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 Haviar**, 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 (galld@rpi.edu)*,** Rensselaer Polytechnic 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 base-centered monoclinic stoichiometric MoN. Epitaxial WC_x layers exhibit a cubic phase that is stabilized by carbon vacancies but phase competition involving hexagonal and orthorhombic W_2C and amorphous carbon lead to an epitaxial breakdown. Epitaxial MoC_x shows a similar phase competition between cubic δ-MoC_x(111) and hexagonal β-Mo_2C(0001) as a function of CH_4 content in the processing gas. In contrast, epitaxial TiC_x 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 $TiC_{1-x}N_x$ (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-TiC 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 (juliana.kessler@kemi.uu.se),*** 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 N_2 flow or by sputtering solely from a Ti-target under N_2 and CH_4 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 (rebecca.janknecht@tuwien.ac.at),*** *K. Weiss, N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria*; E. Ntemou,* Department of Physics and Astronomy, Uppsala University, Sweden*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; P. 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 $MPa*m^{0.5}$). Assisted by ab-initio DFT calculations, we previously demonstrated that additional Ti (to deviate from the TiN–TiB tie-line) is required to fully incorporate more B (up to 8.7 at%) in the TiN lattice while minimizing 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 (paul.mayrhofer@tuwien.ac.at),*** 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 (Λ) of 2–23 nm and a bilayer ratio (ℓ_{TiN}:ℓ_{MoN}) of 1:1, 1:0.5, 1:1, 1:2, and 1:2.7. This work is aim to explore the influence of bilayer periods and ratios, and the vacancies 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 β-Mo_2N signal is also detected for the SLs with Λ = 7.3 nm (ℓ_{TiN}:ℓ_{MoN} = 1:2). The SLs with bilayer ratios of 1:0.5 and 1:2 do not show superlattice effect and bilayer-period-dependent. The SLs with ℓ_{TiN}:ℓ_{MoN} = 1:2.7 provide highest hardness due to a higher nitrogen supply during deposition. Contrary, the SLs with ℓ_{TiN}:ℓ_{MoN} = 1:2 have the worst mechanical properties due to the tetragonal β-Mo_2N phase exist. Among all SLs investigated, those with ℓ_{TiN}:ℓ_{MoN} = 1:1 provide the best blend of mechanical properties, such as H = 34.8 ± 1.6 GPa, K_{IC} = 4.1 ± 0.2 MPa√m, and μ = 0.27, when Λ = 9.9 nm. This study extends our understanding of superlattice effect in general, especially on the influence of bilayer periods and bilayer ratios, as well as nitrogen supply and heterogeneous microstructures, which is benefit to next SL design.

11:40am **MA3-1-MoM-6 TiN/CrN and TiSiN/CrN Multilayer Coatings Deposited in an Industrial–scale HiPIMS System*, Neus Sala (neus.sala@iqs.url.edu),*** IQS School of Engineering - Universitat Ramon Llull, Spain*; M. Abad,* IQS School of Engineering - Universitat Ramon LLull, Spain*; C. Colominas,* FLUBETECH, S.L., Spain*; R. Franz, C. Kainz, M. Rebelo de Figueiredo,* Montanuniversität Leoben, Austria*; C. Rojas, J. Sánchez-López,* CSIC-Universidad de Sevilla, Spain

TiN/CrN and TiSiN/CrN multilayer coatings of varying bilayer period (Λ) were deposited in an industrial-scale deposition system by means of reactive High Power Impulse Magnetron Sputtering (R–HIPIMS). For each composition, three different coatings were deposited with bilayer periods of approximately 85 nm, 15 nm and 5 nm by alternating the sputtering of the different metallic targets in a nitrogen-containing atmosphere.

The influence of the Λ is investigated in regard of the chemical composition, microstructure, and mechanical properties of the coatings.

All coatings present a very smooth and compact structure in SEM images. XRD showed separate crystalline phases for the samples with high bilayer periods. However, as the bilayer period decreases, the crystalline peaks overlap, which would suggest epitaxial growth of the two crystalline phases.

A superlattice structure is confirmed by satellite peaks in the X-ray diffractograms for the TiN/CrN coatings with Λ ≤ 15 nm. TEM and EELS of the TiSiN/CrN coatings show that Si is substitutionally incorporated into the TiN crystalline lattice without segregation of amorphous SiN_X phases. However, epitaxial growth is interrupted by amorphous zones, particularly in samples with smaller bilayer periods.

For the TiN/CrN system, the highest nanoindentation hardness value obtained is 32 GPa while for TiSiN/CrN coatings, it is 28 GPa. In both cases, the maximum hardness value is found for the samples with Λ 15 nm regardless of the composition.

12:00pm **MA3-1-MoM-7 Residual Stress Measurement and Effective Deformation Thickness of Metal Interlayer in Multilayer Hard Coatings - Using TiN/Ti/TiN/Ti as a Model Architecture***, I-Sheng Ting* ***(gary820902@yahoo.com.tw)****, J. Huang,* National Tsing Hua University, Taiwan

High residual stress is one of the critical problems encountered in hard coatings deposited by physical vapor deposition. In industrial applications, introducing a metal interlayer, such as Ti and Cr, is a common practice to relieve the residual stress, thereby enhancing the adhesion and life span of the hard coatings. Our previous studies [1,2] proposed an energy-balance physical model to evaluate the stress and energy relief efficiency of metal interlayers in hard coatings. The assumption of the model was that the relief of stored elastic energy (G_S) in the hard coating and the bending energy of the Si substrate are balanced by the plastic work done by the metal interlayer. The results showed that the energy relief efficiency of the metal interlayer depends on the plastic behavior of the metal, where Zr interlayer has a lower extent of stress relief in ZrN/Zr coating than Ti interlayer in ZrN/Ti coating [1], because the strength coefficient (k) of Zr is higher than that of Ti. In addition, the results indicated that the plastic deformation capability of the metal interlayers is not fully consumed, and the plastic deformation of the metal interlayer is localized within a narrow layer nearby the coating/interlayer interface, which was named as effective deformation thickness (EDT). The EDT was used to depict the energy relief extent in the bilayer coatings [2]. However, whether the energy-balance model and the concept of EDT could be applied in a multilayer structure is still unclear. In this study, the alternated four layered TiN/Ti/TiN/Ti coating was selected as a model architecture to investigate the stress relief and stress distribution of multilayer hard coatings. TiN coating with Ti interlayer was deposited on Si substrate using dc unbalanced magnetron sputtering, where the TiN film and Ti interlayer were alternately stacked to produce structure, TiN, TiN/Ti, TiN/Ti/TiN and TiN/Ti/TiN/Ti. 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.

[1] J.-H. Huang et al., Surf. Coat. Technol., 434 (2022) 128224.

[2] J.-H. Huang et al., J. Vac. Sci. Technol. A, 41 (2023) 023104.

[3] C.-H. Ma et al., Thin Solid Films, 418 (2002) 73.

[4] A.-N. Wang et al., Surf. Coat. Technol., 262 (2015) 40.

[5] A.-N. Wang et al., Surf. Coat. Technol., 280 (2015) 43.

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 Environments***, Kuiying Chen* ***(kuiying_chen@hotmail.ca)****,* National Research Council of Canada*; K. Lee,* NASA Glenn Research Center, USA **INVITED**

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 ytterbium disilicate (YbDS) topcoat and thermally grown oxide (TGO) silicon dioxide in EBCs plays a key role in determining EBCs durability and lifespan. Using physics-based model and thermodynamics along with defect reaction formulae, oxygen permeabilities under both dry oxygen and water vapor conditions, as well as different temperatures, partial pressures and topcoat modifiers, are investigated. Results show that oxygen permeability of YbDS is an order of magnitude larger than that for TGO, indicating TGO hinders the oxidant diffusion stronger, proving to be diffusion rate controlling layer while water vapor strongly increases oxidant permeation.

Solid particle erosion of EBCs was numerically evaluated using mechanics-based formulae where the model parameters are fitted to the test data. The cutting wear, the deformation wear and their relationship with erosion rate are elaborated, while possible mechanisms of erosion rate correlated with EBCs microstructures are explored. The failure mechanisms of EBCs under solid particle erosion processes are discussed combining microstructures, internal cracking within topcoat and external erosion on the topcoat 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-3 Effect of Thermal Barrier Coatings on the Thermal Management of a Jet Engine Combustion Chamber***, Rodrigue Beaini* ***(rodrigue.beaini@polymtl.ca)****,* 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.

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 gardon 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

2:40pm **MA2-1-MoA-4 Elevated Temperature Micro-Scale Impact Testing of Thermal Barrier Coatings for Erosion Simulation***, Ben Beake* ***(ben@micromaterials.co.uk)****, J. Roberts,* Micro Materials Ltd, UK*; L. Isern, C. Chalk, J. Nicholls,* Cranfield University, UK

Higher engine operating temperatures will increase the efficiency of gas turbines, saving fuel and reducing CO_2 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 due to the softening of the TBC. Although the final impact depths were greater at higher temperatures, the increase with continued impact was smaller than at room temperature. 7YSZ impact behaviour at 825 °C is compared to previously reported erosion data obtained with a high temperature erosion rig at Cranfield and in the literature [3].

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.

[1]UK Patent Application #2217939.4. [2] BD Beake et al, ICMCTF, 2023. [3] RG Wellman, JR Nicholls, J Phys D: Appl Phys. 40 (2007) R293-R305 and Tribol. Int. 41 (2008) 657-662.

3:00pm **MA2-1-MoA-5 Influence of Coating Variables on the Steam Oxidation of Modified Si / $Yb_2Si_2O_7$ Environmental Barrier Coatings***, Kang Lee* ***(ken.k.lee@nasa.gov)****, R. Webster, J. Stuckner, A. Garg, L. Wilson,* NASA Glenn Research Center, USA

Environmental barrier coatings (EBCs) have enabled the implementation of SiC/SiC ceramic matrix composites (CMCs) in gas turbines by protecting CMCs from H_2O. Improving the reliability of CMC components requires long-life EBCs and accurate EBC lifing. Steam oxidation-induced failure is one of the most critical EBC failure modes. NASA has developed modified Si / $Yb_2Si_2O_7$ EBCs by adding dopants such as Al_2O_3, mullite, and/or YAG ($Y_3Al_5O_{12}$) in the $Yb_2Si_2O_7$ 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 SiO_2 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 the rapid quenching of molten droplets during the coating formation. Annealing is often employed to stabilize the EBC phase by crystalizing 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 diffractometry and transmission electron microscopy are used to help understand the relationship.

3:20pm **MA2-1-MoA-6 Effect of Pre-Oxidation on the Growth of Thermally Grown Oxide and High Temperature Durability of Thermal Barrier Coatings***, **Do Hyun Kim (dohyunkim@kims.re.kr)**, Y. Kang, H. Kwon, Y. Yoo, Y. Park, S. Lee,* Korea Institute of Materials Science, Republic of Korea

Thermal barrier coatings(TBCs) are widely applied in turbine components of modern jet engines and land base gas turbine to reduces the surface temperature of superalloy substrate. Typically, TBCs consist of a ceramic top coat with low thermal conductivity and an Al-rich and oxidation-resistant metallic bond coat. Upon exposure at high temperature over 1,000℃, a protective thermally grown oxide(TGO) layer, predominately α-Al_2O_3, is formed between the top coat and the bond coat, which is considered to be the most crucial factor that determine the durability and life of TBCs system. Therefore, to enhance the durability and reliability of turbine component in high temperature, the formation of a slow growing TGO is substantial.In this study, we performed the pre-oxidation of bond coat to improve the oxidation resistance of bond coat in TBCs. As coated bond coats were pre-oxidized with different heat treatment conditions of atmosphere, low oxygen, and vacuum for the initial formation of TGO, and then TBC samples were exposed to high temperature during isothermal oxidation. The results showed that the growth behavior of the TGO layer on the bond coat surface during isothermal oxidation was significantly changed by the pre-oxidation heat treatments. In order to explore the mechanism of the improved oxidation resistance of pre-oxidized bond coats, the chemical composition, phase constitutes and thickness of TGO(α-Al_2O_3 and spinel oxide), and microstructural changes of bond coat were characterized. Finally, furnace cycle test(FCT) were performed to evaluate the TBC lifetime.

4:00pm **MA2-1-MoA-8 Correlative Microscopy and AI-assisted Image Analysis Synergetic Approach on High Temperature Applications Coatings***, **Hugues Francois-Saint-Cyr (hugues.fsc@thermofisher.com)**,* Thermo Fisher Scientific, USA*; A. Scarpellini,* Thermo Fisher Scientific, Netherlands*; B. Winiarski,* Thermo Fisher Scientific, Czechia*; J. Yorston, R. Pelapur,* Thermo Fisher Scientific, USA

High-temperature applications coatings require the validation of a thorough checklist regarding their chemical and mechanical properties, as-deposited and within the environments they are designed for.

In order to gain a solid understanding of those complex structures, the use of correlative microscopy (CM) workflows provide a structured approach to integrating microscopy and analytical techniques, delivering a multi-dimensional and multi-modal view of the analyzed samples.

Beside the traditional CM approach where X-ray, Electron-beam, and Ion beam techniques complement each other, today engineers and scientists expect additional help from the image analysis (IA) linking those techniques. Namely, Artificial Intelligence (AI)-assisted IA has become a must-have, allowing specialists, and non-specialists alike, to quickly produce results.

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.

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.

This example was chosen because of its complexity where several ceramic layers (top coats, bond coats) together with metallic substrates were designed to maintain their efficiency at high temperatures and extremely oxidizing environments. Since their performance and durability are intimately linked to their microstructure and composition, the CM workflow encompasses broad ion beam (BIB) milling, Scanning electron microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS), as well as a cross-section using a Focused-Ion Beam (FIB) system.

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.

4:20pm **MA2-1-MoA-9 Characterization of SiO_2 Thermally Grown Oxide Kinetics and Stress Evolution of EBCs with Al-Containing Dopants***, **Michael Lance (lancem@ornl.gov)**, 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 SiO_2 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 SiO_2 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.

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 (M12188037@mail2.mcut.edu.tw)**,* 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*; P. 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

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 B_4C targets in Ar + N_2 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 O_2/Ar at 650℃. We found that an optimized $Si_{26}B_5C_{26}N_{43}$ (at.%) coatings protected the 6wt% Co-WC substrate against oxidation. Stable amorphous structure of Si–B–C–N coatings hindered inward oxidation of O.

5:00pm **MA2-1-MoA-11 Influence of Gas Composition on the Growth Behavior of CVD Processed HfC Coatings for Ultra-high Temperature Application***, **Byung-Hyuk Jun (bhjun@kaeri.re.kr)**, J. Lee, D. Kim, H. Lee,* Korea Atomic Energy Research Institute, Republic of Korea

Refractory metal carbides for thermal protection under ultra-high temperature condition have attracted much attention due to their potential applications in field of advanced aerospace hypersonic vehicles, such as rocket and scramjet components. Hafnium carbide (HfC) has high melting point of 4163 K, low thermal conductivity, high mechanical properties, excellent resistance to oxidation and thermal corrosion, which make it very attractive for coating applications in improving the ablation resistance of carbon/carbon composites in extremely combustion environment. The deposition of coatings was performed in a hot-wall type low pressure CVD furnace under the working pressure of 50 Torr. $HfCl_4$-C_3H_6-H_2-Ar system was applied to deposit HfC coatings on graphite substrate. $HfCl_4$ powder (99.9%) was used as the hafnium source and C_3H_6 instead of CH_4 as the carbon source was used to lower the deposition temperature. H_2 and Ar were used as reducing gas and diluting gas, respectively. In this work, a special powder feeder was designed to supply $HfCl_4$ powder into the reaction zone constantly. The delivery rate of $HfCl_4$ powder was fixed to be about 1 g/min. The gas composition of $HfCl_4$-C_3H_6-H_2-Ar and deposition temperature were mainly varied to optimize the HfC deposition condition for the purpose of obtaining dense and superior oxidation resistant HfC coatings with high deposition rate. Phase, crystal structure and crystallinity of the HfC coating layers were investigated by X-ray diffraction, and the results showed good crystalline phase with different preferred orientations depending on the deposition condition. Surface morphology and microstructure for the plane and cross-section were observed by a scanning electron microscopy. Raman spectroscopy analysis was performed to find out the C-deficit/-excess of HfC coatings. Quantitative analysis of the HfC composition including impurities inside coating layer was performed using Rutherford backscattering spectrometry (RBS) and elastic recoil detection-time of flight (ERD-TOF) methods. Mechanical properties of the HfC coatings including hardness and Young's modulus were examined with nanoindentor. These results of the growth behavior depending on the deposition parameters including gas composition are described.

5:20pm **MA2-1-MoA-12 Promising SiOxNyCz Coatings for Glass Protection in Aggressive Chemical Media***, **Farah Inoubli (farah.inoubli@cnrs-orleans.fr)**, B. Diallo,* CNRS/Université D'Orleans, France*; K. Topka,* Air Liquide Laboratories, Japan*; T. Sauvage,* CNRS/Université D'Orleans, France*; R. Laloo, V. Turq,* CNRS-CIRIMAT, France*; B. Caussat,* CNRS, France*; N. Pellerin,* CNRS/Université D'Orleans, 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 limiting this interaction. But how?

In this work, we expose very promoting 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 tetraethylorthosilicate (TEOS) precursor. However, tris(dimethylsilyl)amine (TDMSA) and a novel proprietary trisilylamine-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 td).

Films deposited on the two sides of a flat silicon monocrystalline substrate were subjected to moderately long alteration of one month in a citric acid aqueous 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.

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, **Stanislav 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 (lina.rogstrom@liu.se)**,* Linköping University, IFM, Sweden **INVITED**

Wear resistant coatings covering tools used for metal machining experiences tough conditions during application, such as high temperatures and stresses. The detailed nature of tool wear is still largely unknown. One limitation to access the material behavior in the contact zone between the tool and the workpiece is the lack of line-of-sight to this area. The contact zone is in the order of 1 mm^2 and characterized by steep gradients in temperature and stress. The material behavior is thus expected to vary significantly within the contact zone, why local analysis is crucial to understand the relation between material properties and wear behavior. Due to the complex situation, model studies at high temperature and/or pressure do not provide a full understanding of the material behavior, instead, real-time methods to access the contact area are needed.

High-energy x-rays are highly suitable for studies of the hidden contact area between tool and workpiece since they can penetrate several mm of coating and workpiece, and in some case also the substrate material. TiAlN is one of the most common materials for wear resistant coatings. It's favorable mechanical properties at high temperatures are related to the spinodal decomposition of the fcc-TiAlN phase, the details of which successfully have been characterized by high-energy x-ray scattering techniques [1].

To study the tool in real time during metal machining, we have designed a small-scale lathe that can be placed at the high-energy materials science x-ray beamline P07 at Petra III [2]. The lathe allows for longitudinal and orthogonal turning using industrial tooling systems and is built for industrial cutting parameters such as cutting speed and feed. Its design enable access to the tool-chip interface with an x-ray beam during turning. In this presentation, results will be presented from in operando experiments performed (i) with the x-ray beam parallel to the tool flank side and (ii) with the x-ray beam parallel to the tool rake face. The results will be discussed in terms of possibilities and limitations of in operando high-energy x-ray diffraction techniques to access the material behavior in real time during metal machining.

[1] M. Odén, L. Rogström et al., Appl. Phys. Lett. 94, 053114 (2009); L. Rogström et al., Thin Solid Films 520, 5542 (2012); A. Knutsson, L. Rogström et al., J. Appl. Phys. 113, 213518 (2013); N. Norrby, L. Rogström et el., Acta Mater. 73, 205 (2014).

[2] L. Rogström et al., Rev. Sci. Instr., 90, 103901 (2019); L. Rogström et al., Submitted for publication (2023).

2:20pm **MA3-2-MoA-3 Exploring High Temperature Decomposition and Age Hardening in Wurtzite $Ti_{1-X}Al_XN_Y$ (X=0.75 to 0.98, Y=0.82 to 1) Thin Films***, **Janella Mae Rosario Salamania (janella.salamania@secotools.com)**,* Seco Tools AB, Sweden*; F. Bock,* Linköping University, Sweden*; L. Johnson, K. Calamba Kwick, I. Schramm,* Sandvik Coromant, Sweden*; A. Farhadizadeh,* Linköping University, Sweden*; T. Hsu,* Sandvik Coromant, Sweden*; F. Tasnadi, I. Abrikosov, L. Rogström, M. Odén,* Linköping University, Sweden

Wurtzite TiAlN is an intriguing material. It forms in high Al-content industrial grade tool coatings and has potential as a semiconductor with adjustable band gap and can serve as an insulating motif for superconductors and piezoelectric crystals. The characterization of wurtzite TiAlN 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 TiAlN alloys. It covers the challenges associated with synthesizing single-phase solid solutions of wurtzite TiAlN and the unknown thermodynamic, elastic properties, and high-temperature behavior of wurtzite $Ti_{1-x}Al_xN$. First-principles calculations were used to predict a phase diagram encompassing miscibility gaps and spinodals for both cubic and wurtzite $Ti_{1-x}Al_xN$ and the full elasticity tensor. Metastable stoichiometric wurtzite $Ti_{1-x}Al_xN$ 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 $Ti_{1-x}Al_xN$, resulting in nanoscale compositional modulations and age hardening of 1-2 GPa.

The high-temperature behavior of wurtzite TiAlN is affected by the presence of nitrogen vacancies. To study this in HRSTEM we grew nitrogen-deficient epitaxial wurtzite $Ti_{1-x}Al_xN_yy$ films, which revealed decomposition into intermediary MAX-phases, segregating into c-TiN, w-AlN phases, and TiAl nanoprecipitates 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 TiAlN, offering valuable insights into the behavior of these materials under extreme conditions.

2:40pm **MA3-2-MoA-4 Enhancing the Thermal Stability of $V_{0.25}Al_{0.25}N_{0.50}$ by Oxygen Incorporation**, ***Matej Fekete (fekete@physics.muni.cz)**, 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. Primetzhofer,* 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 $V_{0.25}Al_{0.25}N_{0.50}$ coatings, oxygen is integrated into the material system. High power pulsed magnetron sputtering at 450°C is utilized to synthesize metastable fcc $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ coating and reference $V_{0.25}Al_{0.25}N_{0.50}$. Coatings are annealed in a vacuum for 30 minutes to up to 950 °C and 1300 °C for $V_{0.25}Al_{0.25}N_{0.50}$ and $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$, respectively.

Decomposition of V and Al within the nitride phase is observed to start at 800 and 900 °C in $V_{0.25}Al_{0.25}N_{0.50}$ and $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$, respectively, although a formation of a few nm scale aluminum-rich regions in as deposited $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ is detected by atom probe tomography. Selected area electron diffraction data reveal the presence of wurtzite phase in the $V_{0.25}Al_{0.25}N_{0.50}$ annealed at 950 °C, while in $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ annealed at 1300 °C no secondary phase is 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-$Ti_{0.5}Al_{0.5}N$ Coatings**, ***Michael Tkadletz (michael.tkadletz@unileoben.ac.at)**, N. Schalk, H. Waldl,* Montanuniversität Leoben, Austria*; B. Sartory, J. Wosik,* Materials Center Leoben Forschung GmbH, Austria*; J. Keckes, J. Todt,* Montanuniversität Leoben, Austria*; M. Burghammer,* European Synchrotron Radiation Facility, France*; C. Czettl,* CERATIZIT 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-$Ti_{0.5}Al_{0.5}N$ 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 revealed that implementation of a suitable base 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 $Hf_{1-x}Al_xN$ Films Grown at High Temperatures and the Effect on Mechanical Properties**, ***Marcus Lorentzon (marcus.lorentzon@liu.se)**,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; T. Zhu,* Nagoya University, Japan, China*; 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 TiAlN 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 with a melting point of ~3300°C. In this study we have grown single crystal cubic $Hf_{1-x}Al_xN_y$ on MgO(001) substrates at 800°C using reactive magnetron co-sputtering from elemental Hf and Al targets. A high flux (J_{ion}/J_{metal}>9.2) of low energy (20 eV < E_{ion} <26 eV) ion assistance was employed with -30V substrate bias. An improved crystalline quality of HfAlN films was obtained on adding up to 30 at.% Al. Similar to the case of annealed TiAlN [1], 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 HfAlN film which is lower concentrations than previously reported [2]. The fracture mechanics of $HfN_{1.22}$ and $Hf_{0.93}Al_{0.07}N_{1.15}$ 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 $HfN_{1.22}$ in relation to the stoichiometry of the film and point defect formation, in particular anti-site point defects which affect the physical properties of HfN_y[3]. We will highlight the impact of increasing Al content on the size of the check-patterned modulation in the cubic phase films and preliminary results of spinodal decomposition in high Al-content wurtzite $Hf_{0.59}Al_{0.41}N_{1.23}$.

[1] P. H. Mayrhofer *et al.*, *Appl. Phys. Lett.*, vol. 83, no. 10, Sep. 2003

[2]B. Howe *et al.*, *Surface and Coatings Technology*, vol. 202, no. 4, Dec. 2007

[3]H.-S. Seo *et al.*, *Journal of Applied Physics*, vol. 97, no. 8, Apr. 2005

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 (stachowski@iot.rwth-aachen.de)**,* Surface Engineering Institute (IOT) - RWTH Aachen University, Germany*; B. Breidenstein, B. Bergmann, F. Grzeschik,* Institute of Production Engineering and Machine Tools (IFW) - Leibniz Universität Hannover, Germany

Hard coatings like TiAlN 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 Elemente (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 θ = 20 °C, θ = 200 °C,θ = 400 °C and θ = 600 °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 $\leq d_s \leq$ 6 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 (balint.hajas@tuwien.ac.at), S. Bermanschläger, 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_2-partial pressure used. Alternatively, such nitrides 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 $(TiN)_{0.5}(AlN)_{0.5}$ target were single-phase face centered cubic (fcc) structured those obtained from the $(TiN)_{0.2}(AlN)_{0.8}$ target were single-phase hexagonal close packed (hcp) wurtzite-type structured. The hcp-phase fraction within the (Ti,Al)N coatings prepared with the $(TiN)_{0.34}(AlN)_{0.66}$ target strongly depends on the deposition conditions. 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 (jilek.jr@shm-cz.cz), 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 10um 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 decoated.

5:00pm **MA3-2-MoA-11 Synthesis and Investigation of Crystalline (Ta,Al)B_2 and AlB_2 Thin Films***, Chun Hu (chun.hu@tuwien.ac.at)*[1]*, S. Lin,* Institute of Materials Science and Technology, TU Wien, Austria*; P. Pöllmann, S. Mráz,* 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 TMB_2 thin films is challenging, since their composition typically deviates from 1:2 metal-to-boron stoichiometry. We developed $(Ta_{1-x}Al_x)B_y$ (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 1.64 leads to the highest hardness (38.8 GPa) among $(Ta_{1-x}Al_x)B_y$ studied here due to promoted formation of the AlB_2-prototype phase. $(Ta_{1-x}Al_x)B_y$ with y=1.97-2.29, 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 $Ta_{1-x}Al_xB_y$ solid solutions, we also synthesized crystalline AlB_x (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 $AlB_{2.27}$ 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 Sun (ysun98@uic.edu)*[2]*, 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 tribocorrosivedamages 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 proteins was selected 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-2phenylindole (DAPI) staining assay live/dead assay.

As a result, the produced CDC shows an excellent tribocorrosion performance, presenting around 30-fold lower potential variation than Ti6Al4V. 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 um was observed; however, a distinct layer of CDC was not showing under SEM. Regarding the biocompatibility

[1] **Graduate Student Award Finalist**
[2] **Graduate Student Award Finalist**

analysis, no significant difference was found in CDC's cell proliferation compared to the control group Ti6Al4V, and living cells were shown on the sample. According to the amount and the cell shapes, no noticeable difference was found between CDC and the Ti6Al4V, verifying CDC's biocompatibility on the Ti6Al4V substrate.

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

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

Moderator: Francisco Javier Pérez Trujillo, Universidad Complutense de Madrid, Spain

8:20am **MA1-1-TuM-2 Tunable Aluminide Coatings for Surface Finish and Improved Oxidation and Hot Corrosion Behaviour of Additive Manufactured Ni-Based Superalloys*, Fernando Pedraza (fpedraza@univ-lr.fr), 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 metallurgical 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 examples will be given for different additive manufactured nickel-based alloy systems including the popular equiaxed or single crystalline nickel-based superalloys.

Simple nickel aluminide coatings will be shown to dramatically improve the oxidation resistance of IN-718 at temperatures as high as 800°C and of Alloy 699XA at 950°C through the development of a thin and adherent Al_2O_3 scale. The application of Al/Si slurry coatings improves dramatically the hot corrosion resistance under Na_2SO_4 against conventional vapour phase and simple Al slurries due to the layered segregation of Si_xW_y. The incorporation of microreservoirs made of MCrAlY 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 Aluminide Diffusion Coatings and to Predict their Ageing Behavior*, Vladislav Kolarik (vladislav.kolarik@ict.fraunhofer.de)***, *M. Juez Lorenzo,* Fraunhofer Institute for Chemical Technology ICT, Germany*; P. Praks,* IT4Innovations National Supercomputing Center, VSB - Technical University of Ostrava, Czechia*; R. Praksova,* IT4Innovation National Supercomputing Center, VSB - Technical University of Ostrava, Czechia

Aluminide 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 Fe_2Al_5 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 (sofmat@ufpr.br)***, 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 processed surfaces depend on the microstructure of AM parts 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-aluminization was applied to AM AISI316L stainless steel processed by PTA-DED, L-DED and L-PBF. Pack-aluminizing was carried out at 850°C for 1h and with a pack-mixture composition of 10%Al-3%NH_4Cl-87%Al_2O_3. Results show that, regardless of the substrate condition, aluminized coatings are composed of an external Fe_2Al_5 intermetallic layer and an interdiffusion region exhibiting two sub-layers, an intermediate layer of the intermetallic FeAl and an internal layer of α-Fe(Al) close to the substrate. The first evidences of the impact of additive multilayer structures is the non uniform interface with the substrate associated with the interlayer regions. Changes in the microstructure in these regions 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-DED (3,6± 0,4 µm): It is interesting to point out that inspite of the differences in microstructure L-DED and L-PBF AM materials exhibit very similar features that differ from PTA-DED that has a thinner external, 15,7±0,9 µm of the set of materials processed. The observed differences between coatings can be accounted for by the non-uniform characteristics of microstructure of the multilayer additive materials as opposed to the more uniform grain structure of the rolled substrate. Between additive materials, the finer microstructure of L-AM materials induced a larger density of diffusion paths forming a thicker external layer ±19 µm. Results allow to conclude that thicker external layers are accompanied by a thinner interdiffusion region behavior associated with an earlier formation of two compositional gradients in the coarser PTA-DED microstructure, at the surface and at the interface between the Fe_2Al_5 /substrate, accounting for the thicker sublayers in the interdiffusion region.

9:40am **MA1-1-TuM-6 Synthesis of Novel Multi-Element TM-Aluminides by Multilayer Magnetron Sputtering*, Vincent Ott (vincent.ott@kit.edu)***, *M. Duerrschnabel, U. Jaentsch, M. Klimenkov, S. Ulrich, M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal Aluminides in the B2 structure like NiAl and FeAl are well known for their combination of mechanical properties and oxidation resistance which make them suitable materials for high temperature applications. However, these materials often suffer from brittle material behavior at room temperature, hampering their machinability and utilization. The RuAl phase shows improved RT ductility due to its greater number of available slip systems compared to other binary aluminides in the B2 structure. To investigate and potentially further improve the mechanical and protective behavior of transition metal aluminide thin films, a multi-layer approach was used to synthesize novel multi-elemental solid-solution aluminides of the type (Ru_x, Me_{1-x})Al. The deposition of nanoscale multilayer films thereby allows to circumvent thermodynamic restrictions in equilibrium bulk conditions to generate supersaturated aluminide phases in thin films outside the phase boundaries. The correlation between the thin films microstructure and the mechanical properties is discussed. The phase formation is observed by HT-in-situ-XRD, while the mechanical properties as well as the microstructure are examined by microindentation and TEM analysis respectively.

10:00am **MA1-1-TuM-7 Structural Evolution and Oxidation Resistance of Al/Si Alloyed Transition Metal Carbide Thin Films**, ***Sophie Richter (sophie.richter@tuwien.ac.at)***, 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. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *S. Kolozsvári, 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 TMCs. This comprehensive study covers a wide range of structural and chemical compositions, which are thoroughly characterized by X-ray diffraction (XRD), nanoindentation, 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 oxidization 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.

10:20am **MA1-1-TuM-8 Hot Corrosion of Arc Evaporated $Ti_{1-x}Al_xN$ on Ni-Cr-Co Based Superalloys**, *O. Hudak, A. Scheiber, P. Kutrowatz, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany; ***Helmut Riedl (helmut.riedl@tuwien.ac.at)***, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Hot corrosion is an accelerated oxidation process that occurs in high-temperature environments (650-950 °C) in the presence of sulfur-rich exhaust gases and salt-impurities. The subsequent formation of high-melting sulfate salts and their deposition on machine components induces accelerated degradation of operating parts through the formation of a porous and non-protective corrosion scale. Notably, Ni-, Co-, and Fe-base superalloys used in aerospace and power generation industry are particularly susceptible to hot-corrosion attacks.

This research explores arc-evaporated $Ti_{1-x}Al_xN$ as a promising protective coating material mitigating hot-corrosion effects on superalloys. $Ti_{1-x}Al_xN$ 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 Na_2SO_4-$MgSO_4$ salt mixture, both coated and uncoated samples were thermally treated in an SO_x-rich atmospheres for a duration of up to 30 h. The primary objective was to enhance the understanding of the corrosion mechanisms of $Ti_{1-x}Al_xN$ 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 a variety of high-resolution characterization techniques ranging form XRD, SEM, to HR-TEM.

Results revealed that arc evaporated Ti_{1-x}AlxN exhibits superior corrosion resistance compared to the bare NiCoCr-based alloy in both temperature regimes. Under LTHC conditions, a localized and accelerated attack was observed, driven by an initial nitride-to-sulfate transformation and followed by a synergistic fluxing mechanism. This mechanism involved the formation of layered oxide domains rich in TiO_2 and Al_2O_3, due to the acidic nature of the liquid salt interface. The obtained scale was dominated by Al_2O_3, known for its enhanced stability under acidic conditions. In contrast, under HTHC conditions, a more uniform development of the corrosion scale was noted. Similar to LTHC, a sequential fluxing produced Ti-rich and Al-rich oxide domains that over time formed a layered corrosion scale. The stability of TiO_2 under basic conditions resulted in the primary formation of a porous TiO_2 scale at the scale-salt interface, followed by a substantial band of Al-rich oxide.

This research contributes valuable insights into the hot corrosion behavior of arc evaporated $Ti_{1-x}Al_xN$ coatings, and highlights their potential as protective coatings for components exposed to aggressive high-temperature environments.

10:40am **MA1-1-TuM-9 Characterization of Li-rich Corrosion Products Formed onto Aluminized and Uncoated Steels after Molten Carbonates Exposure**, *P. Audigié, S. Rodríguez,* ***Alina Agüero (agueroba@inta.es)***, Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Public authorities are strongly encouraging the adoption of new thermal energy storage (TES) systems in order to meet the requirements for clean energy worldwide. However, installation, maintenance and materials for such TES imply rather high costs which can hinder their implementation. To remedy this, various corrosion resistance slurry aluminide coatings have been developed at INTA onto ferritic and austenitic steels as low-cost alternative materials for structural components in contact with molten salt. Emphasis has been placed on Li-rich molten carbonate exposure at high temperature of such coated and uncoated materials and expressly on the identification and characterization by advanced techniques (GDOES, TEM) of Li-rich corrosion products as Li cannot be detected by conventional techniques. Microstructural features of $LiFeO_2$, $LiFe_5O_8$, $LiAlO_2$ both alpha- and gamma- phases among others and Li effect will be discussed. Presence of two distinct peaks of Li were detected in the $LiAlO_2$ oxide formed onto the slurry aluminide coated T92 heat treated at low temperature and exposed 2000h at 650ºC with Li, Na and K carbonates. Similar behavior was observed with the aluminized 310H austenitic steel after 1000h of exposure in the same environment at 700ºC. Li penetration into the different studied materials will thus be described.

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 Haviar**, University of West Bohemia, Czechia, **Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

8:00am **MA3-3-TuM-1 Physical Properties of Pure Tantalum Nitrides Thin Films**, ***Angeline Poulon-Quintin (angeline.poulon@icmcb.cnrs.fr)***, 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 tantalum 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-HiPIMS) 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 $Cr_{1-x}Ta_x$ Coatings**, ***Jan-Ove Söhngen (jan-ove.soehngen@kit.edu)***, *V. Ott, S. Ulrich, M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Refractory 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. $Cr_{1-x}Ta_x$ coatings with various Ta contents weresynthesized 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 mm^3 were placed in a horizontal line opposite to the target. Thus, we obtained different $Cr_{1-x}Ta_x$ 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:

1. All coatings are crystalline.
2. 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.
3. In contrast to the coatings with a lower amount of Ta, the XRD reflections of coatings with 68.5 at.% Ta content show a broader (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 $TaCr_2$ 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 $Cr_{1-x}Ta_x$ 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 $Cr_{1-x}Ta_x$ 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 (denis.kurapov@oerlikon.com)**,* Oerlikon Surface Solutions AG Pfäffikon, 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 resent 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-5 Enhancing the Thermal Stability and Cutting Performance of fcc-AlCrN by Oxygen Incorporation***,* *A. Michau,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; **Tomasz Wojcik (tomasz.wojcik@tuwien.ac.at)**, 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 $(Ti,Al)(O_xN_{1-x})$ compared to (Ti,Al)N.

Based on these results, we thoroughly investigated the decomposition behaviour of oxygen-doped $Al_{0.70}Cr_{0.30}(O_{1-x}N_x)$ coatings grown by arc evaporation. During the reactive growth, the oxygen was incorporated by varying the flow rates between 15 to 70 sccm compared to 940 to 990 sccm nitrogen (p_{dep} around 4 Pa). All coatings were grown using an Oerlikon Balzers INNOVENTA kila equipped with AlCr 70/30 targets. These variations lead to purely fcc structured $Al_{0.70}Cr_{0.30}(O_{1-x}N_x)$ 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 oxygen-containing 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-AlN 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 progression 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 (kevin.kutlesa@unileoben.ac.at)**, M. Meindlhumer,* Montanuniversität Leoben, Austria*; A. Lassnig,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; R. Daniel,* Montanuniversität Leoben, Austria*; A. Medjahed,* ESRF, France*; J. Keckes,* 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 monolithic thin films, namely $Al_{0.63}Cr_{0.27}Si_{0.1}N$ and $Al_{0.675}Cr_{0.075}Si_{0.25}N$, 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 nanocomposite microstructure composed of cubic Cr(Al)N and wurtzite 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 Nanostructured Multilayer Coatings***,* ***Ming-Xun Yang (u6au6vmp711@gmail.com)**, Y. Chang,* National Formosa University, Taiwan

A TiSiN coating with a nanocomposite structure where TiN grains are surrounded by a SiN_x 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 ball-on-disc wear tests at room temperature and 500 °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.

10:20am **MA3-3-TuM-8 Influence of Deposition Pressure and Gas Mixture on the Microstructure and Phase Composition of Arc Evaporated TiSiN Coatings**, ***Nina Schalk (nina.schalk@unileoben.ac.at)***, *Y. Moritz, G. Nayak, D. Holec,* Montanuniversität Leoben, Austria; *C. Hugenschmidt,* Technical University of Munich, Germany; *V. Burwitz,* Technical University Munich, Germany; *L. Mathes,* Technical University of Munich, Germany; *C. Saringer,* Montanuniversitat Leoben, Austria; *C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria; *M. Tkadletz,* Montanuniversitat Leoben, Austria

Owing to their advantageous properties including excellent hardness and high oxidation stability, arc evaporated TiSiN coatings are frequently used as protective hard coatings for various machining applications in the metal cutting industry. Within this work, the influence of a varying N_2 deposition pressure and the addition of Ar to the deposition atmosphere on the microstructure and phase composition of TiSiN coatings was studied in detail. All coatings exhibited a feather-like and fine-grained structure and showed an amorphous SiN_x phase fraction. Further investigation of powdered TiSiN coatings revealed a significant decrease of the lattice parameter with increasing N_2 deposition pressure, while the elemental composition was identical for all coatings. Consequently, the changes of the lattice parameter can either be attributed to the formation of a TiSiN solid solution and/or to the formation of vacancies during the deposition process. Neither atom probe tomography nor Doppler position annihilation broadening could unambiguously clarify the presence of either a TiSiN solid solution or vacancies. Thus, the powdered TiSiN coatings were studied by *in-situ* XRD in vacuum up to 1200 °C in order to gain insight into the evolution of the lattice parameter at elevated temperatures, which suggests that at lower temperatures vacancies are annihilated and then at higher temperatures Si diffuses out of the TiSiN solid solution. The coating synthesized at the lowest pressure and the one grown in a mixed N_2 and Ar atmosphere already reached the lattice parameter of pure TiN after the high temperature XRD experiment, while for the coatings grown at higher pressures an additional annealing treatment was necessary to reach this value, which might indicate that more Si is incorporated into the TiSiN solid solution at higher deposition pressures and that the additional kinetic activation stemming from the Ar ions results in less Si incorporation. The assumption that at lower annealing temperatures defects are annihilated and at higher temperatures Si diffuses out of the solid solution could be corroborated by differential scanning calorimetry and complimentary investigations of annealed coatings on substrates using energy dispersive X-ray spectroscopy and atom probe tomography. Density Functional Theory (DFT) calculations indicate that defects only play a subordinate role for the low observed lattice parameters in as-deposited state and that the addition of Ar to the deposition atmosphere results in a different incorporation of Si into the TiSiN solid solution.

10:40am **MA3-3-TuM-9 Enhanced Mechanical Properties and Thermal Stability of Novel Nanocrystalline AlNi / Al_2O_3 Multi-layered Coatings Deposited by a Combined Physical Vapour Deposition and Atomic Layer Deposition Approach**, ***Hendrik Constantin Jansen (hendrik.jansen@empa.ch)***, *B. Putz, A. Sharma,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; *M. Hans,* RWTH Aachen University, Germany; *S. Lellig,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, RWTH Aachen University, Germany; *J. Schneider,* RWTH Aachen University, Germany; *J. Schwiedrzik, J. Michler,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; *T. Edwards,* NIMS (National Institute for Materials Science), Japan

A one-chamber-design combining physical vapour deposition (PVD) and atomic layer deposition (ALD) without breaking vacuum allows deposition of Al coatings with Al_2O_3 interlayers. These novel Al coatings possess enhanced thermal stability and mechanical properties compared to their pure PVD nanocrystalline counter-parts. Further recent advances involve multi-layered $Al_{98}Ni_2$ / Al_2O_3 and $Al_{95}Ni_5$ / Al_2O3 (25 / 1 nm) coatings as well as their respective pure $Al_{98}Ni_2$ and $Al_{95}Ni_5$ PVD counterparts, which were deposited to evaluate the influence of grain boundary complexion engineering and the unique crystalline / amorphous interface on mechanical properties and thermal stability. The coatings were annealed at 160°C and 210°C to allow not only grain growth but also segregation enrichment at grain boundaries and triple junctions. Subsequently, microstructural stability was investigated based on lateral grain growth by X-Ray Diffraction χ-scanning and GIWAXS – out-of-plane Al grain size being limited by the 1 nm Al_2O_3 interlayers. Mechanical testing by both nanoindentation and micropillar compression at multiple strain rates allowed mechanical property analysis of the high-strength AlNi / Al_2O_3 multilayer coatings, which reached a yield strength of more than 1.3 GPa, outperforming a previously reported Al / Al_2O_3 (25 / 1 nm) coating achieving 1 GPa. Ultimately, high-resolution analyses by trans-mission electron microscopy and atom probe tomography allowed the enhanced properties to be linked to both grain boundary decoration and secondary phases that hinder dislocation and grain boundary movement.

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

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

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Germany, **Francisco Javier Pérez Trujillo**, Universidad Complutense de Madrid, Spain

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 (peter.kelly@mmu.ac.uk)**,* 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 Cr_2O_3 Coating Deposited by DLI-MOCVD on Zircaloy-2 Substrate***, **Kenza Zougagh (kenza.zougagh@cea.fr)**,* 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, physico-chemical and microstructural properties of the coating are characterized. The performance of the chromia layer against Zircaloy – UO_2 interaction is investigated at high temperature between 400 and 800°C using diffusion couple testing with natural UO_2 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.

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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 Concepción del Uruguay, Argentina*; S. Farina,* CNEA and CONICET, Buenos Aires, Argentina*; J. Quintana,* CNEA (CAC), Buenos Aires, Argentina*; **Sonia P. Brühl (sbruhl@gmail.com)**,* National University of Technology (UTN), Faculty of Concepción 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.

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 H_2SO_4 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) $HV_{0.05,}$ 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 HF1 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 x 10^{-3} mm^3 for the nitrided steel and 150 x 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 H_2SO_4 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 (radoslaw.swadzba@git.lukasiewicz.gov.pl)**,* Lukasiewicz Research Network – Uppersilesian Institute of Technology, Poland*; B. Mendala, L. Swadzba,* Silesian University of Technology, Poland*; U. Schulz, N. Laska, P. 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 48-2-2 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 nominal composition Ti-54Al-14Cr-0.5Si-0.5Y (at. %). The study involved the detailed analysis of the coating's growth mechanism, initial microstructure as well as phase transformations using high resolution Transmission and Scanning Transmission Electron Microscopy (HRTEM and STEM) as well as Scanning Electron Microscopy (SEM) and high temperature X-ray diffraction (HT-XRD). In the as-deposited state the obtained CHC-PVD TiAlCrYSi bond coating was found to be characterized by a columnar microstructure that contained both amorphous and crystalline regions. It has been found that the latter were composed of a strongly textured, hexagonal C14 $Ti(Al,Cr)_2$ Laves phase. It was shown that upon high temperature exposure the coating forms a dual phase microstructure composed of the $Ti(Al,Cr)_2$ Laves and TiAl phases. The coatings were pre-oxidized in pure oxygen atmosphere at 900 °C for 2 hours to form an adherent and stable Thermally Grown Oxide (TGO) and were then coated with Thermal Barrier Coatings (TBCs) using EB-PVD. The obtained coatings were tested under isothermal (50 hours) and cyclic oxidation (1000 1h cycles) conditions at 900 °C. Detailed microstructural investigations using STEM allowed to characterize the thermally grown oxide (TGO) scale. These investigations provided microstructural evidence for the Cr effect on the formation of Al_2O_3 during pre-oxidation treatment. Yttrium was found to segregate to the grain boundaries of alumina oxide scale during high temperature oxidation, indicating the occurrence of the reactive element (RE) effect.

3:00pm **MA1-2-TuA-5 The Influence of Molten Pool Behaviour on the Microstructure and Characteristics of Additive Manufactured Ti-6Al-4V Alloy Composite Coatings***, Olawale Samuel Fatoba (proffatobasameni@gmail.com), T. Jen,* University of Johannesburg, South Africa

Numerous varied engineering applications make use of titanium and its alloys. Its low density, strong specific strength, and excellent resistance to corrosion make it one of the best materials for industrial use. Its low hardness and weak tribological qualities, however, limit its applications and shorten its life service. Surface modification can increase the surface's integrity and increase its availability for a wider range of industry applications. Additive manufacturing efficiently produces and repairs intricate geometrical components in the aerospace, biomedical, and automotive industries. The ultimate quality and structure of the manufactured coatings are influenced by a multitude of powder particle factors and properties; the powder flow rate is also dependent upon the powder morphology, distribution, porosity, angularity, motional interaction of the particles, and their hardness property. The microstructural morphology of the α- and β-phases of titanium alloys is determined by the arrangement of lamellar and equiaxed structures, as well as the fine and coarse texture of the structures. The lamellar structures become fine or coarse depending on the pace of cooling.

The coated specimens were created using direct laser metal deposition (DLMD), and X-ray diffraction (XRD), optical microscopy (OPM), electron dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) were used to characterize the microstructure of the as-received samples. The Vickers hardness tester and the DY2300 Series potentiostat were used to measure the microhardness and corrosion behavior, respectively. The findings demonstrated that Ti-6Al-4V's ultimate tensile strength can advance significantly in terms of surface integrity. The micrographs demonstrate how the α-phase's unique characteristics, which set it apart from earlier beta phases, caused anisotropy in the mechanical characteristics and the coarsened structures made of a high concentration of Ti, Al, and Si. The titanium-aluminide intermetallic compounds are the most prevalent crystallographic phases, and this is what is responsible for the materials' increased hardness. The right proportion of Si and Cu weight percentage in the reinforcing powder, along with an ideal laser intensity and scanning speed, results in a coating with enhanced corrosion resistance; the material corrodes more slowly than a Ti-6Al-4V substrate.

Keywords: Ti-6Al-4V alloy, microhardness, microstructure, additive manufacturing, molten-pool, mechanical properties.

4:00pm **MA1-2-TuA-8 Investigations of Water Vapor Enhanced Oxidation on TiAl-Based Alloys: Evaluation of Protective Coating Systems***, Ronja Anton (ronja.anton@dlr.de), N. Laska,* German Aerospace Center (DLR), Germany

Currently, intermetallic γ-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 due to their comparatively half the density. Their 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, Al_2O_3. However, new turbine engine concepts, such as the Water Enhanced Turbofan (WET) engine concept or the use of hydrogen-based fuels in jet engines, introduce higher amounts of water vapor. Now, not only the γ-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 γ-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 SiO_2 as an 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 γ-TiAl alloys with Al_2O_3-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, γ-TiAl alloys were tested isothermally under water vapor enhanced oxidation up to 30 wt.% water in a tube furnace. The growth of a thick Al_2O_3/TiO_2 mixed oxide scale was analyzed on uncoated γ-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 γ-TiAl alloys in dry oxidation conditions. In water vapor enhanced oxidation processes, the growth of the protective Al_2O_3 oxide scale is increased. In order to assess the need for ann 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 N_2 Flow Rate on Structure and Oxidation Behavior of VN Coatings Deposited by High Power Impulse Magnetron Sputtering***, Ruo-Syuan Chen (pamela.chan34@gmail.com), 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 N_2 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 N_2 flow rates. VN coatings with a thickness of 1 mm were deposited on Si substrate by high power impulse magnetron sputtering (HiPIMS).The duty cycles were controlled to be 3% and 10%. The N_2 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.

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4:40pm **MA1-2-TuA-10 Surface Modification of Copper by Electrical Discharge Coating using 3D-Printed SUS -420 Steel Electrodes***, Siddanna Awarasang (siddanna.awarasang@gmail.com),* National Central University,Taiwan*; J. Hung,* National Central University, Taiwan

This study presents a novel approach to surface science by exploring the integration of 3D-printed SUS-420-steel coatings onto copper substrates through Electric Discharge Coating (EDC) processes. Unlike conventional methods, this approach utilizes 3D Printed electrodes (3DPE) for coating, offering a compact and efficient process. Through systematic optimization of process parameters, including discharge energy levels and coating processes, the study achieves significant improvements in coating thickness from 15.40 to 141.16 µm, microstructure, and composition. Surface analyses and Energy Dispersive X-ray Spectroscopy (EDS) scans reveal steel-rich areas, microcracks, and uniform distribution across the substrate. The resulting coatings exhibit enhanced mechanical properties, including increased hardness and improved resistance to corrosion and thermal degradation. This breakthrough not only opens new avenues in coating industries for complex surfaces but also underscores the potential for further innovation in material deposition technologies.

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

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

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Germany, **Francisco Javier Pérez Trujillo**, Universidad Complutense de Madrid, Spain

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. Lambrecht, D. Maria Teresa, L. Maria Isabel, G. Garcia Martin, J. Chaves,* ***Francisco Pérez Trujillo (fjperez@ucm.es)****,* 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 nitrites 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%$NaNO_3$ - 40%KNO_3, well known as Solar Salt with a freezing point around 220ºC and thermal decomposition at 560ºC [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 about 12ºC and high environmental impact yields the heat to Solar Salt by means of exchangers. The maximum thermal energy storage temperature reached is about 390ºC, 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 $LiNO_3$ and $Ca(NO_3)_2$ 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.$NaNO_3$-19%wt.$Ca(NO_3)_2$- -35%wt.$LiNO_3$ (T1) and 33%wt.$NaNO_3$-22%wt.KNO_3-29%wtCawt.$(NO_3)_2$-16% wt.$LiNO_3$ (Q-1). Life Cycle Assessment (LCA) has been used to calculate the environmental impact of the mixtures through the software tool Simapro7 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, ($LCOE_{TES}$).

The effects of molten salts chemical composition in the high temperature corrosion of metalic materials and coatings will be analized.

In this study, a 50 MW and 6 hours heat storage capacity PT plant has been considered for $LCOE_{TES}$ 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 Cr_3C_2-NiCr-BN Composite Coatings Prepared by a Novel HVOF Process Using Ethanol as a Fuel***, S. Liu,* UTBM, France*; M. Arab Pour Yazdi,* ***Pavel Sedmak (pavel.sedmak@anton-paar.com)****, J. Nohava,* Anton Paar, Switzerland*; M. Moliere, H. Liao,* UTBM, France

Cr_3C_2-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 impact 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 Cr_3C_2-NiCr-BN composite coatings.

8:40am **MA1-3-WeM-3 Oxidation Behavior of Si-Based Coatings on Refractory Multi-Principal Element Alloys***,* ***Brady Bresnahan (bresn047@umn.edu)****, 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***,* ***José D. Castro (jodcastroca@unal.edu.co)****,* 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). SS316L 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 performance regardless of the testing conditions (wet or dry). The findings indicate that the obtained films may be used instead of TBT paint in components used in ships as a potential way to prevent biofouling and corrosion when exposed to seawater.

9:20am **MA1-3-WeM-5 New Black Ceramic Coating on LZ91 Magnesium Alloys by Micro-Arc Oxidation***,* ***Hung-Chi Chen (mouyuan75@yahoo.com.tw)****, S. Jian,* Ming Chi University of Technology, Taiwan

LZ91 Magnesium alloy has improved mechanical properties and a low density but their limited resistance to corrosion limits their application. Therefore, it is a great challenge to increase the stability of LZ91 alloys under corrosive factors and environments. The anodized oxide film of magnesium alloy has many defects (poor bonding strength, low wear and corrosion resistance,) in traditional surface coloring technology. These defects have largely limited the applications of magnesium alloy. Micro-arc oxidation (MAO) is a new electrochemical surface treatment technology, suitable for treating the aluminum, magnesium and titanium and other light metal alloys. In electrolyte by the arc discharge plasma generated of the substrate oxidation and high temperature melting, the film was formed with high hardness and corrosion resistance.

This study uses MAO treatment to increase the corrosion resistance of LZ91 alloy, used copper oxide and $KMnO_4$ to change MAO film color. Then, black ceramic film with uniform color, smooth surface, compact structure and excellent corrosion on LZ91 alloys was successfully obtained by MAO treatment. The aim of this study is to added with various chemical element in MAO electrolyte to change the film color to black and has excellent corrosion resistance.The morphology, structure, adhesion and corrosion behavior of the bi-layered composite coating has been investigated by scanning electron microscopy (SEM), 3D white light interferometry. In this study, MAO coatings were prepared, and the effects of adding $KMnO_4$ and copper oxide to the electrolyte on the corrosion resistance and color of the coating LZ91 magnesium alloy were evaluated.

11:00am **MA1-3-WeM-10 Study on the Characterization of Adding CeO_2 Particles on Micro-arc Oxidation Coated AZ91D Magnesium Alloys***, Po-Wei Lien (lanbow888@gmail.com),* 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 metals, 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 coating solidifies and contracts, resulting in surface structural defects such as microcracks. Hence, the addition of CeO_2 particles in the electrolyte aims to seal micro-pores and introduce self-healing capabilities.

This study uses AZ91Dwas utilized as the research substrate, and CeO_2 was introduced into the electrolyte. The investigation aimed to observe the presence of CeO_2 particles within the micro-pores on the MAO surface and evaluate the self-healing functionality during salt spray experiments. Surface corrosion resistance of AZ91D was examined through scanning electron microscopy (SEM) to assess its microstructure. Corrosion identification was conducted via electrochemical impedance spectroscopy (EIS) and salt spray testing. Surface roughness was measured using atomic force microscopy (AFM).

Keywords: AZ91D alloy; Ceramic oxide layer ; Micro-arc oxidation; CeO_2 particles ; self healing

11:20am **MA1-3-WeM-11 Characteristics Of High-temperature Resistant Coating Prepared By the Liquid Spray Technique***, Yan-Rui Chen (eric19990329@gmail.com),* 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_2), 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_2),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-Che Hung (xauxdy111@gmail.com),* 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 protective coating and also the bond coat for the thermal barrier coatingon 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.

12:00pm **MA1-3-WeM-13 Protection Against Heavy Oil Fouling and Sulfidation: Comparison of PVD and Thermal Sprayed Coatings***, Fellipy Rocha (fellipy.rocha@polymtl.ca),* Polytechnique Montréal, Canada*; L. Vernhes, F. Khelfaoui,* Velan, Canada*; G. Patience, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Valve malfunctions pose a significant and expensive threat to the gas and oil industry, leading to valve position switch failure,poor reactor pressure control, and shutdown. Safety and environmental adverse phenomena are related to worn valve maintenance. The valves are subjected to severe service at high temperature (300 – 450 °C), high pressure drop (20 – 250 bar), and erosive reactor effluents. Heavy crude oil and bitumen hydrocracking require materials that simultaneously withstand wear, oxidation, sulfidation, and coke deposition. In this work, we evaluate the protective efficacy between thin magnetron sputtered films and thermally sprayed Co-based coatings. The samples were submerged in sour crude oil at 450 °C and 110 bar for 2 h to assess their fouling resistance.

In the first part, we evaluated three thermal sprayed Co-based coatings, Co-1, Co-2, and Co-3, varying mostly in Ni, Mo, Si, W, and C contents. The as-sprayed samples exhibited typical lamellae structure, and after fusing they presented an enhanced crystallinity with a Co-Cr-Mo-Si microstructure. Surface image analysis allowed us to quantify the level of surface fouling; specifically, the worst-performing Co-1 coating showed 100% intensity, followed by 89%, and 75% for Co-2 and Co-3. After heat treatment, the same samples exhibited 95%, 15%, and 3% intensity, respectively. SEM-EDS/WDS images confirmed sulfur infiltration into the defects of the as-deposited coatings, as well as a better performance against sulfidation after fusing.

In the second part, we studied room temperature sputtered Al_2O_3 that was initially amorphous with a hardness of 11.1 GPa. Annealing at 1000 °C formed different metastable alumina polymorphs, predominantly γ-Al_2O_3 and α-Al_2O_3. Heat treatment improved alumina adhesion and increased hardness to 20.6 GPa. FIB-SEM-EDS cross-section analyses revealed an interaction between the substrate and the annealed coating. No fouling was observed on the amorphous Al_2O_3, but it was noted on the annealed samples. For comparison, HiPIMS-deposited nitride coatings fabricated with a cylindrical magnetron exhibited a very good adhesion and higher hardness, as well as good fouling protection.

In conclusion, we developed and successfully applied an optical technique to assess fouling on different surfaces. In general, amorphous materials tend to perform better, and especially coatings possessing high hardness are adequate for the heavy oil erosive environment.

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

High Entropy and Other Multi-principal-element Materials I

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

8:40am **MA4-1-WeM-3 Growth and Properties of Epitaxial High-Entropy Alloy Thin Films***, Thomas Seyller (thomas.seyller@physik.tu-chemnitz.de),* Chemnitz University of Technology, Germany **INVITED**

High-entropy alloys (HEAs) are discussed for applications in the fields of corrosion and wear protection as well as electrocatalysis. 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.

[1] H. Schwarz, J. Apell, H. K. Wong, P. Henning, R. Wonneberger, N. Rösch, T. Uhlig, F. Ospald, G. Wagner, A. Undisz, T. Seyller, Advanced Materials 35 (2023) 2301526 (https://doi.org/10.1002/adma.202301526).

[2] H. Schwarz, T. Uhlig, N. Rösch, T. Lindner, F. Ganss, O. Hellwig, T. Lampke, G. Wagner and T. Seyller, Coatings 11 (2021) 468 (https://doi.org/10.3390/coatings11040468).

9:20am **MA4-1-WeM-5 Effect of Elemental Additions (X: Pt, Al, Ti, and Ag) on the Microstructure and Electrical Properties of CrMnFeCoNiX-Based High-Entropy Alloy Thin Films***, **Salah-eddine Benrazzouq (salah-eddine.benrazzouq@univ-lorraine.fr)**, J. Ghanbaja, S. Migot, A. Nominé, J. Pierson, V. Milichko,* 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 phases (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 CrMnFeCoNiAl 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 CrMnFeCoNiAg 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 regions. 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 temperature-dependent electrical resistivity measurements confirm the metallic behavior of our alloys.

9:40am **MA4-1-WeM-6 Property Evaluation of Nd Doped NiCoFeAlTi Non-equiatomic High Entropy Alloy Films and the Influence of Post-annealing Treatment***, **Chia-Lin Li (chialinli@mail.mcut.edu.tw)**,* 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-equiatomic 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 exhibited by all films. The mechanical properties, phases and microstructures of Nd doped HEAFs and annealed films were characterized by the nanoindentation, X-ray diffractometer (XRD) and transmission electron microscopy (TEM), respectively. Based on XRD results, amorphous structures were identified in all Nd doped NiCoFeAlTi HEAFs. After annealing, the films exhibit a mixture of HEA FCC, NdNi HCP and L12 phases due to annealing-induced crystallization. For the mechanical properties of Nd doped HEAFs, both the hardness and elastic modulus showed an initial increase, reaching the maxima of ~9.3 GPa and ~158 GPa at 0.61 at.% Nd addition, respectively,and then decreased with the increasing Nd content. The influence of post-annealing treatment of Nd doped NiCoFeAlTi HEAFs on the microstructures and mechanical properties will be given further in this study.

11:00am **MA4-1-WeM-10 Exploring the Effects of Titanium and Molybdenum Contents, and Enhancing the Crystallinity Through Post-Annealing Treatment on the Microstructure and Mechanical Properties of CoCrNi Medium Entropy Alloy Thin Films***, **Pin-Yu Chen (penny0910152048@gmail.com)**, C. Hsueh,* National Taiwan University, Taiwan

Medium entropy alloys (MEAs), such as CoCrNi, have demonstrated a unique combination of high hardness and excellent ductility, surpassing many high entropy alloys reported to date. In this study, we investigated the effects of Mo and Ti additions on the microstructures and mechanical properties of $(CoCrNi)_{100-x-y}Mo_xTi_y$ medium entropy alloy films (MEAFs). Amorphous and nanocrystalline CoCrNiMoTi MEAFs were deposited on p-type silicon substrates using magnetron three-target co-sputtering. While the power applied to CoCrNi target was fixed at 200 W, the same power was applied on Mo and Ti targets which varied from 0 to 90 W. For simplicity, the film was denoted as MoTi80 when Mo and Ti targets were subjected to 80 W power, and so on.

X-ray diffraction and TEM SAED results revealed a structural transformation from FCC to FCC + HCP at MoTi50 due to HCP Ni_3Ti precipitation. With further increases in Mo and Ti contents, the MoTi80 film exhibited a mixed nanocrystalline and amorphous structure, while the MoTi90 film was fully amorphous. Additionally, the mechanical properties of the films were investigated using nanoindentation and micro-pillar compression tests. 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 and Ti contents. 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. Both hardness and Young’s modulus increased and then decreased with the increasing annealing temperature. 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 (yjyan@gapp.nthu.edu.tw)**, 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 $Ni_{30}Co_{30}Fe_{13}Cr_{15}Al_6Ti_6$ 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 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 (goodelman1@llnl.gov)***, *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 sphero-cylindrical 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 (sfaulhaber@ucsd.edu)***, *M. Patino, D. Nishijima, A. Zaloznik, 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 / electron dispersive x-ray spectroscopy / electron backscatter diffraction (SEM/EDS/EBSD) and Auger electron spectroscopy (AES) before and after exposure to fusion-relevant plasma at deuterium-ion fluences of $2 \cdot 10^{26}$ 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.

[1] El-Atwani O, Li N, Li M, Devaraj A, Baldwin JKS, Schneider MM, Sobieraj D, Wróbel JS, Nguyen-Manh D, Maloy SA, Martinez E. Outstanding radiation resistance of tungsten-based high-entropy alloys. Sci Adv. 2019 Mar 1;5(3):eaav2002. doi: 10.1126/sciadv.aav2002. PMID: 30838329; PMCID: PMC6397024.

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 (jjj881029253@gmail.com)***, 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, academia, 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 AISI304 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 workstation. 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 (yujie.chen@adelaide.edu.au)***, University of Adelaide, Australia

N-supersaturated $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ high-entropy alloys (HEAs) were prepared via magnetron sputtering at various N_2 flow rates (R_N) of 4, 8, 10, 15 and 20 sccm, denoted hereafter as N4, N8, N10, N15 and N20, respectively. It was found that the N content rose up from 6.5 to 28.9 at.% when R_N increased from 4 to 20 sccm. Both N4 and N8 exhibit a face-centred cubic (FCC) structure. An increase inR_N 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 R_N, 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 nitride 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 N 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 Mechanical and Anticorrosive Properties of Laminated (NbTaMoW)N_x Films**, ***Yan-Zhi Liao (11289034@mail.ntou.edu.tw)***, *Y. Chen,* National Taiwan Ocean University, Taiwan

(NbTaMoW)N_x films were prepared through cosputtering with four element targets. The distinction in characterization between the laminated nitride films fabricated at substrate holder rotation speed R_H of 2 and 10 rpm and homogeneous high-entropy alloy nitride films prepared at R_H of 30 rpm were evaluated. The nitrogen flow rate (f_{N2} = [N_2/(N_2+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 f_{N2} from 0.1 to 0.4 at R_H of 2 rpm due to the target poisoning effect, whereas the deposition rate decreased from 46.4 to 34.8 nm/min at R_H of 10 rpm. The phase structures and mechanical and anticorrosive properties of the (NbTaMoW)N_x films were studied. The results indicated that a metallic phase dominated structure was observed for the films prepared at f_{N2} of 0.1, whereas nanocrystalline and face-centered cubic nitride phases were obtained for films fabricated at f_{N2} of 0.2 and 0.4, respectively. The films deposited at f_{N2} of 0.4 exhibited hardness values of 25.2 and 26.1 GPa for the films prepared at R_H of 2 and 10 rpm, respectively, which were lower than 29.9 GPa for the films prepared at R_H of 30 rpm. Potentiodynamic polarization tests were conducted out for evaluating the anticorrosive properties of the films on SUS420 substrate.

3:00pm **MA4-2-WeA-4 Structure and Mechanical Properties of (Al,B,Cr,Si,Ti)-based Thin Films**, ***Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at)***, *P. Konecny,* 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 mostly 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 equiatomic composition and different gas mixtures. All the coatings 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. Debnárová, T. Stasiak, V. Buršíková,* Masaryk University, Czechia; *Z. Czigány, K. Balázsi,* HUN-REN Centre for Energy Research, Hungary; *S. Lin, N. Koutná,* Technische Universität Wien, Austria; ***Pavel Souček (soucek@physics.muni.cz)***, 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.

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/acetylene was used in carbides. This led to 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 multielement carbide 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 GA23-05947S financed by the Grant Agency of the Czech Republic.

3:40pm **MA4-2-WeA-6 Mechanical and Oxidation Properties Evaluation of Equimolar and Non-Equimolar High Entropy Alloy Boron Carbonitride Coatings***, **Igamcha Moirangthem (igamcha@gmail.com)**,* 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 recently for excellent mechanical and chemical properties using physical vapor depositions. In this study, an equimolar TiZrNbTaFe alloy target and a non-equimolar $Al_4Cr_2NbSiTi_2$ 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 TiZrNbTaFeBCN High Entropy Alloy Films***, **Meng-Hsueh Chuang (norman12lin@gmail.com)**,* 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_2 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 an X-ray diffractometer. 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.

Protective and High-temperature Coatings
Room Town & Country C - Session MA5-1-ThM

Boron-containing Coatings I

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

8:20am **MA5-1-ThM-2 Study of W and Zr Interdiffusion in the WB_2 – ZrB_2 System***, Yue Zhou (yznwb@mst.edu), S. Filipovic, D. Lipke, W. Fahrenholtz, G. Hilmas,* Missouri University of Science and Technology, USA **INVITED**

Bulk $WB_2$and ZrB_2 ceramics were fabricated by combining powder synthesis and densification methods. Powder synthesis was executed in a graphite furnace, and SPS was employed for powder densification. The raw powders used for WB_2 synthesis were commercial WO_3, B_4C, and carbon black. WB_2 was synthesized at 1600℃ in vacuum for 2.5 hours. The synthesized powder was densified at 1700℃ in vacuum under a pressure of 50 MPa for 10 minutes. For ZrB_2, the raw powders were ZrO_2, B_4C, and carbon black. Synthesis was performed at 1650℃ in vacuum for 1 hour, and the densification was accomplished at 2050℃ in vacuum under a pressure of 50 MPa for 10 minutes. The fabricated WB_2 and ZrB_2 ceramics were contacted and annealed at 2000 – 2200℃ for different periods for the W and Zr element diffusion study. The morphologies and elements concentrations of the WB_2 - ZrB_2 interfaces were characterized by TEM-EDS. Interdiffusion flux profiles were constructed based on the EDS line scans, and the interdiffusion coefficients were calculated.Finally, Arrhenius plots of the diffusions for each element were established and the corresponding activation energies were calculated.

9:00am **MA5-1-ThM-4 W-Based Thin Film Metallic Glasses Doped with Ni, Zr and B for Industrial Applications***, **Antonin Kubicek (kubicek@shm-cz.cz)**, 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. Schmidtova, 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 Vickers 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 WZrTiB Boride Thin Films***, **Wei-Xiang Fang (wayneisboy14@gmail.com)**,* 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_2B_5 targets were connected with the high power impulse magnetron sputtering (HiPIMS) power and radio frequency power, respectively, to prepare five WZrTiB 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 explore 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 WZrTiB boride thin films. Effects of Ti and Zr contents on the microstructure, mechanical properties, and corrosion resistance of WZrTiB 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 Gocník (marek.gocnik@unileoben.ac.at)**,* Montanuniversität Leoben, Austria*; M. Vidiš, T. Fiantok,* Comenius University Bratislava, Slovakia*; P. Švec, Jr.,* Institute of Physics, Slovak Academy of Sciences, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Slovakia*; M. Truchlý, V. Izai, T. Roch, L. Satrapinskyy, V. Šroba,* Comenius University, Bratislava, Slovakia*; M. Meindlhumer,* Montanuniversität Leoben, Austria*; B. Grančič, P. Kúš,* Comenius University, Bratislava, Slovakia*; J. Kečkéš,* Montanuniversität Leoben, Austria*; M. Mikula,* Comenius University, Slovak Academy of Sciences, Slovakia

Excellent mechanical properties of hard coatings based on transition metals 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 superlattices (SL) and multilayers (ML) TiB_2/TaB_2 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 $TiB_{2.8}$ is typically overstoichiometric, has a nanocomposite character and hardness (H) exceeds 40 GPa. In the case of $TaB_{1.4}$, 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 leads 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 nanostructur. 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 TiB_2/TaB_2coatings had a crystalline character across the entire thickness, and the presence of the hexagonal TiB_2 phase and TaB_2 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 TiB_2 layer is preserved but the TaB_2layer again forms a disordered structure after growing a few nanometers. This softer TaB_2 phase affects the overall hardness values which are lower. Nevertheless, hardness values atthe level of ≈33 GPa still classify these coatings as extremely hard. Fracture-mechanicalbehavior, 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% (K_{IC}= 3.45 MPa $m^{1/2}$) in the TiB_2/TaB_2coating with λ= 8 nm compared to binary $TiB_{2.8}$, where K_{IC}= 2.974 MPa $m^{1/2}$

10:20am **MA5-1-ThM-8 Self-Formation of Dual-Phase Nanocomposite Coatings Within Ternary Zr-Cu-B System***, D. Thakur, M. Cervena, J. Houska, S. Haviar, R. Cerstvy, **Petr Zeman (zemanp@kfy.zcu.cz)**,* University of West Bohemia, Czechia

Transition metal nitride and boride coatings with high hardness and wear resistance prepared by magnetron sputter deposition have become popular materials for many engineering applications. Since these coatings are ceramic materials, they deform predominantly elastically before catastrophic failure. One way to improve their toughness is combining them with a non-ceramic phase in a heterogenous nanocomposite structure that allows them to absorb strain energy to a certain level through plastic deformation. As a result, nanocomposite coatings with balanced mechanical properties, in addition to other functional properties, can be developed.

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 follow up 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 ZrB_2 and ZrCu phases.

The Zr-Cu-B coatings were deposited in argon using four unbalanced magnetrons equipped with two ZrB_2 targets, one Zr target, and one Cu target. The magnetrons with the ZrB_2 and Zr targets were operated in dc regimes, while that 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 variedso 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 ZrB_2 phase and an amorphous ZrCu phase. This effect becomes more pronounced as the volume fraction of the ZrCu phase decreases. 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 (merlo3@llnl.gov)**, 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 **MA5-1-ThM-10 Taking Advantage of Unique Lattice Sites – How to Find New Boron-Based Materials Through Large-Scale Stability Predictions***, **Martin Dahlqvist (martin.dahlqvist@liu.se)**, A. Carlsson, J. Rosen,* Linköping University, IFM, Materials Design, 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_2CrB_2 and W_4CrB_3. 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’ an 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. Almost 200 compounds were identified as stable, and for selected systems mechanical and elastic properties were calculated.

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 **MA5-2-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 (d.karpinski@platit.com)**, P. Karvankova, C. Krieg,* PLATIT AG, Switzerland*; H. Joost, H. Frank,* Gesellschaft für Fertigungstechnik und Entwicklung Schmalkalden e.V., Germany*; A. Lümkemann,* 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 TiB_2) 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 Platit Pi411 coating machine equipped with LACS® 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 (MeB_x) coatings were deposited by concurrent magnetron sputtering of a MeB_2 target and cathodic arc evaporation of a Me target (Me = Ti, TiSi, 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.

1:40pm **MA5-2-ThA-2 Coherent Coexistence of Crystalline Phases Enabled by Planar Defect Formation in Annealed $V_{1-x}W_xB_{2-\delta}$Films**,
***Katarína Viskupová (katarina.viskupova@fmph.uniba.sk)**, B. Grančič,* Comenius University in Bratislava, Slovakia*; P. Švec Jr.,* Slovak Academy of Sciences, Slovakia*; T. Roch, M. Truchlý, V. Šroba, L. Satrapinskyy, M. Mikula, P. Kúš, T. Fiantok,* Comenius University in Bratislava, Slovakia

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/mmm columnar 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 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 $V_{1-x}W_xB_{2-\Delta}$ 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.

[1] P.H. Mayrhofer, C. Mitterer, J.G. Wen, J.E. Greene, I. Petrov, Self-organized nanocolumnar structure in superhard TiB2 thin films, Appl. Phys. Lett. 86 (2005) 1–3, https://doi.org/10.1063/1.1887824.

[2] J. Thörnberg, B. Bakhit, J. Palisaitis, N. Hellgren, L. Hultman, G. Greczynski, P.O. Å. Persson, I. Petrov, J. Rosen, Improved oxidation properties from a reduced B content in sputter-deposited TiBx thin films, Surf. Coat. Technol. 420 (2021), https://doi.org/10.1016/j.surfcoat.2021.127353.

[3] K. Viskupová, B. Grančič, T. Roch, Š. Nagy, L. Satrapinskyy, V. Šroba, M. Truchlý, J. Šilha, P. Kúš, M. Mikula, Thermally induced planar defect formation in sputtered V1-xMoxB2-Δ films, Scripta Materialia, Volume 229, 2023, 115365, ISSN 1359-6462, https://doi.org/10.1016/j.scriptamat.2023.115365.

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).

2:00pm **MA5-2-ThA-3 Powder Synthesis and Application of Atmospheric Plasma Spraying Zirconium Diboride Coating**,
***Ching Lee (tiger881217@gmail.com)**,* National Taipei University of Technology, Taiwan*; Y. Chen,* Researcher of National Chung-Shan Institute of Science & Technology, Taiwan*; Y. Chung,* Researcher of National Chung-Shan Institute of Science & Technology, Taoyuan city, Taiwan*; Y. Yang,* National Taipei University of Technology, Taiwan

Zirconium diboride has excellent properties such as high melting point, high thermal conductivity, high hardness, low theoretical density, good electrical conductivity, etc., making it suitable for the outer shell of supersonic spacecraft and missiles. As spacecraft or missiles will generate heat sources due to friction with the atmosphere at high altitudes, it is necessary to attach a layer of high-temperature refractory materials to prevent the heat generated externally from reaching the inside of the body. This experiment uses Atmospheric Plasma Spray (APS) to prepare self-synthesized zirconium diboride, and explores the coatings prepared under different spray conditions (current, surface speed, working distance). The coating was analyzed such as X-ray Diffraction, Scanning Electron Microscope, Crystallinity Analysis, Bond Strength Analysis, Micro Hardness Analysis, etc.

2:20pm **MA5-2-ThA-4 Annealing Twins in Sputtered Tantalum Boride Coatings**,
***Branislav Grančič (branislav.grancic@fmph.uniba.sk)**, K. Viskupová, T. Fiantok,* Comenius University in Bratislava, Slovakia*; P. Švec Jr.,* Slovak Academy of Sciences, Slovakia*; V. Šroba, V. Izai, T. Roch, M. Truchlý, M. Mikula,* Comenius University in Bratislava, Slovakia

Magnetron sputtered transition metal diboride TMB_{2-x} coatings with significant substoichiometry are often amorphous in the as deposited state [1, 2]. Subsequent annealing at high temperatures can lead to formation of various crystalline phases [3]. In our work, we study the effect of annealing up to 1300°C on structure of substoichiometric $TaB_{1.2}$ films. Analysis by High Resolution Transmission Electron Microscopy revealed crystallization into orthorhombic Cmcm structure with high density of annealing twin lamellae. Using ab-initio calculations we show that the formation of stacking faults on {110} planes are energetically favorable and accumulation of such defects can lead to formation of orthorhombic Pnma phase with similar formation energy as Cmcm phase. Moreover, the thermally induced structural changes were accompanied by coatings' hardness increase from 27 to 34 GPa.

[1] B. Grančič, M. Pleva, M. Mikula, M. Čaplovičová,L. Satrapinskyy, T. Roch, M. Truchlý, M. Sahul, M. Gregor, P. Švec,M. Zahoran, P. Kúš, Stoichiometry, structure and mechanical properties of co-sputtered $Ti_{1-x}Ta_xB_{2\pm\Delta}$ coatings, Surf. Coat. Technol. 367 (2019) 341–348, https://doi.org/10.1016/j.surfcoat.2019.04.017.

[2] K. Viskupová, B. Grančič, T. Roch, L. Satrapinskyy, M. Truchlý, M. Mikula,V. Šroba, P. Ďurina, P. Kúš, Effect of reflected Ar neutrals on tantalum diboride coatings prepared by direct current magnetron sputtering, Surf. Coat. Technol. 421 (2021), https://doi.org/10.1016/j.surfcoat.2021.127463.

[3] K. Viskupová, B. Grančič, T. Roch, Š. Nagy, L. Satrapinskyy, V. Šroba, M. Truchlý, J. Šilha, P. Kúš, M. Mikula, Thermally induced planar defect formation in sputtered $V_{1-x}Mo_xB_{2-\Delta}$ films, Scripta Materialia, Volume 229, 2023, 115365, ISSN 1359-6462, https://doi.org/10.1016/j.scriptamat.2023.115365.

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 **MA5-2-ThA-5 Constitution, Microstructure and Properties of Magnetron Sputtered CrB_2-TiB_2 and CrB_2-ZrB_2 Thin Films**, *V. Ott,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; H. Riedl, T. Wojcik,* Vienna University of Technology, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; P. Mayrhofer,* Vienna University of Technology, Austria*; **Michael Stueber (michael.stueber@kit.edu)**,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal diboride thin film materials can provide interesting property 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 sophisticated 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 CrB_2-TiB_2 and CrB_2-ZrB_2. For both 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 **MA5-2-ThA-6 Fracture Characteristics of Si Containing Ternary and Quaternary Transition Metal Diborides**, ***Anna Hirle (anna.hirle@tuwien.ac.at)**, A. Bahr, O. Beck, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* 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 CrB_2, HfB_2, or TiB_2 [3,4]. Adding these strong oxide formers to diborides results in highly dense and protective SiO_2-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 $TaSi_2$ and $MoSi_2$ into TiB_2 thin films not only reduces the amount of Si needed to provide excellent oxidation resistance but also minorly influences the mechanical properties. For quaternary TiB_2 based coatings, hardness values of 36 GPa ($TaSi_2$) and 27 GPa ($MoSi_2$) compared to around 38 GPa of the binary system have been achieved. Interestingly, for ternary Ti-Si-$B_{2\pm z}$ films the mechanical properties vary in a wide range ceasing 20 GPa while exhibiting similar oxidation stabilities. All these coatings crystalized in the α-AlB_2 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 (K_{IC}) of binary $TiB_{2\pm z}$ is known to be highly dependent on the amount of tissue phase present at the grain boundaries.

Therefore, this study aims to unravel the fracture resistance of Si containing ternary and quaternary TMBs, focusing on alloying routes with disilicides. A set of different coating compositions has been deposited by non-reactively DC magnetron sputtering using a broad set of composite targets TiB_2, TiB_2/$TiSi_2$ (90/10 & 80/20 mol%), TiB_2/$TaSi_2$ (90/10 & 80/20 mol%) and TiB_2/$MoSi_2$ (85/15 & 80/20 mol%). The elastoplastic behaviour involving also fracture characteristics such as K_{IC} are evaluated by micro-mechanical testing methods, such as cantilever bending or pillar compression testing, as well as nanoindentation. For an in-depth understanding, these results are correlated with detailed structure-morphological investigations using XRD, SEM, TEM, or ERDA/RBS.

[1] GB. Raju, et al,. J Am Ceram Soc. 2008;91(10):3320–3327.

[2] GB. Raju, et al., Scr Mater. 2009;61(1):104–107.

[3] T. Glechner, et al., Surf. Coat. Technol. 434 (2022) 128178.

[4] A. Bahr, et al.,Materials Research Letters. 11 (2023) 733–741.

3:20pm **MA5-2-ThA-7 Yttrium Tetraboride Thin Films – Thermal Evolution of the Nanostructure and Mechanical Properties**, ***Marek Vidiš (marek.vidis@fmph.uniba.sk)**, M. Truchlý, V. Izai, T. Fiantok, T. Roch, L. Satrapinskyy,* Comenius University Bratislava, Slovakia*; Š. Nagy,* Slovak Academy of Sciences, Slovakia*; M. Mikula,* Comenius University Bratislava, Slovakia

Ultra-high temperature ceramics based on transition-metal diborides (TMB_2) attract attention due to their excellent chemical and mechanical properties. However, their practical application is limited by their inherent brittleness. The Y-B system offers a number of stoichiometric phases with a wide range of mechanical properties. The YB_2 has the lowest Young's modulus among the TMB_2, while the YB_6 is predicted to be a ductile ceramic. On the other hand, the YB_4 has the highest hardness among the Y-B phases, a melting temperature of 2800 °C, and a high flexural strength of 317 MPa. However, only a limited amount of knowledge is available about its properties in the form of a thin film. In this work, we focus on YB_4 thin film prepared by High Target Utilization Sputtering (HiTUS) technology using a stoichiometric YB_4 target. We report the evolution of the chemical composition, nanostructure, and mechanical properties after vacuum annealing up to 1300 °C. The EDS/WDS analyses show a slight over-stoichiometry of the sputtered film with a B/Y ratio of 4.7, a low oxygen content below 2 at.%, and a stable chemical composition with no boron loss. The as-deposited film is X-ray amorphous with a hardness of 23.4 GPa and a low Young's modulus of 281 GPa. After annealing at 800 °C, a partial crystallization occurs, and small regions with the tetragonal YB_4 phase in the amorphous matrix can be recognized. Further annealing leads to the grain coarsening of the YB_4 phase and formation of smaller grains of the cubic YB_6 phase. According to the XRD and HR-STEM, the coherence domain size increases from 26 nm to 44 nm for the YB_4 phase and from 7 to 53 nm for the YB_6 phase. The changes in the nanostructure are reflected in the mechanical properties of the film. The hardness increases to 26.4 GPa at 1000 °C, while a relatively low Young's modulus of 322 GPa is maintained. The ductile/brittle response to the mechanical loading is examined by cube-corner indentation. In the case of as-deposited film, a material pile-up at the edges with no crack formation is observed, indicating a ductile behavior of the X-ray amorphous film. After annealing, a crack formation is observed at the corners of the indents, which is a sign of a more brittle response. To conclude, the exceptional properties of YB_4 ceramic are confirmed in the form of thin sputtered films and are maintained even after high temperature loading. Therefore, the YB_4 thin film is a suitable candidate for example in superlattice architecture, where it would play the role of a medium-hard but less brittle layer in order to improve the overall toughness and thermal shock resistance of the coating.

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 Benrazzouq (salah-eddine.benrazzouq@univ-lorraine.fr), *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 (CrMnFeCoNi) with additional elements like Pt, Cu, Ti, Zr, Al, and Ag. We found that the CrMnFeCoNi 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+BCC 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 using thermodynamic 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-3 Optimizing Temperature Stability in Non-Reactively Sputtered (Hf,Ta,Ti,V,Zr)B-C-N Coatings by Design of the Non-Metal Sublattice,
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In the past, we have studied the system (Hf,Ta,Ti,V,Zr)B-N with exceptional hardness and thermal stability, but the coatings contained a significant amount of C impurities, which may have influenced the properties [1]. To investigate the impact of C in this system, we have deposited new coatings with a TiN target, on which we placed diboride and/or carbide pieces of the metals Hf, Ta, V, and Zr. We have varied the composition by using either only diborides, 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 42 and 0 at%, the C content between 25 and 0 at%, and the N content is stable at around 30 at% in all coatings. The Ti makes up roughly 20 at%, while the other metals are in the range between 2 and 5 at%. X-ray diffraction (XRD) shows a weakly textured single-phase fcc solid solution in all coatings. The FWHM of the 200 reflex ranges from 2 ° in the C-free coating down to 0.5 ° in the B-free coating, indicating different grain sizes. This is confirmed by transmission electron microscopy, revealing fine columnar growth in the 2.3 to 3.2 µm thick 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_2 phase is formed.

[1] Kretschmer, A., Kirnbauer, A., Pitthan, E., Primetzhofer, D., Yalamanchili, K., Rudigier, H., & Mayrhofer, P. H. (2022). High-entropy alloy inspired development of compositionally complex superhard (Hf,Ta,Ti,V,Zr)-B-N coatings. *Materials & Design*, *218*, 110695. https://doi.org/10.1016/j.matdes.2022.110695

MA-ThP-4 Unravelling Diffusion Processes and Morphology Changes of Ternary and Quaternary Diborides During High-Temperature Oxidation,
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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 (TMB_2) 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 TMB_2 with $MoSi_2$) diborides 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 disilicide 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.

[1] M. Magnuson et al., Review of transition-metal diboride thin films, Vacuum. 196 (2022) 110567.

[2] T. Glechner et al., Influence of Si on the oxidation behavior of TM-Si-B2±z coatings (TM = Ti, Cr, Hf, Ta, W), Surf. Coat. Technol. 434 (2022) 128178.

[3] A. Bahr et al., High-temperature oxidation resistance of ternary and quaternary Cr-(Mo)-Si-B2-z coatings — Influence of Mo addition, Surf. Coat. Technol. 468 (2023) 129733.

MA-ThP-5 Influence of Mo on DCMS and HiPIMS Deposited $TiB_{2\pm z}$ Thin Films,
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Titanium diboridethin films deposited by physical vapor deposition are typically attributed to inherent brittleness. Theoretical predictions by DFT assessing the elastic constants revealed that the formation of ternary Ti-Mo-$B_{2\pm z}$ might be a suitable approach to gain a less brittle character.

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 $Ti_{1-x}Mo_xB_{2\pm z}$ thin films: TiB_2/MoB 95/5 mol%, TiB_2/MoB 90/10 mol%, and TiB_2/MoB 80/20 mol%. The binary $TiB_{2\pm z}$ system was deposited with a TiB_2/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.

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 $Ti_{1-x}Mo_xB_{2\pm z}$ fracture characteristics such K_C or K_{IC}have been determined by cube corner indentation and in-situ micro-mechanical bending tests, respectively. 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 α-structured (SG191) $Ti_{1-x}Mo_xB_{2\pm z}$ solid solutions. An increased hardness for both binary and ternary thin films, with a maximum value of 45 ± 1 GPa (TiB_{2+z}) 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 $TiB_{2\pm z}$ using different growth techniques.

MA-ThP-7 Impact of the B/Ti-ratio on Microstructure, Mechanical Properties, and Thermal Stability of DCMS and HiPIMS TiB_2 Thin Films*,* ***Ludwig Enzlberger (ludwig.enzlberger@tuwien.ac.at),*** TU Wien, Institute of Materials Science and Technology, Austria*; M. Podsednik,* TU Wien, Austria*; S. Kolozsvari,* Plansee SE, Germany*; A. Limbeck,* TU Wien, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Titanium diboride is widely known as a superhard material achieving an indentation hardness of 40 GPa and beyond. Coatings of TiB_2 produced by DC magnetron sputtering (DCMS) are typically in the superstoichiometric regime regarding the B/Ti-ratio in a range of $TiB_{2.4}$ to $TiB_{3.5}$. This surplus in Boron is attributed to a different radial distribution of Boron and Titanium during the deposition process and forms a tissue phase which is highly relevant for the material's mechanical properties.

A reduction of Boron content in the coating would thus mean a reduction of tissue phase formed and consequently a clear change in e.g., hardness or fracture toughness. Earlier works have already shown an increase in fracture toughness (measured by microcantilever bending) of DC-sputtered TiB_2 when reducing the B/Ti-ratio from 4.4 to 2.1. There have also been reports of even higher fracture toughness in understoichiometric $TiB_{1.43}$ produced through high power impulse magnetron sputtering (HiPIMS) and measured by cube corner indentation, while films grown by DCMS showed a decrease in K_C with decreasing B-content.

Here we address this discrepancy, via detailed studies of DCMS as well as HiPIMS developed $TiB_{2\pm z}$ thin films with B/Ti-ratios varying between 1.5 and 3.2. The stoichiometry of DCMS-grown films is adjusted by placing Ti-pieces at the target race track, while that of HiPIMS-grown films is adjusted by varying the pulse on-time. The B/Ti-ratios are measured by ICP-OES and the mechanical properties are characterized by nanoindentation (Hardness, Young's Modulus) as well as cube corner indentation for K_{IC}. Vacuum annealing treatments with subsequent detailed transmission electron microscopy studies as well as nanoindentation experiments clarify the impact of the B/Ti ration on these important characteristics.

MA-ThP-8 Synthesis and Characterization of $AlMgB_{14}$ Thin Films*,* ***Erwin Peck (erwin.peck@tuwien.ac.at),*** *A. Kirnbauer,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

When it comes to the protection of tools and the increase of their lifetime, protective coatings with high hardness, good wear resistance, and low coefficients of friction are commonly used. Typically, nitrides, carbides, and borides –specifically metal-diborides such as TiB_2, ZrB_2, and TaB_2 – are selected as protective coating materials.

Here, we concentrate on more complex borides, $AlMgB_{14}$, and study their microstructure, mechanical properties, thermal stability, and wear resistance.

$AlMgB_{14}$ is a very promising material with reported high hardness (even superhardness, > 40 GPa), high thermal stability, and very low coefficients of friction. We developed $AlMgB_{14}$ coatings by magnetron sputtering, using a single composite $AlMgB_{14}$ target, and varying the substrate temperatures between 300 and 600 °C. All of these coatings were amorphous in their as-deposited state with hardness increasing from 29.3±1.6 GPa to 42.1±1.5 GPa upon increasing the substrate temperature from 300 to 600 °C. Simultaneously, their indentation moduli only increase from 373±17 to 497±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.

MA-ThP-9 Non-Reactive Magnetron Sputtering of Al-N Coatings*,* ***Balint Hajas (balint.hajas@tuwien.ac.at),*** *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

Hard protective coatings allow for increased lifetime of machining tools and more versatile applications. Although AlN-based coatings have a rich history in material science with various improvements for their production, little is known about non-reactive deposition using ceramic AlN compound targets. Aluminium nitride in its hexagonal close packed (hcp) wurtzite-type structure has the highest thermal conductivity among ceramic materials, a large electromechanical coupling factor and temperature stability, as well as a high acoustic velocity.

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-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 plasma condition. Additionally, several experiments were conducted by adding H_2 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 N_2 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-10 Effects of the Modulation Period and Ratio on Mechanical Properties and Oxidation Resistance of WB_2/AlB_2 Superlattices*,* ***Chun Hu (chun.hu@tuwien.ac.at),*** Institute of Materials Science and Technology, TU Wien, Austria*; R. Hahn,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; T. Wojcik, R. Janknecht, N. Koutná, P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Superlattice structures offer a unique playground for simultaneous hardness and fracture toughness enhancements by tuning the layer thicknesses 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 WB_2/AlB_2 system, where already one of the chosen materials, AlB_2, 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 WB_2/AlB_2 superlattice thin films with different modulation periods (λ, 3-50 nm) and thickness ratios (η, WB_2/AlB_2=1, 2, 3). All superlattices reveal single-phase AlB_2-type structure. With the template effect of the WB_2 layers, the AlB_2 layers are supported for their crystallization as single phase AlB_2-type layers, even for deposition parameters which would otherwise result in a dual phase constitution of Al and AlB_{12}. TEM investigations of selected samples reveal clearly coherent interfaces between WB_2 and AlB_2 layers. Nanoindentation studies show that these WB_2/AlB_2 superlattice films facilitate the superlattice effect for hardness, which we rationalize with the shear modulus mismatch and modulation period. Among the WB_2/AlB_2 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 WB_2/AlB_2 superlattices compared with WB_2 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 (sofmat@ufpr.br)**,* 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 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 literature 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. Nanoscratch 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 Combusion Boilers, ***Alina Agüero Bruna (agueroba@inta.es)**,* Ctra. Ajalvir km 4, Spain*; M. Gutierrez, S. Rodríguez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Biomass is a renewable, CO_2 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 550º 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 ºC 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 600º 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 (bdh@cpp.edu)**, 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 adverse 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 (cdsullivan@cpp.edu)**, 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-deposited 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.

MA-ThP-15 Corrosion Behavior of Galvanized Coils in Coastal Warehouse Environment, ***Baiyou Fang (Fangby88@163.com)**,* Baosteel-NSC Automotive steel Sheets Co., Ltd, China

To investigate the corrosion failure of packed galvanized coils in a coastal warehouse, a scanning electron microscope with energy disperse spectroscopy and a Raman spectrometer were employed to observe corrosion morphologies of rusty surfaces and detect their chemical compositions. In general, two types of rusts were distinguished, the white grey and the red brown, in which the white corrosion product was a mixture of ZnO, $Zn(OH)_2$, $Zn_4SO_4(OH)_6$ and $Zn_5(CO_3)_2(OH)_6$, and the brown one was mainly composed of γ-FeOOH. In light of these, the corrosion mechanism was determined for the galvanized sheets. Due to the day-and-night temperature difference and high humidity, condensation took place readily, providing electrolyte for corrosion process. Further the zinc coatings react with O_2, H_2O, CO_2 and SO_2 depositing on the surface of galvanized sheet during the initial stage of corrosion, resulting in the white corrosion product. After the exhausting of galvanizing effect in the local area, the steel substrate started to corrode, and thus the red brown product formed.

MA-ThP-16 Development of Zr-Ta Anticorrosion Coatings for Nuclear Applications Using PVD HiPIMS Technology, ***Cécile Marsal (cecile.marsal@cea.fr)**,* Commissariat à l'Énergie Atomique et aux énergies alternatives Centre de Saclay, France

Reprocessing of spent fuel is essential to establish a sustained nuclear cycle, as it enables reusable materials to be recycled and waste to be limited. This retreatment requires the use of nitric acid, which is particularly corrosive for the materials making up the equipment used for fuel reprocessing. However, most of the materials that efficiently passivates in the reprocessing media are expensive, which hinders their direct use. Alternatively, they can be used as coating, the protective performance on which may be further enhanced by mixing two or more complementary elements.

In this study, the corrosion resistance in a nitric acid environment of zirconium-tantalum and zirconium-chromium coatings of distinct compositions on 304L stainless steel was scrutinized. Coatings were elaborated by High-Power Impulse Magnetron Sputtering (HiPIMS), using a tandem target setup allowing for combinatory synthesis of high quality adherent coatings made of Cr-Zr or Ta-Zr solid solutions. The adherence, composition and microstructure of coatings were then characterized by SEM and XRD. Immersion tests in nitric acid demonstrated the appreciable gain in substrate protection with respect to the aggressive environment used for fuel reprocessing.

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MA-ThP-17 Study on Physical Phenomena During Precise Cutting with Novel WCCo/cBN Composite Cutting Tools Equipped with Various Anti-Wear Coatings*, Szymon Wojciechowski (szymon.wojciechowski@put.poznan.pl), R. Talar, P. Zawadzki,* Poznan University of Technology, Poland

Recent research on the development of modern tool materials with improved cutting-performance focuses on the production of hybrid materials combining the advantages of carbides and superhard materials (cBN and PCD). Examples of such materials are novel WCCo/cBN composites obtained by pulse-plasma sintering (PPS). However, the preliminary studies reveal that during cutting of hard-to-cut materials with these novel WCCo/cBN cutting tools an intense built-up-edge (BUE) formation, together with adhesion wear can appear. Thus, in order to improve the cutting ability of WCCo/cBN materials, the anti-wear coatings can be applied. This work is focused on the analysis of physical phenomena and tool wear during turning of spheroidal cast iron with coated (with TiN and TiAlN coatings) and uncoated WCCo/cBN tools. The conducted studies involved the evaluation of a fundamental cutting process physical indicators, as cutting forces and vibrations. Moreover, an updated Merchant cutting model was applied for a determination of the average coefficient of friction on the rake face. The proposed approach considered both the shearing forces related to the chip formation mechanisms, as well as the edge forces related directly to rubbing phenomena occurring between the flank face of a tool and workpiece. Ultimately, the tool wear mechanisms and tool life of the uncoated and coated WCCo/cBN inserts were identified and compared with ones obtained during cutting with a coated and uncoated cemented carbide tools. The obtained results showed the presence of a built-up-edge (BUE) on the flank face of the uncoated WCCo/cBN tool throughout the entire range of cutting speed. In the case of WCCo/cBN inserts with TiN and TiAlN coatings, a BUE was also observed, however, its intensity was significantly lower comparing to that obtained during cutting with the uncoated BNDCC tool. The highest tool life was obtained during grooving with the WCCo/cBN inserts with TiAlN coatings and then with WCCo/cBN inserts equipped with TiN coatings. The tool life obtained for a cemented carbide inserts with TiAlN coating was significantly lower than that for a WCCo/cBN TiAlN insert.

MA-ThP-18 Fabrication and Characterization of Titanium-doped Indium Tin Oxide Thin Film*, Mohammad Kamal Hossain (kamalhossain@kfupm.edu.sa), A. Ulhamid,* King Fahd University of Petroleum and Minerals, Saudi Arabia

Metal-doped indium tin oxide (M-ITO), particularly Gd, In and Al-doped ITO has emerged as an efficient transparent conducting oxide (TCO) to facilitate high mobility and transparency as needed for photo-active devices such as solar cell and a light-emitting diode. However, most of these metals are scarce, and such M-ITO thin film requires special care to fabricate and achieve the best optoelectronic properties suitable for solar cell applications. In this work, we have fabricated tin (Ti)-doped ultrathin ITO film (called hereafter ITO:Ti) through a co-sputtering technique with and without nitrogen (N_2). A detailed and systematic study has been carried out by changing the doping percentage and treating it at different annealing temperatures. Ti doping within ITO thin films was controlled by changing the deposition power provided to the DC gun. Field emission electron scanning microscope (FESEM), SEM-aided energy dispersion spectroscopy (EDS), UV-absorption and transmission, X-ray diffraction (XRD), Hall effect, and ellipsometry were used to perform topographical, optical, and electrical characterizations. The samples were annealed for 2 hours at 200, 400, and 600 °C before being investigated. The impact of Ti doping inside ITO with and without N_2 has been elaborated. Preliminary visual inspection confirmed that the degree of Ti doping altered transparency and shifted the specimen toward opaqueness. The same samples, however, were more transparent after being annealed at higher temperatures. In the instance of N_2 environment, Ti doping was shown to have less of an effect on lowering transparency. UV-Vis measurements revealed that the transparency decreased with increasing Ti doping. The band gap and Urbach energy were estimated for samples containing and not containing N_2. SEM and SEM-aided EDS were used to explore detailed topography and elemental confirmation, respectively. A solar simulator was used to assess the performance of a conventional solar cell with and without the presence of the aforementioned thin films. Due to space limitations, more information is not included in this article. Experimental details and further elaboration of the results will be presented at the event and in the conference proceedings.

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