may involve the reaction of an organonit oxide with carbon dioxide. Notably, organotin compounds exhibit high sensitivity to extreme ultraviolet (EUV), facilitating the attainment of high-resolution patterning. The strength and dissociation mechanism of carbon bonds are factors that can be associated with EUV photosensitivity in dry photoresist. SnO2 photoresists are introduced as materials for EUV resist with high absorptivity and excellent etch resistance. A comparative analysis was conducted on SnO2 thin films deposited via TALD and PEALD at various deposition temperatures and reactant ratios. We focus on the optical, chemical, and electrical properties of the SnO2 thin films under various deposition conditions, with a specific emphasis on the influence of the SnO2 ratio. Additionally, we will evaluate and discuss their etch properties.

MB-Thp-16 Vertical Graphene Deposited on Stainless Steels for Anti-Biological Adhesion. Aidan An-Cheng Sun, Department of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li 32003, Taiwan; S. Wang, Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei 106, Taiwan

The research focuses on the wide application of anti-biological adhesion materials, particularly in the medical field. The goal is to utilize graphene material on the surface of surgical blades to reduce bioadhesion during tissue cutting, improve wound healing rates, shorten healing times, and simultaneously reduce the risk of postoperative infections.

The study employs Plasma-Enhanced Chemical Vapor Deposition (PECVD) to deposit graphene. By adjusting parameters such as graphene growth temperature, growth time, and the ratio of acetylene to argon flow, the vertical arrangement of carbon atoms on the substrate surface is achieved. This structure exhibits high surface area and excellent electrical and thermal conductivity in the vertical direction. The research emphasizes measuring changes in contact angle and electrical properties under different conditions, utilizing tools such as contact angle measurement, four-point probe resistance measurement, scanning electron microscopy, X-ray diffraction, and atomic force microscopy.

Increasing the substrate temperature during film deposition enhances the growth of vertical graphene. At lower temperatures, graphene grows slowly and with insufficient density. As the temperature rises, growth density increases, and the length of graphene also extends. A better graphene density is achieved at 700 oC. Regarding deposition time, at 700 oC, growth for 30 minutes results in graphene that has grown but is still in a planar or spherical state. However, when the time is extended to 60 minutes, three-dimensional graphene structures begin to grow vertically toward the substrate surface, forming vertical graphene films. Water contact angle measurements show that at 700 oC and 30 minutes, an approximately 800 hydrophilic water droplet angle is obtained. However, when the time is extended to 60 minutes, an approximately 1200 hydrophobic water droplet angle is achieved, meeting the standards for anti-biological adhesion.

The study reveals the mechanism behind the formation of high water droplet angles in anti-biological adhesion and explores the correlation between various physical and chemical properties of graphene and the fabrication process. Additionally, the possibility of recycling and redeposition of surgical blades is discussed.


NiO thin films were deposited by RF sputtering in Ar atmosphere on n-Si and glass substrates. During the deposition the RF power was varied between 5 W and 60 W, while the deposition time was fixed at 9 min. Three deposition temperature of 25°C, 50°C and 100°C were used. The samples deposited on Si were separated in three groups. The first group was furnace annealed at 450 °C in N2 atmosphere for 1 h. The second one was treated by Rapid Thermal Annealing (6 min, 550 °C), while the third group was kept as control. Metal/NiO/n-Si heterostructures were prepared by deposition of Au electrodes through a mask.

The thicknesses and optical constants of the layers were determined by spectrocoposcopic ellipsometry. XRD measurements were used to determine the effect of deposition temperature and thermal annealing on the crystallinity of the films. The Au/NiO/n-Si structures were electrically characterized by current-voltage (I-V) and capacitance-voltage (C-V) measurements. The I-V dependences showed formation of p-n heterojunction diodes with properties, which depend on the r.f. power, deposition temperature and annealing.
Thursday Afternoon, May 23, 2024

MB-ThP-18 Nanocrystalline MoO$_3$ Thin Films Prepared by Reactive DC Magnetron Sputtering for NO$_2$ Gas Sensing. S. Singh, D. Kaur, Ramesh Chandra, S. Issar, Indian Institute of Technology Roorkee, India

We report on a molybdenum trioxide (MoO$_3$) thin film sensor fabricated using a reactive DC magnetron sputtering technique to detect of NO$_2$ gas. The crystalline quality and morphology of the films were characterized via XRD and FE-SEM, respectively. To get insights into elemental composition and oxidation states, XPS studies were conducted. Further, the gas sensing performance of the MoO$_3$ thin film sensor was evaluated. The highest sensor response ($R_H/R_O$) of ~9.15 for 200 ppm of NO$_2$ gas at the optimum operating temperature ($T_{opt}$) of 300 °C. Moreover, the sensor’s calculated response and recovery time at $T_{opt}$ were recorded as 114 s and 106 s, respectively. Thus, the fabricated MoO$_3$ thin film sensor had excellent sensing performance and good selectivity for NO$_2$ gas.

MB-ThP-19 Vernier Ellipsometry Sensing with Ultrawide Limit-of-Detection and Large Dynamic Range by Tuning of Zero-Reflection Points, Yun Zhang, M. Thawda Phoo, F. Yishu, X. Li, Y. Lam, J. Zapien, City University of Hong Kong

Optical sensors using zero-reflection points (ZRPs) enable excellent sensitivity due to accompanying phase singularities and the steepest slope of the reflectivity curve. Reflection zeros have been demonstrated at different spectral regions under very specific conditions in the angle of incidence (AoI) and polarization state. However, manipulation of the darkness points for multiple spectral positions and polarizations has not been achieved yet. Here, we report the collaborative and synergic operation of three ZRPs in a simple platform formed by a lithography-free, three-layer, metal-dielectric-metal structure where careful design and efficient manipulation of these ZRPs results in an optical sensor with unsurpassed, experimentally demonstrated, limit of detection ~2x10$^{-8}$ RIU. The synergic operation of the proposed sensor relies on: i) strong coupling between p-pol surface plasmon polariton and p-pol photonic waveguide modes with experimentally demonstrated reflection suppression, Rabi splitting and phase singularities; ii) simultaneous implementation of two orthogonally polarized ZRPs and wavelength-interrogation mode of operation leads to spectral overlap of s-pol photonic modes with the coupled, p-pol resonances; and iii) ellipsometry-based sensing where the relatively insensitive s-pol ZRPs provide internal references to boost the sensor performance in terms of the amplitude ratio ($\Delta$) and phase difference ($\delta$) of the s- and p-polarized reflection thereby naturally forming a refinement measuring scale akin to a Vernier scale. Remarkably, the precise manipulation of the double dark points via the AoI control enables a second metric that yields ultrahigh sensitivity and can be reset to the original spot over a large dynamic range, thereby avoiding the trade-off between sensitivity and dynamic range. This occurs because the AoI acts an additional degree of freedom to tune and reset the sensor to its original ZRPs while keeping track of the total accumulated change. The strength of these capabilities has been demonstrated for a biosensor of SARS-CoV-2 spike (S2) protein that can track the full functionalization process of the chip surface and then reset to its best sensing conditions to perform real-time dose-dependent detection of the S2 spike protein. Our work provides a new and powerful strategy for the development of optical sensors, perfect light absorbers, pyroelectric detectors, and phase modulators. This work was supported by the Research Grants Council of Hong Kong, SAR, Project number CityU 12119919.

MB-ThP-20 Nano Indentation Pop-in Response on Basal Plane of 4H Hexagonal SiC Surface, Jacob C. Huang, National Sun Yat-sen University, Taiwan

The nano-scaled mechanics for the hexagonal 4H SiC single-crystal surface (with a bandgap of 3.26 eV) is examined by using nanoindentation testing on the (0001) basal plane. The 4H SiC material was prepared by Prof. M. C. Chou via the Czochralski process. The as-grown crystal surface has been examined carefully by X-ray diffraction (XRD) to confirm the 4H hexagonal structure, with the basal plane lying on the horizon plane and the c-axis parallel to the growth direction. The (0004) peak at 2$\theta$=35.5$^\circ$ is the only peak appeared, ensuring the well-grown surface orientation with minimum defects. The lattice parameters, a and c, are determined to be 0.3073 and 0.1006 nm, respectively. Through the analysis of XRD rocking curves, it is confirmed that there should be minimum defects inside the as-grown SiC surface.

Nanoindentation tests were performed using the continuous stiffness method (CSM), up to a maximum depth of ~950 nm on the (0001) basal plane surface. The average elastic modulus and hardness calculated from depth ranging from 300×800 nm over nine indents were ~500 GPa and ~42.5 GPa, respectively. In addition, the first few pop-in loads and displacements are captured from the deviations from a perfect Hertzian contact curve fitted to the load-displacement curve. By using rough estimation for the yield stress from hardens by a factor about 2.5 (Tabor’s assumption), we estimate the yield stress to be about 42.5/2.5 ~ 17.0 GPa. The first pop-in loads, pop-in hardness, and pop-in stresses can all be measured. The first pop-in stress is usually termed as the incipient stress, associated with the first initiation of the activation of dislocations (nucleation or gliding of dislocations). The average incipient stress for the first dislocation activity is about 16.1 GPa, slightly below the overall yield stress. From the first pop-in displacement, about 10 nm, it is likely to be a result of the micropipe threading screw dislocations (with a Burger’s vector of c-axis, namely, ~1 nm). This suggests that the first pop-in could be caused by these screw dislocations gliding for 10 Burger’s vectors. The understanding of dislocation incipient pop-in as a function of applied load would give the insight for subsequent influence for various functional properties of 4H SiC.

Tribology and Mechanicals of Coatings and Surfaces Room Golden State Ballroom - Session MC-ThP

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

MC-ThP-1 Influence of Cobalt Content on the Adhesion of TiAIN and AlTiN/TiSiN Coatings on WC-Co Substrates, Brunna Michelle de Freitas, R. Diego Torres, D. Stolle da Luz Weiss, P. Cesar Soares Junior, C. Augusto Henning Laurindo, Pontifícia Universidade Católica do Paraná, Brazil; F. Lacerda Amorim, Pontifícia Universidade Católica do Paraná, Brazil

Coatings based on Ti-Al-N-Si, deposited by the physical vapor deposition (PVD) process, aim to increase the working life of machining tools. In this way, the mechanical properties of the substrate interfere with the adhesion of these coatings, reflecting on their performance. Cemented carbide, one of the most used materials for cutting tool manufacturing, is a composite consisting of tungsten carbide (WC) plus a binder phase. The binder content, typically cobalt (Co), defines its main characteristics: hardness, elastic modulus and determining its application [1]. However, the effect of cobalt composition in the cemented carbide substrate and how its variation affects the mechanical properties and adhesion of PVD coatings is not extensively investigated [2]. Therefore, the objective of this study is to evaluate the adhesion and mechanical properties (hardness (H), elastic modulus (E), and the H/E ratio) of Ti-Al-N-Si-based coatings (TiAIN and AlTiN/TiSiN) deposited by the PVD process on cemented carbide substrates with different Co concentrations (6, 8, and 10%). The surface properties of the substrates and coatings were assessed using scanning electron microscopy (SEM) with an attached energy-dispersive X-ray spectroscopy (EDS) system, X-ray diffraction (XRD), and roughness measurements. For the evaluation of mechanical properties, nanoindentation tests were performed, and adhesion was evaluated through indentation testing and scratch testing. The results show that the hardness and elastic modulus of the substrates are affected by the Co content, and the AlTiN/TiSiN coating has the highest hardness due to the presence of Si in its composition, along with higher roughness from the deposition process. In general, higher Co content in the substrate negatively affects adhesion. Through the scratch test, it was observed that the TiAIN coating has better adhesion to the substrate. Additionally, for a higher H/E ratio, there is greater adhesion for both coatings (TiAIN and AlTiN/TiSiN), and this adhesion is higher in cemented carbide substrates with low Co content. 


MC-ThP-2 The Multi-Component Alloy Powder Manufacturing and Coating on Router Cutters for Carbon Fiber Composite Materials, Sung-Mao Chiu, H. Hsueh, Metal Industries R&D Centre, Taiwan

This research focuses on the manufacturing of the key component of high-end cutting manufacturing in aerospace, the milling tools for cutting carbon fiber composite materials. By integrating the multi-component alloy AlCr,NbSiTi coatings, including alloy composition design, simulation, powder manufacturing and sputtering target block manufacturing to
establish the customized long-life and high value performance special coating technology of cutting tools. Multi-component alloy nitride coating by PVD sputtering process shows high hardness ≥30 GPa, water droplet contact angle: ≥ 90°, high temperature resistance ≥1000°C, coating adhesion: ≥ 60N. After field verification of composite cutting tools show increasing the tool life by more than 30% compared with the current tool life used by the industry.

The developed technology will fill the gap in coating technology in domestic cutting tool manufacturing industry, and finally integrate with the verification of cutting performance in the laboratory and field test, to achieve the goal of significant improving cutting performance in cutting aircraft parts made by carbon fiber composite materials.

**MC-ThP-3 Application of In Situ Hydrogen Charging During Micromechanical Testing of Thin Films, Szilvia Kalácska, CNRS LGF, Mines St. Etienne, France**

Understanding mechanisms of deformation in thin films at the sub-micron scale is the key for designing new composites for industrial applications. It requires the determination of strains/stresses [1], dislocation distribution [2] and the overall microstructure evolution, which is often extremely challenging. Microstructural processes during external mechanical loading are hard to observe due to the complex multiscale nature of the phenomenon. If hydrogen is present in the solid, it can cause embrittlement or enhanced cracking, when the material is subjected to stress. This would eventually lead to the reduced lifetime or critical failure of the component. Although it is known for a long time that hydrogen causes degradation of mechanical performance in metals, the microscale mechanisms remain a subject of debate. Direct H-detection within the lattice is an extremely challenging task, (continuous diffusion and outgassing issues). Microstructure observations are still mostly performed post mortem on bulk samples.

In situ H-charging is therefore essential for thin film experiments. Samples can be loaded electrochemically through the back surface [3], using a cell compatible with high-vacuum (HV) scanning electron microscopes (SEM). This way, H diffuses into the lattice from the back, avoiding contamination to the surface of interest. The developed system will be presented, focusing on the coupling of the cell with the nanodeformation stage by performing nanoindentation experiments on H-charged thin films.

**References:**


**MC-ThP-4 Shrouding Gas Plasma Deposition Technique for Generating Wear Resistant ZnO/Ws**

Composite Films on PEEK, Dietmar Kopp, Leobener Straße 94a, Austria

In this study, zinc oxide/tungsten disulphide (ZnO/Ws) composite films were generated by an atmospheric pressure plasma jet (APPI) equipped with a shrouding gas attachment on polymer ether ketone (PEEK) discs. The friction and wear properties of the ZnO/Ws10 composite sliding against 100Cr6 counterpart balls were intensively investigated by using a rotational ball-on-disk setup under dry sliding conditions at ambient room conditions. The deposited and worn coating areas were observed with a scanning electron microscope (SEM). The results indicated that low friction ZnO/Ws10 composite films have the potential to PEK against mechanical motion. However, the tribological performance of the coatings are strongly dependent on the plasma-process settings (i.e. plasma current, dwell time of the powder particles in the plasma jet). In fact, there is a significant tribological improvement of the composite films in contrast to the uncoated PEEK by a factor of three.

**MC-ThP-5 Wear and Corrosion Characterization and Parametric Optimization of Nb-doped Hydrogenated Diamond-like Carbon (a-C:H) Coatings, Ihsan Efeoglu, Y. Totik, G. Gulten, B. Yaylali, M. Yesilyurt, Ataturk University, Turkey; R. Gunay, G. Kara, B. Altintas, TUSAS ENGINE INDUSTRIES (TEI), Turkey**

This study focuses on enhancing the wear and corrosion resistance of AISI 4130, a chromium-molybdenum alloy steel, through the application of a functional coating. Targeting various industrial uses, notably in the aerospaced and automotive industries, the research aims to improve the durability and performance of AISI 4130. As the functional coating, niobium-doped hydrogenated diamond-like carbon (a-C:H:Nb) coatings were deposited using a closed-field unbalanced magnetron sputtering technique under various parameters, which were systematically optimized following the Taguchi L9 orthogonal array method. The microstructural properties of the coatings were analyzed using a scanning electron microscope, and their crystallographic characteristics were determined using X-ray diffraction, providing a comprehensive understanding of the coating structure. To evaluate the mechanical properties, nanoindentation tests were employed, offering precise measurements of hardness and elasticity. The tribological characteristics of the DLC films were assessed using a pin-on-disc tribometer, examining their wear resistance and frictional behavior under ambient air. These comprehensive analyses reveal the a-C:H:Nb coating potential for applications requiring enhanced surface properties, combining enhanced superior tribological and corrosion performance.

**MC-ThP-6 Improving Tribological Properties of Al 7075 Alloy by Two-Step Soft Plasma Electrolytic Oxidation, Thiago de Lima Gontarski, G. Gaetano, J. dos Santos Junior, B. Leandro Pereira, R. Diego Torres, P. Soares, Pontifical Catholic University of Paraná, Brazil**

The trend of using aluminum (Al) alloys in various industrial sectors, including naval, automotive, and aerospace, can be attributed mainly to their high specific strength. However, their relatively lower resistance to wear and corrosion could limit their applications. To address this, Plasma Electrolytic Oxidation (PEO) has emerged as an effective method to enhance the mechanical, chemical, and thermal properties of Al alloys. Hence, this study aims to evaluate the impact of sample exposure time during the PEO process on the tribological properties of the Al7075. Specimens of Al7075 were abraded with silicon carbide sandpapers of 220 grit. Subsequently, all samples were cleaned with acetone and air-dried at ambient temperature. The PEO procedure was carried out in two stages. It employed a unipolar power source, a stainless steel counter electrode, and a silicate-based electrolyte. The first stage of PEO was the same for all samples, and it involved applying a voltage of 300V and a current of 0.5 A for one minute. The second stage was carried out with a voltage of 350V, and a current of 0.3 A, with varied exposure durations for each sample: 3, 5, 10, and 20 min. The morphology, chemical composition, and crystalline phases were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-ray Diffraction. The friction and wear properties of the samples were determined by dry linear reciprocating sliding tests in a ball-on-plate setup, using an Anton-Paar Universal tribometer. An applied load of 5 N and a sliding speed of 2.5 cm/s were maintained, with a reciprocating stroke of 6 mm. The test distance was set at 40 m at 25°C and a relative humidity of 50%. SEM analyses post-PEO process revealed that surface layers of the Al substrate were characterized by numerous pores and a flattened topography. The smoothest and thickest layer was achieved with the 20 minute PEO treatment. EDS results indicated that Al and O elements were predominantly present in all coatings after various exposure times. The coefficients of friction recorded were 0.557 for the substrate, and 0.501, 0.540, 0.442, and 0.427 for the PEO treatments of 3, 5, 10, and 20 min, respectively. Concurrently, wear rates were measured at 2.84, 1.79, 2.06, 1.97, and 1.4 x 10^-8 mm/Nm for the same conditions. The oxidation layer with the most advantageous tribological performance was that which formed over 20 min; it withstood rupture for in excess of 1600 cycles, compared to the other layers, which failed between 700 to 800 cycles. In conclusion, the longest exposure time during the mild PEO treatment correlated with the most favorable tribological properties.

**MC-ThP-7 Influence of Surface Treatment on the Interfacial Structure of Fe-Ni/Mn/Fe-Ni Bimetallic Strips, Jin Kyu Lee, H. Choi, Kongju National University, Republic of Korea**

Bimetals consist of two or more metallic components with different thermal expansion coefficients that bend when subjected to changes in temperature. Thanks to this property, bimetal strips are widely used in
many equipment items such as thermometers, circuit breakers, and home applications for similar purposes.

In this study, we report the influence of surface treatment on the interfacial structure of Fe-Ni-Mn/Fe-Ni bimetallic strips post-rolling through diffusion bonding. The microstructure of the interface for Fe-Ni-Mn/Fe-Ni bimetallic strips treated with surface treatment and diffusion annealing was investigated. Comprehensive analyses involving X-ray diffractometry, scanning electron microscopy, and electron backscatter diffraction are employed to investigate the microstructure and phase characteristics of the bonding interface. Furthermore, mechanical properties are evaluated through Vickers hardness measurements and deflection assessments at elevated temperatures.

MC-Thp-8 Mechanical and Tribological Behavior of Nanolayered Sputtering MoN/MoWN Coatings, Wan-Chang Hsu, F. Wu, Department of Materials Science and Engineering, National United University, Taiwan

This research investigated the microstructure, mechanical and tribological behavior of the molybdenum nitride, MoN, molybdenum tungsten nitride, MoWN, single layers and the nanolayered MoN/MoWN, films through reactive radio frequency magnetron sputtering, RFMS, technique. The nanolayered MoN/MoWN was prepared with fixed 50 nm MoWN building layers and MoN building layers with a thickness of 25 to 50 nm. These layers were alternately stacked to form a multilayer film with a total thickness of approximately 1 μm. The MoN single building layers presented a nanocrystalline structure while well crystalline feature was found for the MoWN layers. Through microstructure analysis, the nanolayered MoN/MoWN with a building bilayer of 25/50 nm/mm possessed continuous growth of MoWN columnar crystals along B1-MoN(111). On the contrary, the through-layer columnar grain was suppressed by the 50/50 nm/mm MoN/MoWN stacking. For mechanical and tribological behavior, the wear track of the MoN/MoWN multilayer film was shallower and narrower as compared to those of the 25/50 MoN/MoWN multilayer film. The superior wear resistance was attributable to the effective inhibition of continuous growth of columnar crystals by a thicker MoN building layer. Additionally, the 50/50 multilayer MoN/MoWN film exhibited larger compressive residual stress which was beneficial for hardness and tribological characteristics.

MC-Thp-9 MXene Nanosheets Exhibiting Layer-Dependent Friction Properties, Ankitendran Mishra, P. Pendyala, E. Yoon, Korea Institute of Science and Technology (KIST), Republic of Korea

MXenes are a new class of 2D solid-state frictional materials with atomically thin multi-layered structures. The layers of MXenes were shown to exhibit large inter-layer binding due to the presence of a large number of functional groups. How such large inter-layer binding affects the nanoscale friction was not understood. We experimentally investigated the nanoscale frictional properties of layers of MXene nanosheets using friction force microscopy. We showed that the friction of MXenes reduced as the number of layers increased. Using the puckering mechanism of friction, we showed that out-of-plane mechanical properties of MXene layers primarily influence the friction behavior of MXenes. Furthermore, contrary to the prevalent understanding, we showed that higher inter-layer binding in MXenes helps the layer-dependent behavior enhancing the overall frictional performance. Our study critically enables further exploration of MXenes as nanoscale solid-state lubricants.

MC-Thp-10 Influence of Carbon and Boron Additions on the Wear Resistance of Fe₃Al Based Laser Claddings, Harald Rojacz, K. Pichelbauer, M. Varga, AC2T Research GmbH, Austria; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Strengthened iron aluminides exhibit excellent mechanical properties up to 600°C, and are promising candidates to replace Co-, Cr- and Ni-rich coatings for high temperature wear protection. To improve their hardness, different strengthening mechanisms can be chosen accordingly. For this study, precipitation hardening with carbon and/or boron was used to strengthen Fe₃Al-based iron aluminides. Carbon and boron were alloyed in the range from 0-20 at.%, as well as combined up to 10 at.% each to precipitate carbides, borides and carboborides to show the influence on microstructural evolution, hardness, as well as wear resistance. A thorough material analysis of the developed laser claddings materials and the present phases was conducted using scanning electron microscopy, electron backscatter diffraction, hot hardness testing, nanoindentation as well as high temperature abrasion testing. Results show that the hardness can be significantly increased from ~260 HV10 (claddings without any strengthening of the Fe₃Al phase) to ~850 HV10 with boride precipitations (20 at.% B). Strengthening with carbon and boron leads to a hardness of ~670 HV10 due to the formation of carboborides as well as graphite islands (10 at.% B and 10at.% C). Alloying with carbon causes the formation of graphite lamellae as well as perovskite-type carbides Fe₃AlC₀.₆ and lower hardness of a max. of ~350 HV10 at 20 at.% C. Wear results indicate a strong dependence on the present phases, whereas a significant reduction of the wear rates can be pointed out when strengthened, comparable to classical FeCrC₉-based hardfacings, but with the advantage of a significantly reduced ecological impact.

Coatings for Biomedical and Healthcare Applications Room Golden State Ballroom - Session MD-Thp

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

MD-Thp-1 Investigation of Silver/Copper Diffusions in the Matrix of Amorphous Carbon Thin Films Produced by Magnetron Sputtering, Hailinx Sun, Teler Coatings Ltd, UK

The environment inside a spacecraft is ideal not only for the members of the crew onboard, but also for bacteria and fungi to grow. The proliferation of harmful microorganisms can become a hazard for the human crew as well as for the safe running of equipment. In our previous work, we used magnetron sputtering to develop amorphous carbon coatings doped with silver and copper for antimicrobial application in space stations, and the benefits of the bactericidal properties added by silver- and copper-doping were shown under both terrestrial gravity and micro-gravity conditions [1]. In addition, these thin films are scratch-resistant and wear-resistant with high hardness, providing a long lifetime which is critical for the applications in a space station.

The prepared Ag- and Cu-doped amorphous carbon coatings showed a slow diffusion of Ag from the carbon matrix to the surface, eventually replenishing the Ag at the surface lost due to daily wear and tear. Such diffusion process is a key factor in the coating performance: if too fast, the antimicrobial lifetime of the coating would be shorter, if too slow the bactericidal efficiency of the coating would be affected. Therefore, it becomes apparent and critical to identify the key factors that influence the Ag diffusion rate in a carbon matrix, and also to understand how they influence it.

In this work we report the latest study on Ag and Cu diffusion in Ag- and Ag/Cu-doped amorphous carbon coatings. Samples with the same concentration of Ag and different concentrations of Cu have been prepared and annealed in oven at 100 °C, 150 °C and 200 °C to speed up the diffusion process of the metals. With the combination of RBS (Rutherford Backscattering Spectrometry) and ToF-ERD (time of flight elastic recoil detection) the elemental depth profile is accurately measured, which is supported by XPS data to investigate the chemical state of the species at the surface. Preliminary results have shown that higher temperature causes a higher diffusion rate, and the addition of copper has slowed down the diffusion rate of silver, which is confirmed also by cross-section SEM images. Interestingly, XPS data show how Ag retains always its metal state and does not oxidize, while Cu bonds with carbon, oxygen and hydrogen to form more complex molecules such as Cu(II) carbonate dihydroxide.

References


MD-Thp-2 Enhanced Biomedical Implant Surfaces: Stainless Steel Modification Through Hiplims-Coated Titanium and PEO Treatment, Bruno Pereira, Pontificia Universidade Católica do Paraná, Brazil; L. Fontana, Universidade do Estado de Santa Catarina, Brazil; C. Lepienski, Universidade Federal do Paraná, Brazil; P. Soares, Pontificia Universidade Católica do Paraná, Brazil

The main causes of failures in implantable devices are often attributed to bone reabsorption, due to a mismatch in elastic modulus at the implant-bone interface, as well as and bacterial infections. Plasma electrolytic oxidation (PEO) is a versatile surface modification technique for metals, such as Titanium (Ti), and is capable of producing coatings that exhibit a reduced elastic modulus. Moreover, this method can incorporate bactericidal elements, such as Copper (Cu), achieving a durable antibacterial effect. However, PEO is not directly applicable to stainless steel, which is frequently employed as biomaterial. In this study, austenitic
stainless steel was coated with titanium using High Power Impulse Magnetron Sputtering (HiPIMS). The Ti-coated steel (SS-Ti) was subsequently subjected to the PEO process to improve the surface properties essential for implantable devices. The PEO process involved an electrolyte mixture of calcium acetate, calcium glycerophosphate, and copper sulphate. Post-PEO surfaces were examined by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Crystalline structures were characterized using X-ray diffraction (XRD), while the thickness of the layers was measured through cross-sectional analysis. Nanoidentation tests were employed to measure the hardness (H) and elastic modulus (E) of the layer, while nano-scratch tests were performed to evaluate the layer adhesion. The resulting coating presented a homogeneous, porous oxide structure containing calcium (Ca), phosphorus (P), sulphur (S), copper (Cu), and crystalline anatase (TiO2). The modified oxide layer was approximately 4 µm thick. Nanoidentation tests indicated a considerable reduction in the elastic modulus (~50%) compared to SS, while the scratch tests showed strong adhesion of the Ti-oxide layer to the SS substrate, with no exposure of the SS substrate in the scratched regions. The resulting coating, due its properties, displayed potential for use in biomedical applications.


Nanosized and nanostructured monolayers (SAMs) on solids are common platforms for functionalizing and controlling chemical and physical properties of surfaces with applications in diverse fields such as corrosion, catalysis and bio-sensors. Here Resonance enhanced AFM-IR is used to obtain nanoscale topographic information and spectroscopic, i.e. chemical information on such systems [1], in order to better understand the interplay between nanostructure and function. A tunable pulsed quantum cascade including four chips and a fast optical parametric lasers provides the IR source in the ranges of 910-1900 cm⁻¹ and 2700-3900 cm⁻¹. Using a gold coated silicon cantilever on gold substrate provided high sensitivity to detect monolayer and single molecule.

First, results on aptamer SAMs on gold used as SARS-CoV-2 biosensors will be presented. Tapping mode AFM-IR was employed to characterize the surface after each fabrication step and after analyte binding to the receptor layer to provide insight to molecular conformational and structural variation as well as chemical composition of this system. Binding of single molecule proteins was detected.

Second, biomolecule-repellent oligoethylene glycol (OEG)-based SAMs on gold were studied. In such systems the molecular conformation of OEG and the structure of interfacial water are thought to strongly influence the repellent character [3]. Tapping mode AFM-IR investigation of water films adsorbed on nano-domains of OEG SAMs were performed under elevated relative humidity and provided structural details of the OEG moieties and adsorbed H₂O.


MD-ThP-4 Development of Hierarchical Surfaces Coated with Zinc Nanoparticle-Doped Polycaprolactone on 316LVM Stainless Steel Substrate for Biomedical Applications, Tarciana Diel Toscana, Pontificia Universidade Católica do Paraná (PUCPR), Brazil; A. Bhattacharjee, Colorado State University, USA; K. C. Popat, George Mason University, USA; P. Soares, Pontificia Universidade Católica do Paraná (PUCPR), Brazil.

The use of 316LVM stainless steel in medical implants, while advantageous due to its mechanical strength and biocompatibility, poses a significant challenge in the form of bacterial infections. These infections occur when bacteria adhere to the implant surface, forming biofilms that are resistant to antibiotics and immune responses. This can lead to persistent infections, causing complications such as implant failure, the need for surgical revision, and prolonged patient suffering. It is known that nanostructured and biologically textured surfaces have demonstrated superior over smooth surfaces in bacterial inactivation and reduction of bacterial adhesion. Bacterial inactivation through surface morphology can occur through a physical-mechanical mechanism. By integrating bacterial elements into these nanostructured surfaces, it is possible to create a route for physical-mechanical and chemical inactivation. Thus, the surface of 316LVM steel was modified using the cathodic plasma electrolytic oxidation process, followed by acid etching to promote surface nanostructuring. This nanostructured surface was subsequently coated with polycaprolactone doped with zinc oxide nanoparticles (nZnO/PCL). The objective of this study is to evaluate the morphological, topographical, and chemical properties, along with the wettability and electrochemical response of the textured surfaces. Additionally, the effect of surface texturing on the adhesion of the nZnO/PCL coating was investigated. The bactericidal effect of the nanostructured and nZnO/PCL-coated surfaces was also assessed using Staphylococcus aureus bacteria. For this purpose, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), contact angle measurements using a sessile drop goniometer, and evaluation of the electrochemical response through potentiodynamic polarization tests were employed. Coating adhesion to the substrate was assessed through scratch tests. The bactericidal effect was evaluated using colorimetric assays and live/dead bacterial quantification. The results showed that the application of cathodic plasma electrolytic processes in conjunction with acid treatment successfully induced surface nanostructuring. There was an improvement in corrosion resistance properties and increased adhesion in surface contact angle for the textured and coated samples, along with a significant reduction in bacterial adhesion. It was also observed that the zinc oxide-doped polymeric coating exhibited better adhesion on textured surfaces compared to polished material.

MD-ThP-5 Catastrophic Corrosion in Metal Guitar Strings with or Without DLC Films Using Artificial Sweat, C. Andres Veldsquez Andrade, Universidade do Vale do Paraíba, Brazil; N. Pereira Alves Granado, IGTIPAN, Brazil; Lucia Vieira, Universidade do Vale do Paraíba - Univap, Brazil.

Diamond-like carbon (DLC) film was deposited on electric guitar strings to evaluate corrosion under the impact of artificial sweat at a constant temperature of 37 degrees Celsius. The objective was to assess the effect of corrosion on the change in string mass over time and the string tonality variation. The process involves the application of a DLC by plasma-enhanced chemical vapor deposition (PECVD), recognized for its corrosion-resistant film. The strings' mass changes due to exposure to artificial sweat were measured over 240 hours, focusing on mass variation to obtain information on the strings' durability and corrosion resistance. The results show that all strings suffered corrosion, and the tonality (frequency variation of the notes) varied due to the film of the strings. The results can help design electric guitar strings with better tonal qualities and corrosion resistance. Understanding how external elements such as sweat affect the integrity of the DLC film contributes to the sound quality and longevity of the strings.

Keywords: mass variation; Corrosion; artificial sweat; nickel plated steel; Raman; guitar strings; DLC; PECVD

Plasma and Vapor Deposition Processes

Room Golden State Ballroom - Session PP-ThP

Plasma and Vapor Deposition Processes (Symposium PP) Poster Session

PP-ThP-1 Topological Insulator Bi₂Se₃ Nanoplatelets Enhanced Photo-Detectivity of UV and Visible Light by Ag Depositing, Chih-Chiang Wang, A. Lo, National Chin-Yi University of Technology, Taiwan; P. Lin, Texas A&M University, USA; F. Shieu, National Chung Hsing University, Taiwan; H. Shih, Chinese Culture University, Taiwan

Bi₂Se₃ is a promising material for photodetectors because it possesses several favorable properties, including a narrow band gap (~0.35eV), conducting surface states, and an insulating bulk. Bi₂Se₃ nanoplatelets were synthesized on Al₂O₃(100) substrates through thermal evaporation, followed by the deposition of Ag using the magnetron sputtering technique. The rhombohedral Bi₂Se₃ crystal structure was confirmed through XRD, HRTEM, Raman spectroscopy, and XPS. The presence of Ag on the surface of Bi₂Se₃ nanoplatelet was determined using FESEM-EDS, XPS, and HRTEM. The optical absorbance of Bi₂Se₃ nanoplatelets in the UV-visible range decreased with the Ag content exceeded 7.1 at.%. The photocurrent measured under zero-bias conditions exhibited a notable effect due to the presence of Ag. The photocurrent under UV and visible light for the Bi₂Se₃ nanoplatelets with 7.1 at.% Ag was approximately 4.3 and 4.6 times higher than that of Ag-free Bi₂Se₃ nanoplatelets. The possible factors could contribute to this enhancement in photocurrent. (1) narrow band gap (~0.35 eV) of Bi₂Se₃, (2) Schottky field rise between Ag and Bi₂Se₃, (3) SPR effect caused by Ag, and (4) highly conductive surface
between Ag and Bi$_2$Se$_3$. As a result, proper Ag deposition can significantly enhance the photosensitivity of Bi$_2$Se$_3$ nanoplatelets under both UV and visible light, making them promising materials for photodetector applications.

**PP-ThP-2** Modeling and Synthesis of Long Scale Coherence Time Vacancy Defects in Silicon Carbide via Pulsed UV Laser and Photonic Curing for Industrial Scale Qubit Manufacturing, N. Khatoon, S. Khalili, Douglas Chrisey, Tulane University, USA

Qubits have unique capability to exhibit superposition and entanglement which makes them stand out to exist in multiples states simultaneously with ability to perform parallel computations. Serving as a fundamental building block of Quantum computers (QC) which leverages the superposition and entanglement of Qubits to perform quantum parallel operations at exponential speed. The applications of QC include cryptography, solving optimization problems, materials science, drug discovery and materials science. IBM Quantum System One is the first QC powered by 127-Qubits reported by RPI of Troy, NY. The unmatching wonders of Qubits comes with certain challenges to make and build QC such as their susceptibility to environmental noise and decohering, and difficulty in their fabrication and scalability. In this work we utilized pulsed UV laser and a broad spectrum (220-1500 nm) intense and short (0.03–100 ms) pulsed light (called photonic curing) to create and anneal the vacancy defects in silicon carbide (SiC) respectively. The study of vacancy formation will help to explore the mechanism of defect formation after laser irradiation as well as the mechanism of the subsequent photonic annealing of residual damage. The combination of these processes will give us an extensive combinatorial library of data to be used to train a deep learning neural network algorithm to predict the best possible Qubit defect architectures, processing conditions, and their expected performance. Excimer lasers like ArF (10 nsec, 193 nm) are efficient in creating color centers with 6.42 eV photons and can even etch SiC at a high enough laser fluence, < 2 J/cm$^2$. We propose to use an ArF excimer laser or a quintupled YAG (266 nm) and to optimize the conditions for different defect constructs and test their efficacy as defect-based Qubits. The as created defects will then be selectively annealed using photonic curing, which initiates rapid transformations, and reactions due to non-equilibrium processes. The acquired dataset will serve as the foundation for crafting a machine learning algorithm. This algorithm will be trained using innovative open-ended material selections to ensure statistically reliable predictions for future Qubit outcomes, with accuracy that can be empirically verified. Combination of Pulsed UV laser and photonic curing offers an instantaneous and roll-to-roll compatible approach for large-scale synthesis of Qubits.

**PP-ThP-3** Comparison of Metal Drift in SiO$_2$ film for Co, Ru, and CoRu, Yi-Lung Cheng, H. Zhang, B. Liao, National Chi-Nan University, Taiwan

Cobalt (Co) and ruthenium (Ru) have been proposed to replace copper (Cu) as a conductor in the next generation interconnects. In this study, the drift of Co, Ru, and CoRu in the SiO$_2$ film was investigated by flatband voltage ($V_b$) shift and time-dependence-dielectric-breakdown (Tddb) measurements. After constant-voltage-stress at positive polarity, larger negative $V_b$ shift was observed for Co, while Ru and CoRu had positive $V_b$ shift. Moreover, TDDb lifetimes stressed at positive and negative polarities were significantly divergent for Co, indicating that Co is affected by metal drift. Therefore, Ru and CoRu are suitable for barrierless integration schemes.

**PP-ThP-4** Recirculating Atmospheric Inductively Coupled Plasma (Icp) Beam Systems for Conversion of Si Sawdust in Si Nanoanode, Michael ryaboy, UC Berkeley, USA

Policies encouraging the reuse of waste products are becoming increasingly popular so as to avoid the negative impact on the environment and human health. Nowadays, silicon ingots are into strips a few hundreds of microns thick (wafers) that are the base of solar cells. Inefficiently, ca. 45% of Qubits reported by RPI of Troy, NY. The unmatching wonders of Qubits comes with certain challenges to make and build QC such as their susceptibility to environmental noise and decohering, and difficulty in their fabrication and scalability. In this work we utilized pulsed UV laser and a broad spectrum (220-1500 nm) intense and short (0.03–100 ms) pulsed light (called photonic curing) to create and anneal the vacancy defects in silicon carbide (SiC) respectively. The study of vacancy formation will help to explore the mechanism of defect formation after laser irradiation as well as the mechanism of the subsequent photonic annealing of residual damage. The combination of these processes will give us an extensive combinatorial library of data to be used to train a deep learning neural network algorithm to predict the best possible Qubit defect architectures, processing conditions, and their expected performance. Excimer lasers like ArF (10 nsec, 193 nm) are efficient in creating color centers with 6.42 eV photons and can even etch SiC at a high enough laser fluence, < 2 J/cm$^2$. We propose to use an ArF excimer laser or a quintupled YAG (266 nm) and to optimize the conditions for different defect constructs and test their efficacy as defect-based Qubits. The as created defects will then be selectively annealed using photonic curing, which initiates rapid transformations, and reactions due to non-equilibrium processes. The acquired dataset will serve as the foundation for crafting a machine learning algorithm. This algorithm will be trained using innovative open-ended material selections to ensure statistically reliable predictions for future Qubit outcomes, with accuracy that can be empirically verified. Combination of Pulsed UV laser and photonic curing offers an instantaneous and roll-to-roll compatible approach for large-scale synthesis of Qubits.

The FTIR spectra of the Si-coated films exhibited a characteristic band at around 1075 cm$^{-1}$, corresponding to the asymmetric stretching vibrations of Si–O–Si. Carbon based coatings displayed a broad band at around 1600 cm$^{-1}$ related to C–C bonding vibrations. Raman spectra of carbon coatings showed the typical D and G bands which are characteristic of amorphous carbon. SFE was about 45 mN/m for carbon- and about 20 mN/m for silicon-based coatings, while that of the untreated polymers is in average 30 mN/m. SEM cross-sections allowed for an estimation of coating thickness between 50 and 150 nm, which is considered to be neglected in conventional recycling processes. Depending on thickness and chemical composition, barrier properties improved by 20 to 50%, with Al-PVD coating showing the best performance with an improvement of up to 10 times.

**PP-ThP-6** Design and Manufacturing of Low-Cost Atomic Layer Deposition System to obtain Semiconductor and Dielectric Thin Films, J. Navarro-Rodriguez, F. Mateos-Anzaldo, Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico; Jesús Román Martínez-Castelo, Facultad de Ingeniería, Mexican-Universidad Autónoma de Baja California, Mexico; A. Pérez-Sánchez, J. Ruiz-Ochoa, Facultad de Ciencias de la Ingeniería y Tecnología, Valle de las Palmas-Universidad Autónoma de Baja California, Mexico; A. Gaytán-Pérez, Facultad de Ciencias de la Ingeniería y Tecnología-Valle de las Palmas-Universidad Autónoma de Baja California, Mexico; H. Tiznado-Vázquez, Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México; N. Nedy, Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico

This work describes the design and manufacturing of a lab-made ALD system. In the system, the chamber reactor was designed using SolidWorks software and machined with a lathe. The chamber is of aluminum and has temperature area of the swirling plasma stream for incremental downsizing is more rational.

The first objective of this proposal is to develop a method of recycling of Si waste in the high-temperature in the plasma loop using the multi-step plasma-thermal plasma recirculation process. Such recycling involves three stages. The first stage consists of in the conversion of the Si sawdust into the Si melted droplets in thermal plasma flowing in a non-oxidant environment; the second stage consisted in the superficial incremental vaporization of the shells of the melted droplets; the third stage consisted in collecting the downsized Si nanoparticles on the current collector to manufacture the Si anode, simultaneously preventing its oxidizing during the whole process operation.
an internal diameter of 3.5 inches, with two entries for precursors with a diameter of 1/64 inch, and one exit with a diameter of 1/2 inch. To dose the precursor and the oxidant, two 3-way diaphragm valves were used. This type of valves allow a continuous flow of nitrogen as carrier gas and permit formation of high- and low-pressure zones, which allow a high-speed deposit. To heat the system, a flat circular resistance controlled by a PID was used. The control of all the system is carried out using a graphical interface of LabView.

PP-ThP-7 Neon Addition to the Plasma for Enhanced Ionization in the Deposition of Cr films by HiPIMS-DOMS, João Carlos Oliveira, University of Coimbra, Portugal; S. Adebayo, University of Coimbra, Nigeria; R. Serra, University of Coimbra, Portugal

In magnetron sputtering-based deposition processes, particles that arrive at oblique angles relative to the growing film’s surface promote the atomic shadowing effect which, ultimately, results in porous and underdense columnar microstructures. Energetic particles bombardment helps to prevent this effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and/or triggering re-deposition processes. However, bombarding the film’s surface with highly energetic particles comes with a heavy cost: the formation of a high density of defects, which disrupts the crystalline structure of the films, and the creation of compressive stresses.

In a previous work, the authors have shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material[1]. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment. The most straightforward route to achieve high ionization of the sputtered species in HiPIMS is to increase the peak power. However, this also increases the average energy of the sputtered species and brings about energetic bombardment. Partially replacing Ar by Ne in the process gas promotes an increased mean electron energy which increases plasma ionization, as the ionization energy of Ne (21.56 eV) is significantly higher than that of Ar (15.75 eV). In this work, partial substitution of Ar by Ne in the DOMS process gas was investigated as a mean to increase the ionization degree of the sputtered species without increasing their average energy.

In this work, Cr thin films were deposited by DOMS in pure Ar and mixed Ar + Ne plasmas up to 60 % Ne. Adding Ne to the plasma resulted in 25 % increase in the ions saturation current density (ISCD) as measured by an electrostatic flat probe placed at the substrate location. All the deposited films have a dense and compact columnar microstructure with an almost complete (110) out of the plane preferential orientation. The lattice parameter of the films increased with increasing Ne content in the plasma while their surface roughness decreased from 6 to 3 nm. The hardness and young’s modulus of the Cr films were evaluated by nanoindentation.

PP-ThP-8 Study of Transitional Element Dopants on CeO2 Thin Films for Resistance Random Access Memory Application, A. Sun, Department of Chemical Engineering and Materials Science, Yuan Ze University, Taiwan; Sea-Fue Wang, Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei 106, Taiwan

In this study, an RF magnetron sputtering method was employed to fabricate a 60 nm CeO2 film as the insulating layer for Resistive Random-Access Memory (RRAM). Platinum (Pt) layers, each 100 nm thick, were utilized as the upper and lower electrodes. To investigate the impact of doping elements on device characteristics, elements such as La, Nd, Sm, Gd, and Y were introduced into the insulating layer. The findings revealed that La doping resulted in the most stable operation with the lowest operating voltage. The device exhibited excellent non-volatile properties, achieving over 2000 switching cycles, and maintained data storage for more than $10^7$ seconds.

X-ray Photoelectron Spectroscopy (XPS) analysis indicated that the metal elements in the doped film were bound with oxygen rather than existing in a pure metal state. Based on these results, it is hypothesized that the conductive path in the film is composed of oxygen vacancies. The controlled formation and breakage of conductive filaments by the input voltage allow the device to undergo high and low resistance state changes, showcasing its potential application in resistive memory technologies.

Furthermore, XPS analysis of bond energies suggested that doping weakened the interaction between Ce and O, making it easier for oxygen ions to migrate. This effect contributes to a reduction in the working voltage of the device.

PP-ThP-9 Mechanical Properties Thermal Stabilities of Multilayered AIcBN/AITiSiN Hard Coatings, Chung-En Chang, T. Tsai, H. Feng, M. Yang, Y. Chang, National Formosa University, Taiwan

AIcN and AITiN coatings have been applied widely in cutting tools and mold dies because of good mechanical properties, tribological properties and oxidation resistance as resulting from the incorporation of Al into CrN and TiN. The AIcBN coating possesses good oxidation resistance even at 1000 °C while the AITiN has high hardness at high temperature. To make further improvement of these two coatings, multilayer coatings with alternate AITiN and AIcBN layers have been designed. In addition, it is known that adding Si and B to coatings can effectively enhance their mechanical properties. Through combining the characteristics of Si and B, multicomponent and multilayer AIcBN/AITiSiN coatings were prepared using an electro-magnetic controlled cathodic arc ion plating method, and their thermal stabilities at high temperature up to 900 °C and 1000 °C were studied to align with the requirements of high-temperature applications. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM) equipped with energy-dispersive X-ray spectroscopy (EDS). In this study, multilayered AIcBN/AITiSiN coatings were deposited using cathodic arc evaporation with periodic layering structures. Nanoindentation measurements and SEM/TEM observations revealed that when the samples were subjected to vacuum annealing at 900 °C, the addition of Si and B not only suppressed the unfavorable formation of h-CrN and w-AlN phases that would deteriorated mechanical properties, but also resulted in the phenomenon of increased coating hardness due to the formation of nanometer-sized c-TiN and c-AlN after the phase decomposition of the coating. In comparison, the hardness of AIcBN coatings decreased continuously with increasing temperature due to the absence of inhibiting h-CrN formation. And, strengthening mechanisms from the phase decomposition was not observed in this AIcBN at high temperature. The AIcBN/AITiSiN coatings exhibited the capability to maintain or even enhance their mechanical properties at high temperature. In addition to the improved oxidation resistance, secondary hardening mechanism at high temperature could contribute to the successful application of such coatings in high-temperature environments.

PP-ThP-10 CVD Equipment: Yesterday, Today and Tomorrow, Anne Zhang, H. Strakov, IHI Bernex AG, Switzerland

Bernex coating systems are used for the coating of tools and components with a thin (less than 0.1 mm) coating on the basis of metal-ceramic compounds for the purpose of reducing wear and/or friction, providing corrosion and oxidation protection or to obtain other specific surface characteristics. The CVD coating processes are based on chemical reactions on hot surfaces between reactant gases, which directly yield the solid coating material.

Bernex coating systems are highly modular and provide significant process flexibility. Based on customer requirements, the systems can be pre-configured upon purchase, or extended at any time. This not only includes hardware and software components, but also comprises external units and accessories.

New process modules and general improvements on hardware and software modules have been made available and will be presented, including future developments.

PP-ThP-11 Target Erosion Simulation in Full 3D for Optimization of Target Utilization in Magnetron Sputtering, Krystof Mrózek, P. Zikán, A. Obrusnik, PlasmaSolve s.r.o., Czechia

Target utilization – fraction of target material sputtered over its lifetime - is one of the important factors in total cost of magnetron sputtering processes. One approach to increasing target utilization is movement of target surface, relative to magnetic field – for example rotation of cylindrical target. However, this approach is not always possible (e.g., for planar targets), or cost-efficient as it adds complexity and moving parts to the cathode design.

Another way of optimizing the target utilization is through the magnetic field. Electrons are trapped by the magnetic field, move above target, and ionize the gas. Created ions then impact the target surface and sputter its material. By changing the shape of the magnetic field, it might be possible to extend the ionization region, thus increasing the area of target impacted...
by ions (therefore eroded). However, it is very difficult, time-consuming, and expensive to do this optimization experimentally. Each magnetic field configuration has to be tested on separate cathode, the cathode has to be eroded for a long time in order for erosion groove to be visible, only several cathodes can be tested at a time (4-8, depending on the coater), and large part of the target material is wasted.

Reliable target erosion model solves all of the aforementioned issues. Presented model, developed by PlasmaSolve within the OPTIMISM project, predicts the shape of racetrack and profile of an erosion groove based on full 3D geometry of a cathode (cylindrical, planar), pressure, power level, and, most importantly, shape and strength of an arbitrary external magnetic field. The model is based on an iterative Monte Carlo algorithm. The computation takes from a few hours (for ca 50 cm cathodes) to about a day (for 4 m glass coater cathodes). Thanks to this, the model can serve as a fast prototyping tool for target erosion optimization studies in real geometries.

This contribution will present a brief overview of the model and its results for different cathode geometries, metallic and poisoned state of the target and different topologies of the magnetic field, with focus on the effect of the magnetic field on racetrack shape and target utilization.

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Topical Symposium on Sustainable Surface Engineering
Room Golden State Ballroom - Session TS1-ThP
Coatings for Batteries and Hydrogen Applications - TS1 Poster Session

TS1-ThP-1 Formulating Advanced Materials for Energy Storage using Composite Solid-State Electrolyte Incorporating Al-Doped LLZO (Al-LLZO) in NCM811 for Solid State Lithium-Metal Batteries. C. Yang, Ming Chi University of Technology, Taiwan; Adele Tarekegn Habte, Ming Chi University of Technology, Ethiopia

The development of advanced materials for energy storage devices has been of utmost importance for the transition towards clean and renewable sources of energy. In this context, solid-state lithium metal batteries have shown promising features such as high energy density, good ionic conductivity, and safer performance than conventional batteries. The primary aim of this research work is to develop a free-standing composite solid-state electrolyte (CSE) that incorporates Al-doped Lithium Lanthanum Zirconium Oxide (LLZO) into NCM811 for solid-state lithium-metal batteries followed by solution casting method. The researcher used various characterization techniques such as XRD, FT-IR, EIS, and SEM to analyze the structural and morphological properties as well as the impedance of the solid-state composite electrolyte. This material gives 4.9 × 10⁻⁴ Scm⁻¹ ionic conductivity at room temperature. The NCM811/CSE/Li exhibited after 100 cycles a specific capacity of 125.35 mAhg⁻¹ and a capacity retention of 99.08 % at ambient temperature and with the rate of 0.2C.

TS1-ThP-2 Corrosion Stability and Electrical Conductivity of PVD Coated Electrolyzer Bipolar Plates, Martin Welter, KCS Europe GmbH, Germany; N. Krupe, Schaeffler Technologies AG & Co. KG, Germany; R. Cremer, KCS Europe GmbH, Germany; M. Öze, N. Bagcivan, Schaeffler Technologies AG & Co. KG, Germany

Bipolar plates (BPP) are one of the essential components of electrolyzer stacks for the generation of pure hydrogen by water electrolysis. In order to replace conventional and expensive titanium based BPP, stainless steel becomes more and more important against the background of increasing production volume due to cost and functional reasons. On the other hand, some requirements exist, which limit the use of stainless steel BPP in electrolyzers. Firstly, due to harsh corrosive conditions, the application of the stainless steel BPP requires the protection against corrosion. Secondly, the electrical conductivity of BPP must remain constantly low over the entire service life.

As part of the H2Giga StacIE joint project, KCS Europe developed titanium-based PVD protection layers for stainless steel BPP in order to fulfill the demanding requirements of water electrolysis. In addition to the functional suitability of the coatings, the economic viability and suitability for large-scale production was kept in mind. Therefore, the coatings were deposited by means of a tailored inline coating system, applying PVD technology. The coating system enables an easy scale up to larger production quantities in future. Measurement of Interfacial Contact Resistance at 10 bar and Linear Sweep Voltammetry of the coatings revealed promising results regarding corrosion stability and electrical conductivity prior and after electrochemical cell tests on laboratory scale adapting electrolyzer cell conditions.

TS1-ThP-3 PVD Core-Shell-Catalysts for Water Electrolysis, Jan-Ole Achenbach, KCS Europe GmbH, Germany; M. Berger, Institute of Technical and Macromolecular Chemistry, Germany; P. Pilaski, The Hydrogen and Fuel Cell Center - ZBT, Germany; R. Cremer, KCS Europe GmbH, Germany

The expected increasing demand of hydrogen in the upcoming years requires adequate electrolysis capacities in order to be able to serve the market. One technology for mass production of hydrogen is the alkaline polymer membrane water electrolysis (AEM-WE). Heart of AEM-WE are the catalysts, which enable the decomposition of water at low energy input. Therefore, the availability of sufficient and suitable catalysts is a limiting factor for high H₂ production volumes.

Within the research project H2Giga AlFaKat, KCS Europe follows up the approach of replacing the usual expensive catalysts containing precious metals by cheaper core-shell particles. Therefore, particles of a suitable low-cost material are activated by the deposition of a more expensive catalyst material by means of physical vapor deposition (PVD). For the realization, a coating demonstrator was developed and validated in the project. Thereby, the basic suitability, the efficiency and useability for mass production of the concept as well as the coating growth, homogeneity and properties were investigated. Analyses of the core-shell-particles showed a homogeneous coating of the core particles after processing by PVD coating demonstrator. Further investigations regarding catalytic activity revealed high activity of new PVD catalyst. In this context, a comparison confirmed similar activity of PVD core-shell-catalyst and pure catalyst. Therefore, only the top layer of the core-shell-catalyst is active, meaning the same performance at significantly less material input. The results prove that a reduction of catalyst material by Core-Shell-concept is possible.

Topical Symposium on Sustainable Surface Engineering
Room Golden State Ballroom - Session TS3-ThP
Solar Thermal Conversion - TS3 Poster Session

TS3-ThP-1 Tailoring the Structural, Optical and Electrical Properties in Perovskite Nickelates Through the Tilt Control of Nd₃Sm₃NiO₁₀ Thin Films, Zil Fernández-Gutiérrez, T. Easwarakhantham, S. Bruyère, D. Pilloud, S. Barrat, F. Capon, Institut Jean Lamour - Université de Lorraine, France

Rare-earth nickelates (RNiO₃) are functional oxides with a vast landscape of properties, with the metal-insulator transition (MIT) being the most attractive one. This latter can be modified by varying the rare-earth atomic composition (R²⁺₉Au₃NiO₁₀) and the consequent tilt of the crystalline structure. However, obtaining solid solutions of this perovskite family is even more complex due to the specific composition control and the bottleneck that has been their synthesis over the years. Even so, this work aims to customize the thermochromic behavior of the layers to enhance infrared thermal regulation in solar collectors between 60 and 80 °C. Therefore, Nd₃Sm₃NiO₁₀ thin films were synthesized using reactive magnetron sputtering and air-annealing. Comprehensive XRD and TEM analysis confirms the efficient synthesis of various crystallized nickelates within the SmNiO₃ to NdNiO₃ range. This methodology facilitates the tunability of MIT temperatures between -80 and 120 °C as Sm atoms progressively replace Nd atoms. Optical performance, assessed through FTIR spectroscopy, aligns with literature-reported MIT temperatures. Additionally, a detailed examination of the structural, electrical, and electronic properties of the NdₓSm₃₋ₓNiO₁₀ combination is presented. Lastly, ellipsometry measurements reveal a metal-like to dielectric-like phase change in the imaginary part of the dielectric function with photon energy, while the real part indicates oxidation in the upper film volume. These findings advance the understanding of NdₓSm₃NiO₁₀ nickelate thin films and their potential applications in thermochromic devices for solar energy utilization.
Coatings and Surfaces for Thermoelectrical Energy Conversion and (Photo)electrocatalysis - TS4 Poster Session

**TS4-ThP-1** Dopant-defect engineering in SnS$_2$ Thin Films for Improved Gas-phase Photocatalytic CO$_2$ Reduction, **Tadios Tesfaye Mama**, Department of Chemistry, National Taiwan University, Taiwan; **M. Qorbani**, Center for Condensed Matter Sciences, National Taiwan University, Taiwan; **A. Hailemariam**, Department of Applied Chemistry, National Yang-Ming Chiao Tung University, Taiwan; **A. Sabbah**, Center for Condensed Matter Sciences, National Taiwan University, Taiwan; **S. Kholidattussadiah**, Department of Physics, National Taiwan University, Taiwan; **C. Huang**, Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan; **L. Chen**, Center for Condensed Matter Sciences, National Taiwan University, Taiwan; **K. Chen**, Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan

To address the issue of CO$_2$ amount increment in the Earth’s atmosphere, various semiconductor photocatalysts have been employed to convert CO$_2$ into valuable products. Designing an efficient photocatalyst that can activate the CO$_2$ molecule with the least amount of activation energy is one of the challenging problems. In this regard, we report a combined experimental and computational analysis on a thin film of SnS$_2$ doped with phosphorous ions at various ion doses. Thermal evaporation followed by sulfurization and ion implantation processes were used to prepare the regulated amount of phosphorous ion-implanted 20-nm SnS$_2$ thick thin films. Our findings reveal that phosphorous doping synergistically enhances light harvesting by lowering the band gap and energetically stable CO$_2$ binding sites with the lowest activation energy. The optimized P-SnS$_2$ photocatalyst has a three times higher CO$_2$ conversion rate than the pristine one, with a high selectivity of about 92% towards CH$_4$ formation. Because Phosphorous play a vital role in the activation of CO$_2$ by serving as an active site and due to its low electronegativity, it increases the charge density of the Sn atom adjacent to it. Also, P-doping affects the charge density of the neighboring S atom by serving as a bridge to improve the charge distribution between Sn and S. This degree of electron density alteration would facilitate the electron transfer in the photocatalytic reaction. NAP- In-situ XPS and XAS results with formation energy, Bader charge, and Gibb's free energy calculations are used to carefully assess the overall impact of phosphorus in the SnS$_2$ sample. DFT calculations accord well with the experimental findings and help us to know the reaction pathway. We anticipate that our result will motivate additional ion implantation research to modify the material’s active site for CO$_2$ reduction and examine its CO$_2$ conversion capability and related optical and charge transfer behavior.

**TS4-ThP-2** Copper-Based Coatings on Polyactic Acid for Electrocatalytic CO$_2$ Reduction, **Maria José Lima**, University of Minho, Portugal; **J. Castro**, **S. Carvalho**, University of Coimbra, Portugal

The climate crisis caused by global warming is recognized by the United Nations (UN) as a trigger for catastrophic effects such as weather extremes and natural disasters. Carbon dioxide (CO$_2$) emissions constitute about three-quarters of the total greenhouse gases (GHG) released and have gathered global attention due to their significant contribution to global warming.

Developing new catalytic processes can accelerate the transition to a more sustainable Earth. Electrocatalytic methods are the most promising of all the catalytic processes because they are energy efficient, selective, easy to control, and flexible. They are also known as the most viable solution for the CO$_2$ reduction reaction (CO$_2$RR).

Metallic copper has notable electrical conductivity, making it suitable for many electrode-based applications. Additionally, copper-based materials were reported to be active and selective electrocatalysts capable of producing hydrocarbons from the CO$_2$RR. However, the updated version of the Element Scarcity—EuChemS Periodic Table by the European Chemical Society brings attention to the limited abundance of copper. Ensuring a sustained supply of this element is a significant challenge. Utilizing thin film coatings to produce electrodes is a potentially practical approach to mitigating element shortages. Furthermore, Cu-based electrodes using a polymeric skeleton can provide several benefits concerning cost, material accessibility, and weight.

This work used polyactic acid (PLA) as the substrate for Cu-based electrodes. PLA is widely used in additive manufacturing, a low-cost technique that enables the fabrication of 3D-structured electrodes. Magnetron sputtering (PVD technique) was applied to develop copper metallic surfaces on PLA. Different coatings with Cu/CuO/Cu layers were produced. Anodization was a secondary technique applied to enhance the electrochemical active surface area. The CuO in the middle of the coating might act as a barrier material to stop the oxidation reaction during the anodization process while maintaining film adhesion. The chemical and morphological characterization of the resulting films will be discussed, as well as the electrochemical properties for CO$_2$RR applications.
Coatings for Biomedical and Healthcare Applications
Room Palm 3-4 - Session MD3-FrM
Bioactive Surfaces
Moderators: Valentin A.R. Barão, University of Campinas (UNICAMP), Brazil; Sandra E. Rodil, Universidad Nacional Autónoma de México
8:00am MD3-FrM-1 The Investigation and Application of Carbon-Based Composite Electrochemical Biosensor for Parkinson's Disease, Tzu-Yu Chen, Y Shen, J. Huang, National Cheng Kung University (NCKU), Taylor Parkinson's disease (PD) mainly causes symptoms such as involuntary tremors and hypokinesia in patients. In recent years, the detection method is single emission computed tomography, which the nuclear medicine drug is injected into the patient's body and observing the distribution of dopamine in the brain. However, tomography method can only be performed in hospitals and cannot be popularized in general clinics. Hence, early detection will help prevent the occurrence of the disease. In this project, carbon-based composite materials will be utilized to electrochemical biomedical sensors, which is measuring the amount of dopamine, urea, vitamin C and other key substances for Parkinson's disease to prevent the occurrence early. This study utilized graphite oxide (GO) as a carbon-based composite material, following the method of the Weng group with Modified Hummer’s method for GO preparation. Initially, 2 grams of graphite powder were used as a precursor, mixed with 98 milliliters of concentrated sulfuric acid, stirred for 10 minutes. Subsequently, 2 grams of NaNO3 were added, and the resulting mixture was stirred and cooled in an ice bath for 30 minutes. With the temperature below 15°C, 12 grams of KMnO4 were slowly added, and the stirring continued for 30 minutes. After removing the ice bath, the mixture was heated to 78°C and maintained for 2 hours, followed by the addition of 80 milliliters of deionized water with continued stirring for 15 minutes. The reaction was terminated by adding 200 milliliters of distilled water and 30% H2O2, resulting in a yellow-brown color. Adding 20 milliliters of HCl and stirring until no bubbles were produced, the GO was collected using a filter, washed with alcohol and deionized water several times. The collected GO was then placed in a vacuum oven and dried overnight at 45°C. In Raman spectrum of GO, where the in-phase vibration (G band) of GO is at 1500.48 cm⁻¹ and the disorder band (D band) of GO is at 1331.82 nm. In FT-IR analysis, GO has a peak at 1016 cm⁻¹, which is attributed to the C-O bond, confirming the presence of oxide functional groups after the oxidation process. The peaks in the range of 1623 cm⁻¹ to 1694 cm⁻¹ show that the C= =O bond remained. The broad peak at 2779 cm⁻¹ to 3626 cm⁻¹, which is attributed to the O-H bond. In the future, we will modify GO on a glassy carbon electrode surface to create an electrochemical sensor with high sensitivity. This sensor is designed for the detection of urea, vitamin C, and dopamine. We expect that the sensitivity will reach 10μmol/L and even better.
8:20am MD3-FrM-2 Electrochemical Aspects of Interaction between Surface Engineered Metal Implants and Biological Environment, Aleksey Yerokhin, University of Manchester, UK
INVITED Interfacial redox reactions involving charge transfer between metallic biomaterials and biological environment are of particular interest for development of new generation of biomedical implant devices. Controlling reaction kinetics can help achieving the targeted biological functionality such as osteogenic and biocidal activity, or drug-release ability of surface engineered smart and multifunctional implants; this is also important when minimising corrosion rates to enhance long-term performance of permanent metal implants or controlling degradation behaviour of bioabsorbable implants. Extensive exploratory research at the interface of biomedical and materials engineering often takes advantage of lab-scale electrochemical methods for express assessment of relevant implant properties. However interpreting results of the tests that were originally designed to evaluate aqueous corrosion of metals in engineering applications and are now being adopted to study more complex interactions between implants and biological environment is not straightforward. This talk will revisit electrochemical fundamentals of most common corrosion tests based on potentiodynamic polarisation and frequency response analysis, with a focus on implications for the
MD3-FrM-4 Metal Oxide Coatings on 3D Printed Templates to Promote Osteogenesis, Pheaida Silva-Bermudez, D. Marquecho-Marin, Universidad de Ingeniería y Tecnología, Colorado, USA, M. A. López, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico; S. Rodil, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México; G. Prado-Prone, División de Investigación y Estudios de Posgrado, Facultad de Odontología, Universidad Nacional Autónoma de México; J. Gracia-López, Universidad de Ingeniería de Tefidos, Terapia Celular y Medicina Regenerativa, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico; B. Millán-Ramos, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

Biodegradable materials with suitable properties to direct the biological response and simultaneously meet biomechanical requirements are crucial for the development of orthopedic and dental implants. Implants’ mechanical properties are mainly dependent on the bulk material while biological response is mainly dictated by the surface of the implants. Coatings with biological desirable properties, such as osteoinduction and osteoconduction, in the case of bone tissue repair, represent appropriate options to tailor the surface of biodegradable, three dimensional porous scaffolds, and ultimately develop novel biomaterials appropriate to be used during orthopedic and dental treatments. ZrO2 and TiO2 are of great interest as coatings, since they might promote adequate osteoinductive, osteoconductive and oseointegration processes, in a similar way as it has been proved for the native oxide film formed on Ti- or Ti-Zr-based orthopedic/dental implants upon implantation in the body. Quasi-amorphous TiO2 and semycrystalline ZrO2 thin films were deposited on polyacrylic acid 3D porous scaffolds with different porosity. Deposits were performed by magnetron sputtering using pure metallic targets, reactive Ar/O2 atmospheres, and RF-power. The coated and uncoated samples were characterized by Scanning Electron Microscopy, X-Ray Photoelectron Spectroscopy, Tension Mechanical assays, Differential Scanning Calorimetry, Thermogravimetric analysis and Water Contact Angle. Human mesenchymal stem cells were plated and cultured on coated and uncoated samples to study their biological response. 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. At 7-14 days of culture, cell differentiation to the osteoblastic phenotype was assessed by immunocytochemistry, and quantitative ELSA assays against characteristic markers of the osteoblastic phenotype such as osteopontin and runx2. Phosphatase alkaline expression was also quantified. The findings indicate that the PEO+TiO2 coatings have shown remarkable mechanical and electrochemical properties, the impact of their simultaneous exposure to corrosion and wear remains unexplored. Moreover, the prevalence of antibiotic resistance, fueled by the overuse of antibiotics, necessitates innovative antimicrobial surface coatings. This study focuses on the tribocorrosive behavior of hybrid coatings on titanium, aiming to enhance wear and corrosion resistance, impart antibacterial qualities, and ensure bioactivity. Oxidation of titanium (TiGr2) was performed using the plasma electrolytic oxidation (PEO) technique, followed by the deposition of a biabsorbable polymer film (PCL) embedded with ZnO nanoparticles (NPs). These coatings were characterized through scanning electron microscopy, energy-dispersive spectroscopy, X-ray diffraction, and contact angle analysis. Tribocorrosion tests were performed in an artificial saliva medium, using a ball-on-plane reciprocating sliding configuration in a tribometer (Anton-Paar), connected to a potentiostat (Iwum). Further in vitro evaluations assessed the bioactivity and antibacterial properties of the coatings. The findings indicated that the PEO+PCL+ZnO np coatings not only improved tribocorrosion resistance but also revealed bioactive behavior and were effective against S. aureus and P. aeruginosa. The enhanced tribocorrosion performance, coupled with the bioactive and antibacterial capabilities of the coatings, opens the way for a new generation of implant surfaces with improved clinical performance.

MD3-FrM-9 New Approach for Controlling Peri-Implant Infections Integrates Multifunctional Photocatalytic Coating and Photodynamic Therapy – in Vitro and in Vivo Study, Valentim A. R. Barbó, B. Nagay, R. Costa, C. Dini, A. Santos, University of Campinas (UNICAMP), Brazil; L. Cintra, Sao Paulo State University (UNESP), Brazil; N. da Cruz, L. Faverani, Sao Paulo State University (UNESP), Brazil; J. van den Beuckeen, Radboudumc, Netherlands

Although peri-implant infections reduce the longevity of dental implants, there is still no gold-standard therapeutic strategy. Therefore, here we developed a visible light-responsive multifunctional bismuth (Bi)-TiO2 coating on titanium (Ti) surface to optimize the properties of dental implants and enhance antimicrobial photodynamic therapy (aPDT)-mediated microbial reduction. Bi-TiO2 experimental material was synthesized via plasma electrolytic oxidation (PEO). TiO2 and polished Ti were controls. Topographic, physicochemical, tribological, structural and photocatalytic properties were analyzed. In vitro microbial assays were performed under different light times (0, 1 and 5 min). In vitro cytocompatibility was evaluated in mesenchymal cells and gingival fibroblasts. The antimicrobial activity and inflammatory response were investigated in vivo (in a subcutaneous tissue of rats). PEO created rough, superhydrophilic and crystalline surfaces, with higher hardness values and tribological performance compared to Ti control (p<0.05). Bi-TiO2 was not cytotoxic and enhanced the microbial reduction mediated by aPDT (p<0.05) by promoting photocatalytic activity under visible light. The combination of Bi-TiO2 and aPDTreduced microbial viability and modulated the inflammatory response in vivo (p<0.05). The Bi-TiO2 coating is a promising strategy for rehabilitation with dental implants as it presents optimized surface properties and enhances microbial reduction and inflammatory modulation mediated by aPDT.
Note: This study was supported by the Sao Paulo Research Foundation (FAPESP, Brazil) (grant numbers: 2019/17238-6 and 2022/16267-5).

**Plasma and Vapor Deposition Processes**

**Room Town & Country B - Session PP5-FrM**

**Plasma Surface Interactions and Diagnostics**

Moderators: Yin-Yu Chang, National Formosa University, Taiwan, Arutjun P. Ehiasarian, Sheffield Hallam University, UK

8:00am PP5-FrM-1 The Role of Plasma in Plasma Enhanced Atomic Layer Deposition, Scott Walton, D. Boris, M. Johnson, V. Wheeler, US Naval Research Laboratory, USA; M. Sales, P. Litwin, NRC, USA; J. Woodward, US Naval Research Laboratory, USA; S. Rosenberg, Lockheed Martin Space Advanced Technology Center, USA; J. Hite, D. Pennachio, M. Mastro, US Naval Research Laboratory, USA.

**INVITED**

Plasma-enhanced atomic layer deposition (PE-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of selfterminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce amorphous, crystalline, and epitaxial films of varying types and characteristics. The plasma-based advantages come at the cost of a complex array of process variables that can drastically impact the growth modes and resulting film properties. Accordingly, understanding the process-structure-property relationship is both critical and challenging. We approach this problem by combining plasma diagnostics and material characterization techniques. Plasma diagnostics are used to inform the choice of process conditions for PE-ALD systems including VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the plasma used in commercial and research PE-ALD tools. In particular, we assess the spatial variation of plasma parameters, flux and energy of ions reaching the substrate surface, and the relative fractions of atomic and molecular species generated in the plasma under a variety of operating powers, gas substrate surface, and the relative fractions of atomic and molecular species. Measuring these values for various chamber conditions can not only aid in process development, but also facilitate process transfer, as well as the ability to precisely tailor material properties critical to specific applications. Nevertheless, the complexity introduced by plasma necessitates a more detailed understanding of the deposition environment. This study aims to characterize in situ the surface reactions occurring during electron cyclotron resonance (ECR) microwave plasma-assisted ALD and their influence on the deposited films, in this case using the examples of aluminium nitride (AlN) and titanium nitride (TiN). Trimethylaluminium (TMA) and tetrakis(dimethylamido)titanium (TDMATi) were used as precursors for AlN and TiN, respectively, with plasma-activated nitrogen serving as co-reactant. Two types of time-of-flight mass spectrometers (ToFMS) were used to identify neutral and ionic species produced during the sequential ALD cycles. Optical emission spectroscopy (OES) was utilized to identify the nitrogen species produced during the nitrogen plasma step, while Langmuir probe measurements determined the plasma spatial potential, density, and electron temperature as a function of microwave power and distance from the source. Finally, the chemical composition, thickness, density, and structure, as well as surface uniformity of deposited AlN and TiN thin films were investigated via a combination of scanning and transmission electron microscopy (SEM/TEM), X-ray reflectometry (XRR) and ellipsometry. This work offers insights on the complexity of plasma-assisted ALD processes and paves the way for informed optimisation and application-based customisation of deposited thin films.

9:00am PP5-FrM-4 Quantification of the Negative Oxygen Ion Yield, Diederik Depla, Ghent University, Belgium.

Many thin film applications are based on oxides. The optimization of the oxide properties is an on-going process and requires a deep understanding of the deposition process. A typical feature of reactive (magnetron) sputter deposition is the presence of negative oxygen ions. The presence of negative ions in gas discharges was already postulated in the very first paper on sputtering by Grove. In a magnetron oxygen containing discharge, two groups of ions can be identified based on their energy. Low energy ions are generated in the bulk of the discharge. The high energy ions are emitted from the oxide or oxidizing reactant surface. As these ions are generated at the cathode, they are accelerated by the electric field towards the growing film. Depending on the discharge voltage and the powering method, their energy is typically several tens to hundreds electron volt. As such the ions can have a strong impact on the film properties. Nevertheless, despite the many illustrative studies on the impact of negative oxygen ions, quantification is often lacking as the negative ion yield is only known for a few oxides. A compilation of several literature sources permits not only the prediction of the negative ion yield, but also a comparison amongst different oxides.


**INVITED**

Plasma polymer films are deposited via reactive intermediate species as formed in a low temperature plasma. Over the last decades, the understanding of the mechanisms behind plasma polymerization processes has steadily been improved, which will be discussed. Basically, the highly non-equilibrium conditions provide an average energy per molecule in the plasma, known as specific energy input (SEI), yielding plasma chemical reactions by inelastic collisions (excitation, dissociation, and ionization). Due to the related energy distribution, the probability for the activation mechanism to produce film-forming species can be described by a simple Arrhenius-like equation, where temperature is replaced by SEI. The potential of this approach to optimize plasma polymerization processes for surface functionalization is demonstrated on the basis of siloxanes, hydrocarbons, and further gaseous mixtures. Hexamethyldisiloxane (HMDSO) has been well studied in the past revealing insights into the plasma chemical reaction pathway, which can thus be used as a model monomer following Arrhenius-like behaviour. Nano-scaled controlled film deposition is obtained considering the flux of film-forming radicals, etchants, and energetic species. Thus, dense to porous, hydrophilic to hydrophobic films can be generated. Such films are investigated for the chemical modification of catalytic substrates, as durable barrier layers and bioactive surfaces.

Furthermore hydrocarbon molecules are mixed with reactive gases such as CO2 or NH3 to investigate the penetration of radicals into complex 3D structures, which is studied using cavity techniques. Various applications in technical and biomedical fields will be presented.

Finally, an outlook is given about the applicability of the presented approach for plasma gas conversion based on comparable plasma chemical processes.

10:00am PP5-FrM-7 Advanced Ion Energy Measurement Tools to Understand the Effect of Ion Energy on Film Properties, Angus McCarter, Impedans, Ireland.

In any plasma assisted deposition process, ion surface interactions can influence the film properties significantly. Ion energies determine if deposition, sputtering or implantation occurs, while ion flux determines the rate of this processing. The ion/neutral ratio impacts the thin film properties. Measuring these values for various chamber conditions can not only aid in process development, but also facilitate process transfer, as these ion parameters are the direct process drivers.

We, at Impedans Ltd, offer solutions to the requirements of ion energy and flux measurements. Our collection of sensors includes the Semion, Quantum and Vertex RFEAs for wafer level measurements. In this talk we will demonstrate the role of energetic ions in plasmas and how they affect the properties of materials etched or deposited in plasma processing. We will show how to use measured ion flux, ion energies and ion-neutral fractions to optimize industrial plasma-assisted processes. The Semion RFEA measures the ion energies hitting a surface, the ion flux, negative ions, and bias voltage at any position inside a plasma chamber using an array of integrated sensors [1-3] over a region of 300 mm large size wafer down to 44 ns time resolution. On the other hand, the Quantum system is...
an energy resolving gridded quartz crystal microbalance (QCM), used to measure the ion-neutral fraction hitting a surface inside a plasma reactor. This instrument also measures the etching/deposition rate, ion energy, ion flux and bias voltage [4, 5]. The Vertex RFEA design has a variable aspect ratio (AR), controlled using a potential difference between its grids. A variable AR controls the ion angular spread passing through the sensor for detection. The Vertex product produces a plot of ion energy distribution versus AR [6].

We will highlight the successful measurements done by our RFEA product range in selected applications (like pulsed source and /or bias, tailored waveform biasing, etc) enabling better control of film properties of different materials and various plasma chemistries.

References

Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP7-FrM

Modeling and Data-Driven Methods for Process Design, Analysis and Control
Moderators: Clemens Nyffeler, Evatec AG, Switzerland, Petr Žíkán, PlasmaSolve s r o., Czechia

10:20am PP7-FrM-8 Digitalization Finds Its Way Into PVD Coating Facilities, Ton Hurkmans, A. Heike, IHI Ionbond Group, Netherlands

Company IHI Ionbond provides PVD coating services across many industries. This is done through multiple so-called coating centers across the northern part of the globe. It might come as a surprise, but while running such a coating center, the production of the final coating is the least of the concerns. PVD coating equipment has become more and more reliable with reproducible output. Even with good employees, the human factor is still the weakest link and never consistent. The only way to overcome this is continued digitalization of all production steps, PVD coating being just one of many steps.

An ERP system is pretty much standard in any factory these days, but this can be seen as a bookkeeping tool. For PVD coating manufacturing, most products will go through the following production steps: Incoming inspection, pre-processing, cleaning, racking, coating, post-processing, outgoing inspection, and packaging and shipping. All individual departments add their individual value to the overall chain, but there is limited overview of all steps together. This means that there is limited information of the correlation of these individual steps. Real Industry 4.0 is key to taking full advantage of data generation, interpretation to improve productivity and reduce resources and costs. With that, efficiency gains will be made, and scrap reduced.

Key in all of this is the real time data generation at all production steps to follow the smart factory approach and that is easier said than done. A starting point is creating crucial, digital data at these individual stages. Dashboards become the intermediate step towards the final goal, Industry 4.0 and "big data". Examples will be discussed for improved operations, but also monitoring towards lower energy consumptions and herewith lowering the carbon footprint in PVD production. This is getting pushed by requirements to decrease greenhouse gas emissions combined with increased legislations demands.

11:00am PP7-FrM-10 Insights on Plasma Processing from Multi-Scale Physical and Data-Driven Modeling, L. Vialletto, Stanford University, USA; T. Gergs, Kiel University, Germany; I. Chaerony Siffa, Leibniz Institute for Plasma Science and Technology (INP), Germany; C. Stüwe, Kiel University, Germany; T. Mussenbrock, Ruhr University Bochum, Germany; M. Becker, Leibniz Institute for Plasma Science and Technology (INP), Germany; Jan Trieschmann, Kiel University, Germany

INVITED

The theoretical description of plasma processing provides a formidable task that has been addressed by analytical modeling and numerical simulation for decades. Although the continuous increase in compute power has enabled simulation studies of the gas discharge physics in great detail, many open questions remain. This is reasoned by the extremely complex dynamics of multi-component plasmas facing solid surfaces, involving a large number of processes in the plasma and in the solid, as well as their plasma–surface interaction. The time and length scales of these physico-chemical processes span many orders of magnitude. Well separated scales often allow for the description of a given phenomenon on its respective scales, paired with a hierarchical coupling. This coupling is often rather static and realized via oversimplifying assumptions (e.g., tabulated coefficients), and may be biased-by-experience. Advantage can be taken from more unbiased data-driven approaches, which are derived from high fidelity data obtained from physical models at the lower scales. Moreover, the description of certain physical mechanisms may be substituted by data-driven sub-models (e.g., electric field calculation or transport parameters from a kinetic description). Correspondingly, a hierarchy of physical and data-driven models may be derived, linking global process quantities (e.g., pressure, voltage, current) to microscopic process quantities (e.g., thin film composition, electrical properties).

This approach is exemplified by the investigation of a low-pressure partially-magnetized capacitively coupled radio frequency discharge for the sputter deposition of silicon oxide thin films. The model is implemented in the OpenFOAM framework, extended by a Particle In Cell/Monte Carlo Collisions (PIC/MCC) implementation and coupled to a system of fluid equations for the neutral background. The surface evolution is described by a system of rate equations, which takes into account physical sputtering, chemisorption, physisorption, and surface diffusion of adatoms. The dynamics of physical sputtering are included using an artificial neural network model trained on surface kinetics data with varying stoichiometry from Monte Carlo simulations. It is argued that the versatility of the implementation also allows to use this model in a broader range of applications, such as plasma etching.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 138690629 – TRR 87 and – Project-ID 434434223 – SFB 1461.

11:40am PP7-FrM-12 Utilizing Digital Twin Technology for Automated Coating Recipe Development, Petr Zikan, A. Obrusnik, PlasmaSolve s r o., Czechia

Recent developments in the field of coating technology have seen a rise in the adoption of process modeling and digital twin tools. The primary motivation for this shift is the extended duration and unpredictability of process transfers and scaling in coating applications. Moreover, these technologies are now beginning to contribute to energy reduction in coating processes.

In our previous work, we introduced a Digital Twin model for coaters, integrated into the MatSight framework by PlasmaSolve. This model demonstrated high accuracy in predicting the composition and key performance characteristics (such as hardness and residual stress) of coatings, utilizing a dataset of only eight characterized samples for training. This achievement was made possible by a hybrid process model that merges simulations of physical processes and chemistry with machine learning techniques. By incorporating knowledge of the coater’s physical limitations, the model significantly reduced the need for extensive training experiments.

This contribution advances our research by tackling an inverse problem: using the Digital Twin model to create a coating recipe based on defined material specifications. These specifications include the number of layers, the thickness and composition of each layer, and the target hardness/residual stress for the complete stack. The model generates a recipe file compatible with coater operations, allowing for immediate implementation and validation of model predictions.

Furthermore, we illustrate how the Digital Twin model can be seamlessly integrated with other PVD simulation tools, offering a comprehensive view of the coating process. A case in point is the integration with the MatSight Coating Uniformity App, which enhances understanding of the coating’s thickness distribution and the variations in ion bombardment and composition across a 3D object.
Topical Symposium on Sustainable Surface Engineering
Room Palm 5-6 - Session TS3-FrM

Solar Thermal Conversion

Moderators: Telmo Echániz, University of the Basque Country, Spain; Marcus Hans, RWTH Aachen University, Germany

8:00am TS3-FrM-1 Application of Surface Engineering Solutions in Concentrating Solar Power Key Components, Ramón Escobar-Galindo, University of Seville, Spain; J. Sanchez-Lopez, T. Rojas, CSIC-University Seville, Spain; H. Barshilia, CSIR-National Aerospace Laboratories, India; M. Krause, Helmholtz Zentrum Dresden-Rossendorf, Germany

Thermal conversion of solar energy into electricity is one of the most efficient methods of harvesting renewable energy. In this regard, the development of new materials is crucial to improve the performance of concentrating solar power (CSP) plants. The future developments of thermosolar plants demand, among others, (1) mirrors with higher reflectivity, better protection, and lower costs, (2) absorber receiver components operating at higher temperatures, with wavelength selective capabilities, or (3) more stable materials under corrosive environments (i.e., molten salts) (see Figure 1). In this presentation, a review of surface engineering concepts (i.e., tailoring of multilayer materials, control of the interface design) applied to thermosolar energy will be discussed. Examples from our own research on the design, characterization, and thermal testing of ultra-reflective dielectric multilayer mirrors and solar selective coatings (SSCs) for high-temperature applications will be presented. In the former, we have demonstrated the design, using a genetic algorithm, and manufacturing, using Physical Vapour Deposition (PVD) techniques, of metal-dielectric multilayered solar mirrors that can outperform silver reflectors commonly employed in thermosolar and photovoltaic systems. In the latter, the thermal stability of SSCs based on metal oxynitrides prepared by PVD was studied after high-temperature annealing of the samples performed in air and in vacuum.


8:40am TS3-FrM-3 Development and Thermal Characterization of High-Temperature Coating Materials for Solar Thermal Energy Conversion, Renkun Chen, University of California, San Diego, USA

Coating is fundamentally important and ubiquitous for solar thermal energy conversion. From low temperature solar water heaters to intermediate parabolic trough solar collectors to high temperature solar towers, solar absorbing coatings play an important role. In this presentation, I will introduce our work over the past few years. Specifically, we have developed coatings based on high-temperature stable spinline oxide nanoparticles with ultra-high solar absorbance. The spinline oxide nanoparticles are synthesized with a scalable hydrothermal process. In the first application, the particles are mixed with silica resin to form a slurry for coating. The slurries can be spray coated onto substrates with a scalable process followed by standard curing and sintering processes. The coating on these spray coated substrates shows high solar absorbance (with solar to thermal conversion efficiency over 90% for 1000-sun at 800 °C absorber temperature). The coatings also exhibit superior thermal stability after long thermal isothermal ageing tests at 800 °C and thermal cycling tests from room temperature to 800 °C. This scalable coating process can be applied to cylindrical solar collector tubes with liquid heat transfer fluid (e.g., molten salts) in solar towers. In the second application, the black spineline nanoparticles are coated onto particulate heat transfer media (HTM) based on sand or ceramic particles of a few hundred microns in diameter. The black coating can greatly enhance the solar absorbance of sand HTM, and can also lead to stable solar absorbance of Carbo ceramic particles. We also developed high-entropy version of black nanoparticles which show remarkable stability against grain growth and can be used to coat thermochemically active particles to simultaneously increase the solar absorbance and suppress particle sintering, which is important to sustain high reaction kinetics of the thermochemical materials.

9:20am TS3-FrM-5 Smart Coatings for Concentrated Solar Thermal: from Optical Design and Plasma Synthesis to Performance and Durability Assessment, Audrey Soum-Glaude, A. Diop, PROMES-CNRS, France; A. Mahammou, D. Ngoue, PROMES-CNRS, Perpignan University, France; A. Grossean, EPF Montpellier, France; B. Plujat, S. Quoizola, PROMES-CNRS, Perpignan University, France; A. Bouquet, E. Tomasella, University Clermont Auvergne, France; L. Thomas, PROMES-CNRS, Perpignan University, France

Half of our energy consumption is heat for industrial processes and buildings. Contrary to solar PV and wind where electricity is directly produced, in solar thermal technologies, solar radiation is harvested by a solar receiver and converted into heat. In concentrated solar thermal (CST) technologies, solar radiation is concentrated by mirrors on the receiver to increase temperature. The generated heat can be stored more efficiently and at lower cost than electricity, providing great dispatchability and mitigating the intermittency of the solar resource. Solar thermal is thus a major solution for sustainable energy production, complementary to PV and other renewables. Additionally, the hybridization of PV and CST solar technologies can take advantage of the low cost of PV electrical production and the thermal storage of CST to produce both electricity and heat on demand.

To increase solar-to-heat conversion efficiency, the metallic surface of CST receivers can be covered with Solar Selective Absorber Coatings (SSACs) with high absorbance (i.e., low spectral reflectance) in the solar range, and low thermal emittance (i.e., high spectral reflectance) in the infrared range to limit radiative thermal losses. These coatings must also be resistant to high temperatures in air and high thermomechanical stresses, particularly for CST where they are exposed to harsh working conditions for long durations.

Similarly, for PV/CST hybridization, compact systems where PV cells are installed on solar concentrators to produce electricity, and CST thermal absorbers placed at their focus to produce heat, require spectrally selective mirror coatings. The latter must transmit part of the solar radiation to the underlying PV cells (typically from 400 to 1100 nm) and reflect the rest towards the CST thermal solar receiver.

In both types of surfaces, such spectrally selective behavior is obtained by combining advanced optical design and optimization of the coatings with their experimental synthesis, microstructural and thermo-optical characterization, and aging studies including aging under representative solar irradiation. In this paper, this complete development strategy will be illustrated with two examples of coating developments carried out at PROMES-CNRS laboratory: WSiC/TaOxN, and WSiC/TiOxN, multilayer stacks for CST high temperature SSACs and SiOx/TiOxN selective "PV" mirrors for CST hybridization, deposited by PVD and PECVD techniques.

10:20am TS3-FrM-8 Controlling Infrared Emissivity of Thermochromic Vo2 Films via vN Precursor Thickness for Enhanced Solar Thermal Regulation, A. García-Wong, D. Pilloud, S. Bruyère, S. Migot, S. Hupert, F. Capon, Jean-François Pierson, Institut Jean Lamour - Université de Lorraine, France

The control of infrared (IR) radiation is crucial for applications related to solar radiation. Thanks to the IR properties modification during its metal-insulator transition, monoclinic vanadium dioxide (m-VO2) is an excellent material for solar thermal regulation device development. Yet, these applications are linked to substrate IR properties on which the VO2 is deposited.

In this study, we propose a novel method for tuning the sign of the VO2 IR-emissivity without changing the substrate. Thermochromic VO2 films have been synthesized by air oxidation of reactive sputtered VxN films deposited on silicon substrates. As-deposited vanadium nitride films have been oxidized in air at 550 °C. The structure of the VO2 films has been characterized using X-ray diffraction and Raman spectrometry. Transmission electronic microscopy combined with electron energy loss spectroscopy (EELS) bring relevant information to describe the oxidation mechanism of VxN. At the interface between the remaining VxN film and the formed VO2 one, a thin layer of VN of 20 nm thick has been evidenced. At this oxidation temperature, the annealing duration to obtain efficient thermochromic VO2 films is fixed to 3 minutes. The initial precursor (VxN) thickness is the key parameter for tuning the IR properties. VxN films with low thickness allow the formation of thermochromic VO2 films with negative emissivity switch (approx. -0.2) while thick VN films allow positive emissivity switch (approx. 0.2). Our findings introduce a different strategy for IR emissivity control on thermochromic devices.

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8:00 AM
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Widespread adoption of concentrated solar power relies on lowering its operational costs, which requires efficient absorbing materials capable of withstanding high temperatures. This motivates the development of coating materials based on oxides. Unfortunately, these materials do not always feature appropriate optical properties, which means that strategies to increase their solar absorptances must be carried out. This work reports on the optical characterization of high-absorbing coatings. For that, directional spectral infrared emissivity measurements up to 600 °C, integrating sphere and bidirectional reflectance measurements in the UV-Vis-NIR range at room temperature have been performed. Spectral directional emissivity measurements were performed in the HAIRL emissometer using using a DTLaGS detector between 1.43 and 25 μm and the sample was placed between 10 and 80° every 10° for each directional measurement [1]. This emissometer is equipped with a Bruker Vertex 80v FTIR spectrometer that possesses an IR integrating sphere. Once the spectra were obtained, the emissivities were integrated along the electromagnetic spectrum and the solid angle to obtain total hemispherical emissivity values. Bidirectional reflectance measurements were performed between 350 and 2500 nm in a Cary UMA device. They were measured in both s and p polarizations, from which the unpolarized reflectance function was reconstructed. Measurements in the off-specular directions were also measured to complement these data and allow estimation of the total reflectance, weighted by the solar spectrum. Both the infrared emissivity and the BRDF measurements allowed obtaining the conversion efficiency.

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