New Horizons in Coatings and Thin Films
Room Town & Country B - Session F5-1-MoM

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

Moderators: David Holec, Montanuniversität Leoben, Austria, **Ivan G. Petrov**, University of Illinois at Urbana-Champaign, USA

10:00am **F5-1-MoM-1 Competition between Plasticity and Brittleness in Refractory Ceramics***, **Davide Sangiovanni (davide.sangiovanni@liu.se)**, F. Tasnadi, I. Abrikosov,* Linköping University, Sweden **INVITED**

Understanding the competition between brittleness and plasticity in refractory ceramics is of fundamental importance for screening and design of hard materials with enhanced resistance to fracture from room to elevated temperature.

Ab initio and classical molecular dynamics (AIMD & CMD) simulations are used to investigate fracture mechanisms in defect-free, as well as notched B1 $Ti_{1-x}Al_xN$ ($0 \leq x \leq 0.75$) supercells subject to tensile and shear deformation as a function of temperature. The interatomic potential employed in CMD – thoroughly validated for several structural, mechanical, and thermodynamic properties of Ti-Al-N systems – accurately reproduces the results of AIMD simulations obtained for *small* (1100 atoms) supercells. Hence, the results of relatively large ($\approx 10^5$ atoms) CMD simulations of notched crystals subject to mode-I tension allow gaining a comprehensive understanding of the competition between unstable crack growth vs plasticity mechanisms at crack tips in Ti-Al-N systems.

The talk also briefly introduces an AIMD database (24 investigated systems) of B1-structure ceramic properties calculated for $300 \leq T \leq 1200$K. The database includes both raw *ab initio* data – $\approx 10^9$ phase-space configurations with associated energies, forces, total stresses, and magnetic moments – as well as mechanical properties including elastic constants, tensile and shear strengths, moduli of tensile toughness, Schmid vs non-Schmid lattice-slip mechanisms, and strain-mediated lattice transformation pathways. Taking Ti-Al-N systems as representative case, it is illustrated how indicators (determined from the *ideal* properties of single-crystal ceramics) can reliably predict statistical trends in mechanical performance evaluated for systems that contain native structural flaws.

Sangiovanni, Inherent toughness and fracture mechanisms of refractory transition-metal nitrides via density-functional molecular dynamics, Acta Materialia (2018).

Sangiovanni et al, Strength, transformation toughening, and fracture dynamics of B1 Ti-Al-N alloys, Physical Review Materials (2020).

Mei et al, Adaptive hard and tough mechanical response in single-crystal B1 VNx ceramics via control ofanion vacancies, Acta Materialia (2020).

Almyras et al, Semi-Empirical Force-Field Model for the Ti-Al-N System, Materials (2019).

Sangiovanni et al, Enhancing plasticityin high-entropy refractory ceramics via tailoring valence electron concentration, Materials &Design (2021).

Sangiovanni et al, Temperature-dependent elastic properties of binary and multicomponent high-entropyrefractory carbides, Materials & Design (2021).

10:40am **F5-1-MoM-3 Intriguing Deformation Mechanisms in Nanolayered Ceramics***, **Nikola Koutná (nikola.koutna@tuwien.ac.at)**,* TU Wien, Austria*; L. Löfler,* RWTH Aachen University, Germany*; D. Holec,* Montanuniversitat Leoben, Austria*; Z. Chen, Z. Zhang,* Austrian Academy of Sciences, Austria*; L. Hultman,* Linkoping University, Sweden*; P. Mayrhofer,* TU Wien, Austria*; D. Sangiovanni,* Linkoping University, Sweden

Nanolayered ceramic materials exhibit fascinating properties and can easily overshadow their individual layer components. An excellent example are the superhardening and supertoughening effects experimentally shown for series of nitride superlattices, such as cubic-based TiN/VN, TiN/WN, or TiN/CrN films. Advancing applicability of nanolayered ceramics in extreme conditions—including high mechanical loads—calls for atomic-level understanding of their response to stress. In this talk, we employ multi-method/multi-(length)scale approach that combines density-functional ab initio molecular dynamics, classical molecular dynamics, and experiments to identify elementary mechanisms responsible for tensile strength, plastic deformation, and fracture in transition metal nitride superlattices. The AlN/TiN system—a paradigm protective coating for industrial machining and engine components—represents our model platform. The predicted bilayer-period-dependent trends closely relate to different strain-mediated phase transformations initiating in AlN layers. In particular, the B1-to-B3 transformation is clearly confirmed also by transmission electron microscopy analyses of AlN/TiN superlattice films. The key message of our study is that a simultaneous increase in hardness and toughness can be achieved if the superlattice layer thickness is such that slip across the SL interfaces is impeded at initial stages of deformation, while lattice transformations within AlN layers are gradual and/or local, rather than full polymorph transitions. The AlN/TiN system is well-established and widely studied, however, other TiN-based superlattices, e.g. TaN/TiN, offer even better basis for plasticity enhancement: not only via phase transformations but also via vacancy and valence electron concentration engineering. Different deformation mechanisms arising in these superlattices will be discussed, especially in contrast to AlN/TiN.

11:00am **F5-1-MoM-4 In Silico Testing of AlN/TiN Superlattices Using Molecular Dynamics***, **Lukas Löfler (loefler@mch.rwth-aachen.de)**,* Montanuniversität Leoben, Austria*; N. Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; Z. Chen,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; G. Nayak,* Montanuniversität Leoben, Austria*; O. Renk,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; L. Hultman,* Linköping University, Sweden*; Z. Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; D. Sangiovanni,* Linköping University, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria

The mechanical strength and fracture toughness of thin films can be tuned by microstructure. Superlattices, for example, have shown an increase in both hardness and fracture toughness at small layer thicknesses for a variety of materials. The introduced interfaces in these systems govern the mechanical response of the coating. However, their key role during mechanical loading is not yet understood. In this work, classical molecular dynamics simulations were performed to study the behavior of rocksalt cubic-structured AlN(001)/TiN(001) superlattices under mechanical loading in the form of uniaxial tension and indentation.

The tensile loading simulations aimed at revealing mechanisms behind plasticity and crack growth. Cells with layer thicknesses between 1.25 and 10 nm were put under tensile loading in different crystallographic directions. Depending on the load direction different mechanisms for plastic deformation are activated resulting in anisotropic behavior. Tensile loading perpendicular to the (001)-interface shows only minor plasticity accompanied by the nucleation of only a few dislocations and fracture parallel to the layers near the interface. Strain applied along the [100] and [110] directions on the other hand reveals a significant increase in toughness due to B1-to-B3 or B1-to-B4 phase transformations in AlN and later the development of shear bands. Under these load scenarios, networks of dislocations form that can, for small layer thicknesses, span over the interfaces. The findings were supported by ab initio molecular dynamics and nanoindentation and transmission electron microscopy experiments. From the joint results, we could conclude that the layer thickness of superlattices can impede the formation of cracks.

The indentation simulations focused on the intermixing of the alternating layers in superlattices under the load of the indenter. We were able to reveal that with ongoing deformation, a single phase starts to form near the indenter, degrading the coherent interface. The findings were supported by nanoindentation and high-resolution transmission electron microscopy experiments.

These cutting-edge simulations provided novel insights into the deformation mechanisms and processes of thin bi-layer superlattices at the atomistic level, hence complementing information available through high-end sophisticated experiments.

11:20am **F5-1-MoM-5 Advancing Computational Methods for Heterogeneous Material Systems***, **Susan Sinnott (sinnott@matse.psu.edu)**,* Penn State University, USA **INVITED**

Heterogeneous systems are challenging to investigate with high fidelity at the atomic scale across length scales that are not accessible by first-principles methods. This presentation describes recent developments of classical reactive potentials to enable the modeling of phenomena such as metal catalyst absorption to graphene and carbide-derived carbon supports, the interactions of metal catalysts with water, and the growth of thin films on oxide substrates. The classical simulations that are used to investigate these phenomena are complementary to first-principles, quantum mechanical calculations and experimental measurements. The new insights gained from these investigations are key to enabling the design of new materials and their utilization in applications of technological importance.

12:00pm **F5-1-MoM-7 On the Interplay between Stacking and Stability of Transition-Metal Diborides***, **David Holec (david.holec@unileoben.ac.at)**, T. Leiner,* Montanuniversität Leoben, Austria*; N. Koutná, P. Mayrhofer,* TU Wien, Austria

Transition-metal diborides are a hard and brittle type of materials, which, among others, find their use as protective coatings, because

of their excellent heat conductivity, oxidation stability and wear resistance.

In this work, we apply first-principles calculations to investigate the interplay between the structural properties (stacking of metal planes, puckering of the boron planes), mechanical properties (elasticity) and stability. For the latter, we assessed chemical, mechanical and vibrational stability. The investigated diborides $X\mathrm{B}_2$ included X=Cr, Hf, Mn, Mo, Nb, Re, Ta, Ti, V, Zr. We probed (among others) also the three stackings corresponding to the stable structures of our $X\mathrm{B}_2$, namely the A-A-A-A stacking of, e.g. TiB_2, the A-B-A-B stacking of ReB_2 and the A-B-B-A stacking of WB_2.

We could reveal chemical trends (i.e. related to the position of X element in the periodic table of elements) on the stability and transformation barriers between different stackings.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F5-2-MoA

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

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

3:40pm **F5-2-MoA-7 Theoretical Investigation of Sluggish Diffusion in Nitride Films of High-Entropy Alloys***, **Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at)**,* Montanuniversität Leoben, Austria*; A. Kretschmer, P. Mayrhofer,* TU Wien, Austria*; D. Holec,* Montanuniversität Leoben, Austria

The concept of alloying was revolutionized in multi-component or high-entropy alloys (HEA), where five or more elements are distributed randomly on a crystalline lattice in equiatomic or near-equiatomic composition. Thereby, no element acts as a principal component and four core effects have been postulated to stem from this configuration: high configurational entropy, severe lattice distortion, sluggish diffusion, and cocktail effects. Since we still lack a proper quantification of the sluggish diffusion, this work focuses on this topic applied to the case of high-entropy nitrides (HENs). These ceramic materials possess high hardness and good thermal stability and are hence attractive for high-temperature applications.

The HEN systems that have been considered for this ab initio study are non-magnetic and structurally stable systems with the metals distributed on the metal sublattice by special quasi-random structure (SQS) methods. For each HEN system and each species, we determined migration barriers corresponding to vacancy-driven elementary point-defect migration mechanisms for crystalline solids. The change in diffusion w.r.t. migration barrier, while going up from ternary to hexinary systems, will be presented. Our results suggest that the impact of the local composition and increasing high-entropy environment can significantly alter these results. Our analyses focus on comparing low and high entropy systems (as measured by the number of elements) for systems exhibiting low and large local distortions, and similar and different nominal bond lengths of the forming binary nitrides. From our preliminary results, the claimed sluggishness of the diffusion in HENs should be more composition and/or environment-specific rather than generalizing for all high entropy systems.

4:00pm **F5-2-MoA-8 Simulation of Transport and Mechanical Properties of TiSiN:Ag Self-Lubricating Coatings With Machine Learned Force Fields***, **Veniero Lenzi (veniero.lenzi@fisica.uminho.pt)**,* University of Minho, Portugal*; F. Fernandes,* University of Coimbra, Portugal*; L. Marques,* University of Minho, Portugal

The quest for the environmental impact mitigation of aerospace industry passes through the use of lightweight and high-performance novel materials. However, these materials are hard to work/machine with standard tools. In this regard, a promising solution is the use of nanocomposite self-lubricating thin films on cutting and machining tools, which might enhance their lifetimes while reducing the use of lubricant, with clear economic and environmental advantages.

Titanium Silicon Nitride and Silver (TiSiN:Ag) nanocomposite thin films have been shown to provide good performance as self-lubricating coatings.[1,2] Their performance depends critically on the release rate of silver, the lubricating agent, which is influenced by the nanoscale structure of the thin film. Atomistic simulation methods are thus necessary to investigate and understand the Ag diffusion within the coating. [3] Moreover, it is important to consider the effects of the high temperatures and stresses encountered during the operation conditions on the coating's structure and stability.

To tackle the complexity of this material, we are currently employing machine learning (ML) techniques to obtain force fields capable of ab-initio level accuracy while enabling large-scale simulations. In particular, we are using the FLARE package [4] to perform on-the-fly training over ab-initio calculations. In this way, we obtained force-fields for TiN/Ag, SiN/Ag and TiSiN systems, which we used to calculate not only the diffusion constants for the different transport processes of Ag within the coating, but also the evolution of the nanocomposite structure under high temperatures and stresses. The obtained force fields show a very high degree of accuracy, within range of ab-initio calculations.

This work highlights the importance of ML methods for the simulation of complex materials. Our results shed light into the Ag transport in TiSiN coatings and in their mechanical properties, thereby providing a unique tool to optimize the thin film processing parameters to achieve the best possible performance.

References:

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2: D. Cavaleiro, *et al.*, *Surface and Coatings Technology*, 399:126176, 2020.
3: V. Lenzi, *et al., Applied Surface Science,* 556:149738, 2021.
4: Y. Xie,*et al., Nature Computational Materials,* 7:40, 2021.

4:20pm **F5-2-MoA-9 Machine Learning Assisted Ab Initio Thermodynamics of Novel Materials***, **Prashanth Srinivasan (prashanth.srinivasan@imw.uni-stuttgart.de)**,* University of Stuttgart, Germany*; F. Körmann,* Max-Planck Institut für Eisenforschung, Germany*; B. Grabowski,* University of Stuttgart, Germany **INVITED**

Recent developments in machine learning techniques has immensely benefited *ab initio*modeling of materials. Interatomic potentials such as the moment tensor potential (MTP) (Shapeev, 2016) that are trained to high temperature density-functional theory (DFT) data are able to predict energies and forces of atomic configurations highly accurately. They are thus able to statistically sample a much wider part of the phase space in a fast and efficient manner. In combination with a systematic thermodynamic integration method (Direct Upsampling), they can be used to calculate total free energies of even complicated systems such as high entropy alloys (HEAs) to 1 meV accuracy (Grabowski et al., 2019, Ferrari et al., 2020) up to the melting point. Apart from static and electronic energies, this also includes vibrational contributions including anharmonicity which significantly affect thermodynamic properties such as specific heat capacity and bulk modulus at high temperatures.

Here, firstly, we demonstrate these results for a bunch of refractory BCC systems ranging from single- to five-component alloys. We break-down the total free energies into various individual contributions. We compare a contrasting trend in the anharmonic free energies beyond the quasi-harmonic approximation in certain BCC refractories, some of which show a positive contribution and some a negative contribution. We narrow this feature down to the density of states (DOS) and the first- and second-neighbor forces and illustrate a difference in bonding behavior between the two sets of BCC elements. Secondly, we also show the applicability of the MTPs to design novel shape memory alloy materials, where a MTP trained to DFT data predicts the stress- and temperature-induced phase transformations in these alloys.

5:00pm **F5-2-MoA-11 Materials Design Principles of Amorphous Cathode Coatings for Lithium-ion Battery Applications***, **Jianli Cheng (jianlicheng@lbl.gov)**, K. Persson,* Lawrence Berkeley National Laboratory (LBNL), USA **INVITED**

Cathode surface coatings have been the foremost solution to suppress cathode degradation and improve cycling performance of lithium-ion batteries (LIBs). In this work, we carry out an extensive high-throughput computational study to develop materials design principles governing amorphous cathode coating selections for LIBs. Our high-throughput screening includes descriptors to evaluate the thermodynamic stability, electrochemical stability, chemical reactivity with electrolytes and cathodes, and ionic diffusivities in the cathode coatings. We consider the commonly used Li_3PS_4 and $LiPF_6$ as the solid and liquid electrolytes, respectively, and categorize the coating materials based on their chemical reactivity with the electrolytes. We reveal the formidable challenge of mitigating oxygen diffusion when selecting an ideal cathode coating, and suggest a few promising materials that pass all the criteria in our high-throughput study. Combining the screening results and detailed ionic diffusion analysis of the selected cathode coatings, we summarize the general guidelines for selecting amorphous cathode coatings.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F2-1-TuM

High Entropy and Other Multi-principal-element Materials I

Moderator: Erik Lewin, Uppsala University, Sweden

8:20am **F2-1-TuM-2 Elaboration and Characterization of High Entropy Nitride Al-Ti-Zr-Ta-Hf (-N) Deposited by Reactive Magnetron Sputtering for High Temperature Applications***, **Djallel Eddine TOUAIBIA (djallel_eddine.touaibia@utt.fr)**, M. ELGARAH, S. ACHACHE,* LASMIS, France*; A. MICHAU, F. Schuster,* Commissariat à l'Energie Atomique et aux énergies alternatives (CEA) Saclay, France*; F. SANCHETTE,* University of Technology Troyes (UTT), France

AlTiTaZrHf(-N) high entropy nitrides films were deposited in various argon-nitrogen gas mixtures on glass and silicon substrates. X-ray diffraction analyses reveal a transition from amorphous to an FCC single phase by increasing the nitrogen content.

Films morphology is not influenced by nitrogen content, all films have a compact morphology. Energy dispersive spectroscopy analysis shows an increasing of the film nitrogen content when the flow rates ratio RN2=N2/Ar+N2 varies between 0 and 15% and stabilizes above. Evolution of hardness and Young's modulus are discussed and the maximum values are obtained for a flow rates ratio RN2 of 10% at 27.67 GPa and 205.56 GPa respectively. Chemical bonds and tribological performances will be discussed and high temperatures stability is investigated.

8:40am **F2-1-TuM-3 Strain-Stabilized Al-Containing High-Entropy Sublattice Nitrides***, **Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at)**[1], B. Hajas,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversitat Leoben, Austria*; K. Yalamanchili, H. Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; M. Hans, J. Schneider,* RWTH Aachen University, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The impact of configurational entropy, enthalpy, and strain energy on the phase stability of high-entropy materials has not yet been investigated quantitatively. We used ab-initio calculations to predict the driving force for decomposition of 126 equimolar Al-containing high-entropy sublattice nitrides (HESN), which are all metastable with respect to all corresponding equimolar lower-entropy nitride phases. The entropy stabilization of ≈-0.06 eV/at at 1073 K is overruled by the 0.10-0.27 eV/at enthalpy-governed driving force for decomposition. Stabilization is however predicted for 22 compositions due to the -0.01 to -0.28 eV/at strain energy contribution caused by large differences in equilibrium volume between the HESN and their decomposition products. The predicted stabilities were validated with diffraction and tomography data of 9 annealed nitride systems. Hence, it is evident that only strain enables the stabilization of the here studied Al-containing HESN, while the entropic contribution is overruled by endothermic mixing.

9:00am **F2-1-TuM-4 Structural and Mechanical Properties Investigation of a New TiTaZrHfW(-N) Refractory High Entropy Films Deposited by Reactive Magnetron Sputtering***, **Abdelhakim Bouissil (abdelhakim.bouissil@utt.fr)**, S. Achache, F. Sanchette, M. El Garah,* LASMIS, Antenne de Nogent, Université de Technologie de Troyes, France

In the last decade, refractory high entropy thin films have attracted more attention due their superior proprieties at high temperatures [1]. Besides the thermal stability, these new materials present a good resistant to oxidation and can also keep good mechanical properties, high hardness and elastic modulus etc, at temperature up to 1600 °C, which is interesting compare to conventional alloys [2][3]. TiTaZrHfW(-N) films are synthesized by reactive magnetron sputtering in various argon plus nitrogen atmospheres. The microstructure, mechanical and thermal properties are investigated. Optical emission spectroscopy is performed to analyze the target nitriding conditions and to optimize the deposition parameters. The nitrogen flow rate ratio $R_{N2}=\Phi_{N2}/(\Phi_{N2}+\Phi_{Ar})$ is varied from 0 to 30%. XRD analyses show a transition from an amorphous structure to FCC single phased films once the nitrogen is added (5%). By increasing the nitrogen flow rate, preferential orientation from {111} to {200} is observed. The morphology of the films changes from compact to columnar when the nitrogen ratio exceeds 5%. The hardness and Young's modulus are also studied and the maximum values, 29 GPa and 257 GPa respectively, are obtained at R_{N2}= 9%. All nitrides show a good thermal stability under vacuum at 800 °C for three hours compared to metallic film, for which phase transition occurs.

[1] O. N. Senkov, D. B. Miracle, K. J. Chaput, et J.-P. Couzinie, « Development and exploration of refractory high entropy alloys—A review », *J Mater Res*, vol. 33, nº 19, p. 37, 2018.

[2] P.-K. Huang et J.-W. Yeh, « Inhibition of grain coarsening up to 1000°C in (AlCrNbSiTiV)N superhard coatings », *Scr. Mater.*, vol. 62, nº 2, p. 105–108, janv. 2010, doi: 10.1016/j.scriptamat.2009.09.015.

[3] O. N. Senkov, G. B. Wilks, J. M. Scott, et D. B. Miracle, « Mechanical properties of Nb25Mo25Ta25W25 and V20Nb20Mo20Ta20W20 refractory high entropy alloys », *Intermetallics*, vol. 19, nº 5, p. 698–706, mai 2011, doi: 10.1016/j.intermet.2011.01.004.

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[1] **Graduate Student Award Finalist**

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F2-2-TuA

High Entropy and Other Multi-principal-element Materials II

Moderator: Erik Lewin, Uppsala University, Sweden

2:00pm **F2-2-TuA-2 Structure and Properties of Refractory MoNbTaW+X (X = Ti,V,Cr,Mn,Hf) High Entropy Alloy Thin Films Deposited by HiPIMS***, G. Gruber,* Montanuniversität Leoben, Austria*; A. Lassnig, S. Zak, C. Gammer, M. Cordill,* Austrian Academy of Sciences, Austria*;* ***Robert Franz (robert.franz@unileoben.ac.at),*** Montanuniversität Leoben, Austria

Refractory high entropy alloys (HEAs) represent a new class of materials that show promising properties, such as high hardness, good thermal stability and sluggish diffusion, which makes them suitable for various potential applications. Within this study a series of refractory HEAs was deposited using high power impulse magnetron sputtering keeping the base alloy MoNbTaW constant and adding a fifth element: Ti, V, Cr, Mn or Hf. The targets used for the synthesis of each alloy contained all five elements in an equimolar concentration. As analysed by X-ray diffraction and transmission electron microscopy, all films showed a bcc solid solution phase structure in as-deposited state. Further, the thermal stability of the films was analysed by annealing in vacuum up to 1200 °C revealing that the bcc phase is stable to a temperature of at least 1000 °C. Changes in the residual stress state and mechanical properties due to annealing were studied by the wafer

curvature method and nanoindentation, respectively. The performed work is intended to contribute to a comprehensive understanding about phase and thermal stability of refractory HEA thin films.

2:20pm **F2-2-TuA-3 Effect of Rare-earth yttrium Addition on Microstructure and Thermal Stability of Refractory TiTaZrHfW High Entropy Film***,* ***Mohamed EL GARAH (mohamed.el_garah@utt.fr),*** University of Technology of Troyes , France*; L. PATOUT, A. CHARAI,* Aix Marseille University , France*; F. SANCHETTE,* University of Technology of Troyes , France

High entropy alloys (HEAs) are of considerable interest due to their superior properties. Since 2004, they are defined as quasi- or equimolar alloys and they consist, at least, of five elementary elements with an atomic percentage ranging from 5 to 35 at.% [1-3]. High Entropy Films (HEFs) have been also reported to have excellent properties such as good wear [4] and corrosion resistance [5] and excellent thermal stability [6]. Rare earths have excellent physical and chemical properties. They play an interesting role to improve the performance of the coatings. The effect of the addition of yttrium Y as a rare earth element, on the microstructure, the mechanical properties and on the thermal stability of TiTaZrHfW refractory film is studied. A series of (TiTaZrHfW)$_{100-x}$Y$_x$ films were synthesized using magnetron sputtering technique. Y content is varied by changing the discharge current applied to Y target. No change of the films microstructure is observed when Y is added with small amount, however with high Y content new phases are formed. The phase evolution is evaluated by calculating the thermodynamic criteria ΔHmix, ΔSmix, Ω and δ and the result are compared to the experimental analysis. Nanoindentation measurements indicate a degrading of mechanical properties when the film is doped with Y element. The highest values of hardness and Young's modulus are obtained for TiTaZrHfW film at 9.69 GPa and 111.63 GPa respectively. Moreover, thermally stability of TiTaZrHfW film without and with Y element is investigated.

[1] Yeh,J.-W.; Chen, S.-K.; Lin, S.-J.; Gan, J.-Y.; Chin, T.-S.; Shun, T.-T.; Tsau,C.-H., Chang,S.-Y.; Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, *Adv. Eng. Mater.*, **6**(5), 299-303 (2004)

[2] Cantor, I. Chang, P. Knight, A. Vincent, Microstructural development in equiatomic multicomponent alloys, *Mater. Sci. Eng. A*, **375**, 213-218 (2004)

[3] W. Zhang, P.K. Liaw, Y. Zhang, Science and technology in high-entropy alloys, *Sci. China Mater.*, **61**(1), 2-22 (2018)

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[5] Hsueh, H.-T.; Shen, W.-J.; Tsai, M.-H.; Yeh, J.-W., Effect of nitrogen content and substrate bias on mechanical and corrosion properties of high-entropy films (AlCrSiTiZr)$_{100-x}$N$_x$. Surf. Coat. Tech. 2012, 206 (19-20), 4106-4112

[6] Sheng, W.; Yang, X.; Wang, C.; Zhang, Y., Nano-crystallization of high-entropy amorphous NbTiAlSiW$_x$N$_y$ films prepared by magnetron sputtering. Entropy 2016, 18 (6), 226

2:40pm **F2-2-TuA-4 Investigation of Strain Stabilization in Aluminum-Based High Entropy Sublattice Nitride Films***,* ***Balint Hajas (balint.hajas@tuwien.ac.at),*** *A. Kretschmer, A. Kirnbauer, P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien University, Vienna, Austria

Hard protective coatings allow for increased lifespan of machining tools and more versatile fields of application. Less than two decades ago the world of material science was introduced to the so called "high entropy alloys" (HEAs), a field that has since seen enormous growth in popularity. Applying the concept of metallic HEAs, which typically consist of a solid solution of at least five primary elements in near equiatomic composition, we developed various nitride and oxy-nitride coatings, where at least five different metals (in near equiatomic composition) share the same metal-sublattice. Hence, essentially their metal-sublattice is high entropic, however, for simplicity these will be named high entropy nitrides respectively oxynitrides.

Based on Density Functional Theory calculations, several Al-based single-phase high entropy nitride systems were selected for further experimental investigations. The selection criterion was basically their ability to delay the wurtzite AlN phase formation (essentially through strain stabilization) upon exposure to elevated temperatures. In addition to these high entropy nitrides, also their oxynitrides and Si-alloyed nitrides were developed, all of which by reactive magnetron sputtering.

The primary investigation focused on how the mechanical properties such as hardness and fracture toughness of the nitride coatings changed due to vacuum annealing up to 50 hours, and how the oxynitrides related to those results, and whether the formation of the wurtzite phase could be detected. The secondary investigation was aimed towards the oxidation resistance of the coatings, and if the additional silicon could delay the oxidation process. Their characterization includes X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, nanoindentation and cube-corner indentation.

4:00pm **F2-2-TuA-8 Magnetron Sputtering of Hard and Strong Multicomponent (HfNbTiVZr)C Thin Films***,* ***Barbara Osinger (barbara.osinger@kemi.uu.se),*** *S. Fritze, L. Riekehr, E. Lewin, U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden

Thin films of the high entropy alloy HfNbTiVZr have shown promising mechanical properties and interesting charge transfer effects, reducing atomic size mismatch and in turn the lattice distortion δ. Being able to tune the electronic structure is especially interesting for the design of multicomponent carbides, as their desirable properties are a result of their bond character. This, along with general properties of group 4-6 carbides, like ceramic hardness, high wear resistance and ultra-high temperature strength, motivates the investigation of the (HfNbTiVZr)C system.

This study focused primarily on multicomponent carbide (HfNbTiVZr)C thin films with varying carbon concentrations (0–44 at.%), synthesised by non-reactive DC magnetron sputtering. All carbide films exhibit a single solid solution phase with NaCl-type structure and a lattice parameter of approximately 4.53 Å. The hardness increases to 34 GPa compared to 10 GPa for the metallic films. Additionally, phase stability based on films deposited at elevated temperatures (300-700°C), compared with predictions made by CALPHAD methods, will be discussed.

4:20pm **F2-2-TuA-9 Comparative Study of Reactively and Non-Reactively Sputtered High-Entropy Metal-Sublattice Carbides***,* ***Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at),*** *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany

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. Within this work, we report on the phase formation and thermal stability of high entropy metal-sublattice carbides to provide a further insight to a more extensive understanding of the high-entropy effect, according to which, based on the Gibbs-free energy, such materials should be stabilised in the high-temperature regime. Therefore, (Hf,Ta,Ti,V,Zr)C coatings were reactively and non-reactively sputtered from a single powder-metallurgically produced composite target (either metallic or consisting of the respective binary carbides). Reactively sputtered coatings were synthesised using an C_2H_2 – Ar mixture with different $C_2H_2/(C_2H_2+Ar)$ ratios (f_{C2H2}). After deposition, the coatings were investigated in as-deposited state and after vacuum annealing between 800 and 1200°C. The structure and morphology, the chemical composition, the mechanical properties, and the thermal stability of the coatings were investigated by scanning electron microscopy, X-ray diffraction, and nanoindentation.

The non-reactively sputtered as well as reactively sputtered coatings with f_{C2H2}= 20 % show a single-phased face-centred cubic (fcc) structure. The hardness for the non-reactively sputtered HESCs is with ~41 GPa higher than that of the reactively sputtered one which exhibits a hardness of 35 GPa. This indicates that due to the use of C_2H_2 also regions of amorphous carbon form, which slightly weaken the coating already in the as-deposited state. After vacuum annealing up to 1200 °C the non-reactively sputtered coatings maintain a hardness of ~40 GPa indicating retarded softening mechanisms due to sluggish diffusion. Additionally, powdered free-standing coating material was investigated by XRD in as deposited state and after vacuum annealing up to 1300 °C. The results of these investigations show, independent of the synthesis route, no phase transformation within the investigated temperature range. This behaviour was also observed in previous studies on different material classes such as nitrides, borides, and oxides indicating a stabilisation due to the high-entropy metal sublattice.

New Horizons in Coatings and Thin Films
Room Pacific D - Session F4-1-WeM

New Horizons in Boron-Containing Coatings I

Moderators: Helmut Riedl, TU Wien, Austria, **Johanna Rosén**, Linköping University, Sweden

8:00am **F4-1-WeM-1 Synthesis and Oxidation Behavior of $Ti_{0.35}Al_{0.65}B_y$(y= 1.69- 2.43) Coatings**, *A. Navidi Kashani, S. Mráz, D. Holzapfel, M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; L. Löfler, P. Ondracka,* ***Jochen Schneider (schneider@mch.rwth-aachen.de),*** RWTH Aachen University, Germany

The effect of B concentration on the phase formation and oxidation resistance of $(Ti_{0.35}Al_{0.65})$By with y = 1.69, 2.03, 2.43 coatings was investigated. Elemental B targets in radio frequency (RF) mode and a compound $Ti_{0.4}Al_{0.6}$ target in direct current (DC) mode at floating potential were sputtered. The B concentration was varied systematically by adjusting the applied power to the respective magnetrons while keeping the power supplied to the magnetron with the $Ti_{0.4}Al_{0.6}$ target constant. The oxidation resistance at 700 °C in air for up to 8 hours was compared to a cathodic arc evaporated $(Ti_{0.37}Al_{0.63})_{0.49}N_{0.51}$ coating with an Al/Ti ratio of 1.69 ± 0.19 which is very similar to 1.84 ± 0.42 for the boride coatings. Scanning transmission electron microscopy (STEM) imaging revealed oxide scale thicknesses of 39 ± 7 and 101 ± 25 nm for $(Ti_{0.35}Al_{0.65})B_{2.03}$ and $(Ti_{0.37}Al_{0.63})_{0.49}N_{0.51}$ after 8 hours, respectively. Hence, the close to stoichiometric boride outperforms the nitride coating. This behavior can be understood based on compositional and structural analysis of the oxide scales: While the oxide layer on the diboride is primarily composed of Al and O and protective, the oxide layer on the nitride coating is porous and contains Ti, Al and O.

8:20am **F4-1-WeM-2 Influence of Si Alloying on the High-Temperature Mechanical Properties of CrB_2 Based Thin Films**, ***Lukas Zauner (lukas.zauner@tuwien.ac.at)****, T. Glechner, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold, J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Among transition-metal diboride based thin films CrB_2 is an exciting prospect due to a unique portfolio of materials properties, especially through offering high fracture resistance [1]. However, this class of PVD coatings suffers from an inherently low oxidation resistance. Therefore, establishing pathways to improve the oxidation resistance and thus maintain the mechanical properties to higher temperatures (*i.e.*, above 1000 °C) for these hard-protective coatings is an integral aspect for future high-performance components in thermo-mechanically demanding environments.

In this work, the influence of Si alloying on the high-temperature mechanical properties and fracture toughness of magnetron sputtered CrB_2 thin films is studied for various concentrations. As indicated by thermogravimetric analysis, adding Si to the hexagonal α-AlB_2 structured coatings improves the onset of oxidation by at least 600 °C in lab-air conditions. This drastic improvement in the formation of a stable oxide scale is further correlated with detailed analysis on the thermal stability and phase formation as obtained by non-ambient X-ray diffraction in both vacuum and lab-air atmospheres. The mechanical properties of the synthesised Cr-Si-$B_{2\pm z}$ thin films – including hardness, Young's modulus and fracture toughness – are obtained by nanoindentation and bending of pre-notched, unstrained micro-cantilever beams in the as-deposited as well as the annealed state. Complementary in-situ characterisation of the aforementioned mechanical properties on coated high temperature bulk materials up to 800 °C allowed for a direct identification of changes in the deformation and fracture mechanisms across the investigated temperature regime [2]. Hence, this study showcases the potential of transition-metal diboride thin films – a class previously deemed unsuitable for high-temperature applications – by utilising Si-alloying to preserve the CrB_2 thin films.

[1] Gu, Xinlei, et al. "Sorting transition-metal diborides: New descriptor for mechanical properties." *Acta Materialia* 207 (2021): 116685.

[2] Buchinger, J., et al. "Fracture properties of thin film TiN at elevated temperatures." *Materials & Design* 194 (2020): 108885.

8:40am **F4-1-WeM-3 Design of Novel Transition Metal Diboride-Based Pvd Thin Films: From Pure Compounds to Alloys, Composites and Multilayers***,* ***Michael Stueber (michael.stueber@kit.edu)****, V. Ott, S. Ulrich,* Karlsruhe Institute of Technology (KIT), Germany*; H. Riedl, P. Mayrhofer,* Technische Universität Wien, Austria **INVITED**

Transition metal diboride hard coatings are attractive material candidates for various high performance applications in engineering. Due to their chemical nature and microstructure these materials exhibit interesting multifunctional properties. Unfortunately, their mechanical properties (i.e. toughness and ductility) and the demand for achieving stoichiometric film composition or appropriate adhesion onto various substrates in physical vapor deposition processes make their utilization often a challenge. Thus, such materials and their deposition experience currently a strong revitalization of research efforts. This presentation will review the recent status of PVD transition metal diboride-based thin films, with a focus on magnetron sputtering techniques. It includes a brief retrospect on pioneering developments in the field, covering fundamental materials science aspects of the diborides as well as advanced coating design concepts such as the various Ti-B-C-N thin films. The major part of the presentation will discuss three design concepts for novel boride-based hard and tough coatings for engineering applications. These are mainly based on the model thin film material TiB_2 which is by far the most detailed characterized PVD transition metal diboride. The first approach describes the alloying of TiB_2 with the intention to design ternary solid solutions, $(Ti,X)B_2$ where X is another metal such as Al, Cr, Zr, V or others. The impact of Al content on phase formation, microstructure and mechanical properties of magnetron-sputtered $(Ti,Al)B_2$ thin films will be described. A second approach refers on the formation of TiB_2-metal composite thin films, which covers the objectives of designing thin film material composed either of a boride matrix with dispersed metal nanoclusters or of a metal matrix with dispersed diboride cluster phase. The metal phase used in this part of the description is the superalloy B2 structured NiAl. Phase formation and microstructure evolution of magnetron co-sputtered TiB_2-NiAl thin films will be covered, both in as-deposited and vacuum annealed state. The third approach deals with the integration of TiB_2 layers into nanoscale multilayers when the second layer constituent is also a metal layer. Focus is again on the combination of TiB_2 with NiAl. Multilayers with variation of the bilayer period and its impact on their structure and properties will be considered. Other relevant diboride thin film design concepts and newest progress achieved by advanced PVD techniques such as HIPIMS or hybrid PVD processes will also be reported.

9:20am **F4-1-WeM-5 Tribological Properties and Thermal Stability of $V_{1-x}Mo_xB_y$ Coatings**, ***Katarína Viskupová (katarina.viskupova@fmph.uniba.sk)****, B. Grančič, T. Roch, M. Truchlý, M. Mikula, V. Šroba, L. Satrapinskyy, P. Kúš,* Comenius University, Bratislava, Slovakia

Development of space technology encourages research of new materials that are highly performing in extreme conditions. An important category are low wear resistance solid lubricants with stable properties at temperatures above 1000°C and in oxidative environments. Currently widely studied transition metal diborides (TMB_2) offer high temperature stability and excellent mechanical properties, such as high hardness and wear resistance. Vanadium diboride also shows promising tribological properties due to lubrication effect of oxidation products B_2O_3 and V_2O_5 [1]. Our aim is to study effects of alloying of VB_2 coatings with Mo, which may lead to structural decomposition and hence provide good mechanical properties at high temperatures [2]. Moreover, possible formation of MoO_3 during oxidation may influence the tribological properties of the coatings [3]. In our work, we use physical vapour deposition for preparation of $V_{1-x}Mo_xB_y$ films with different Mo concentration and B/TM ratio. We discuss the relationship between chemical composition, structure formation and structure evolution during vacuum annealing up to 1300°C. We further investigate the influence on hardness, elastic modulus, and friction coefficient at elevated temperature in air. Our results are supported by density functional theory calculations.

[1] A. Erdemir et al., Wear 205 (1997) 236-239

[2] B. Alling et al., Scientific Reports 5 (2015) 9888

[3] W. Gulbiński et al., Wear 254 (2003) 129–135

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New Horizons in Coatings and Thin Films
Room Pacific D - Session F1-WeA

Nanomaterials and Nanofabrication

Moderators: Diederik Depla, Ghent University, Belgium, **Vladimir Popok**, Aalborg University, Denmark

2:00pm **F1-WeA-1 Polymer Films with Gas-Phase Aggregated Nanoparticles: Formation and Applications***, **Vladimir Popok (vp@mp.aau.dk)**,* Aalborg University, Denmark **INVITED**

In the last couple of decades, nanoparticles (NPs) have been widely used in various research fields and industrial branches. Among many physical and chemical ways of nanoparticle synthesis, the gas-phase aggregation method, also known as cluster beam technique, [1, 2] provides a number of advantages allowing for a very good control of composition because ultra-pure targets are used and the particles are aggregated in vacuum. Formation of not only homo-atomic but alloy and compound NPs with tunable structure and shape (core@shell, Janus- and dumbbell-like, spherical or cubic etc.) is possible. Adjusting the aggregation parameters and adding mass-filtering systems brings a capability of size selection. One more advantage is easy tuning the surface coverage or filling factor of NPs on/in the films. Finally, yet importantly is a capability to form patterned nanostructured films or coatings with gradients of NP surface density.

Polymers are very attractive hosting or supporting media for NPs due to plasticity, flexibility, easy processing, low weight and also low cost. Use of polymers also allows to add required functionality [3, 4]. The talk will overview several most important directions, namely on: (i) tuning resistance of the composite films by controlling the coverage or filling factor of metal NPs and use such materials as elastomeric electrodes, strain gauges and gas sensors; (ii) utilizing localized surface plasmon resonance of NPs to design polymer-based metamaterials with controllable transmittance as well as matrices for enhanced sensing and detection; (iii) polymer coatings with ferromagnetic particles demonstrating excellent absorption of GHz waves as well as tunability of magnetic properties; (iv) utilization of polymer films with NPs as advanced membranes in filtering as well as bactericidal media in food packaging and in medicine.

1. V.N. Popok, E.E.B. Campbell, Rev. Adv. Mater. Sci. 11(1) (2006) 19-45.
2. V.N. Popok, O. Kylian, Appl. Nano 1 (2020) 25-58.
3. V.N. Popok, Cluster Beam Synthesis of Polymer Composites with Nanoparticles, in: Polymer-based Multifunctional Nanocomposites and Their Applications, Eds. K. Song, C. Liu and J.Z. Guo, Elsevier, 2019, 35-76.
4. O. Kylián, V.N. Popok, Frontiers of Nanoscience, 15 (2020) 119-162.

2:40pm **F1-WeA-3 Stress Evolution in Particle Strengthened Metal-Oxide Nanolaminates: Insights from in-Situ Synchrotron Diffraction Experiments***, **Barbara Putz (barbara.putz@unileoben.ac.at)**,* Montanuniversität Leoben, Austria*; A. Sharma,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; K. Gradwohl,* Leibniz-Institut für Kristallzüchtung , Germany*; P. Gruber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM)-WBM, Germany*; D. Többens,* Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Germany*; X. Maeder, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Understanding deformation mechanisms of metal-ceramic nanolaminate coatings (NLC) is crucial in order to exploit their promising mechanical, physical and chemical properties, useful for a wide range of thermal, mechanical and environmental conditions (1). We have fabricated unique, particle strengthened metal/oxide nanolaminates, combining three different deposition techniques: Atomic Layer (ALD), Physical Vapor (PVD) and Nanoparticle (NP) Deposition. Ultrathin oxide layers (<1nm, Al_2O_3) confine the grain growth of metallic PVD films (50nm, Au), for grain sizes distinctly lower than the total film thickness (150nm), improving strength and ductility, while incorporated NPs (W, diameter 4 nm) further enhances mechanical properties. The multilayer microstructures and NP concentrations were confirmed and characterized by cross-sectional transmission electron microscopy (TEM). Stress evolution in the nanocomposites was studied with X-ray diffraction and $\sin^2$psi analysis during in-situ tensile experiments on flexible polymer substrates. Two different nanocomposite geometries (Au/Al_2O_3 and Au + W-NP/Al_2O_3, total thickness 150nm) as well as single Au films (50nm and 150nm) with and without NP reinforcement were investigated to study and isolate the influence of layer thickness and nanoparticle concentration. Results indicate a clear strengthening of 150 nm Au films through multi-layering (Au/Al_2O_3), which can be further increased through the addition of NPs (Au+W-NP/Al_2O_3). Post mortem scanning electron imaging (SEM) of the deformation pattern as well as electrical resistance measurements recorded in-situ during straining indicate that no significant embrittlement was introduced by neither ALD nor NP addition. In summary, the novel manufacturing approach and resulting nanocomposites are promising candidates for multifunctional components in next-generation nano-devices.

(1) A. Misra, J.P. Hirth, R.G. Hoagland, Length-scale-dependent deformation mechanisms in incoherent metallic multilayered composites, Acta Mater. 53 (2005) 4817–4824. https://doi.org/10.1016/j.actamat.2005.06.025.

3:00pm **F1-WeA-4 Structure-Processing Relationships of Chiral Organic-Inorganic Thin Films for Circularly Polarized Light Detection***, **Katherine Burzynski (katherine.burzynski.ctr@afrl.af.mil)**,* AFRL / Azimuth Corp., USA*; E. Muller,* AFRL / UES, USA*; A. Trout,* The Ohio State University, USA*; W. Kennedy,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

Photonic quantum information systems (pQIS), optical imaging systems, and analytical spectroscopy tools all benefit from sensitivity to the polarization state of light. Particularly of interest is the detection and discrimination of circularly polarized light (CPL). Currently, the main method to detect CPL requires complex optical systems that cannot easily be incorporated into on-chip circuitry. Direct detection of CPL has been demonstrated by chiral organic semiconductors and metamaterials but suffer from low quantum efficiencies. Chiral organic-inorganic materials are promising for CPL detection due to their ease of fabrication and chiral optoelectronic properties. To date, a limited number of chiral organic metal halide systems possessing intrinsic optoelectronic response to CPL are reported in literature, leaving many chiral systems unexplored. The chiral organic cations, R-(+)- and S-(−)-1-(1-naphtyl)ethylamine (R- and S-NEA+) were incorporated into the lead iodide system. A variety of growth techniques, including spin-coating, confined crystallization, and hydrothermal crystallization, as well as annealing conditions were investigated in an effort to reliably produce functional thin films for CPL photodetection. The fabrication techniques that promote the chiral organic metal halide crystallization and reduce the amount of lead iodide crystallites result in strong chiral optical responses, and ultimately, efficient CPL detection via polarization sensitive photocurrent in thin film devices.

3:20pm **F1-WeA-5 Bio-Inspired Antibacterial Metasurfaces Fabricated by Glancing Angle Deposition***, **Chuang Qu (chuang.qu@louisville.edu)**, J. Rozsa, H. Jung, M. Running, S. McNamara, K. Walsh,* University of Louisville, USA

The goal of this research is to propose an easy and cost-effective fabrication approach of Glancing Angle Deposition (GLAD) for creating antibacterial surfaces, which are inspired by cicada wings. Antibacterial surfaces are known to be applied in a variety of specific interfaces, such as medical implants and food packaging. As Ivanova et al pointed out, bio-inspired surface structuring for antibacterial requires ‘further comprehensive and systematic studies’.

This research begins with the examination of the wings of Neotibicen canicularis (an annual cicada in North America, also known as the dog-day cicada, see Fig 1a). Using a scanning electron microscope (SEM), one can observe that the cicada wing is covered nanopillar cone nanostructures, with the tips of the cones sub-100 nm in diameter, and the height of the cones approximately 200 nm (see Fig 1b). The nanopillar cones are semi-hexagonally distributed on the cicada wings with ~170 nm between the neighboring pillars. These antibacterial surfaces compose of appropriately spaced nanopillars cone features, which puncture into bio cells falling on top and keep the surface bacteria-free. Given the nano-level three-dimensional features on the surface of cicada wings, it is extremely difficult to replicate these naturally occurred nanostructures using conventional top-down nanofabrication processes, especially cost-effectively and in large areas. For this reason, we propose to use GLAD combining self-assembly of nanospheres to solve the fabrication problem. GLAD is a versatile bottom-up process that uses physical vapor deposition while maneuvering with incident angle and rotation of the substrate. Although the GLAD approach has been proposed over decades, there is still a lot to discover about this technique, such as the effective seeding rules. This paper will introduce the new seeding rule and scheme for GLAD to replicate the nanopillar cone structures, along with the whole fabrication process using GLAD. Figure 2 presents our initial effort to replicate the cicada wing nanopillar cone structures using GLAD. Finally, gram-negative bacteria (E Coli) are applied on top of the surface for antibacterial testing. Our preliminary results show the effectiveness of the antibacterial property of our synthetic nanostructured film. The proposed GLAD process with the new seeding scheme provides the flexibility in design and optimization of three-dimensional nanofeatures with periodic/random distributions, which allows the further exploring of functional bio-inspired nanostructures.

3:40pm **F1-WeA-6 Polymer Templates-Assisted Design of ZnO Films via Swelling-Assisted Sequential Infiltration Synthesis (SIS) and Swelling Based Infiltration (SBI): Properties, Adsorption Characteristics, and Performance***, **Khalil Omotosho (khalildolapoomotosho@my.unt.edu)**,* University of North Texas, USA

In this paper, we report the properties and adsorption characteristics of ZnO coatings designed with polymer templates-assisted infiltration approaches and their reactions with the environment. For this, we investigated the infiltration of polymer of amphiphilic block copolymer (BCP) templates with ZnO by comparison of 2 infiltration approaches, the swelling-assisted sequential infiltration synthesis (SIS) and the swelling-based infiltration (SBI), followed by polymer templates removal by oxidative thermal annealing for the design of porous ZnO films. Using the quartz crystal microbalance (QCM), we compared the infiltration efficiency of both methods. The XRD and XPS data revealed that the SBI-based porous ZnO films have a more disordered structure with a high surface concentration of OH groups, leading to a more hydrophilic film. We monitored the chemical interactions of the polymer templates before and after infiltration using the FTIR. Our results indicate that the performance of the ZnO coatings is highly dependent on the infiltration approach adopted, the templates, and their interactions with organic molecules. These results suggest new ways to efficiently design highly porous metal oxide coatings that can be adapted for various applications.

4:00pm **F1-WeA-7 Pulsed Aerosol Assisted Plasma Deposition: Process and Film Composition Characterization Using Nanoparticles Optical Properties***, **Adèle Girardeau (adele.girardeau@laplace.univ-tlse.fr)**,* LAPLACE, LCC, Safran Tech, France*; G. Carnide,* LAPLACE, LCC, IMRCP, France*; A. Mingotaud,* IMRCP, France*; M. Cavarroc,* Safran Tech, France*; M. Kahn,* LCC, France*; R. Clergereaux,* LAPLACE, France

Aerosol-assisted processes enable to deposit thin films, homogeneous[1,2] or nanocomposite[3–6]. For example, the nebulization of colloidal solutions, i.e. liquid solutions containing nanoparticles, in plasma processes have been widely used for nanocomposite thin film deposition. In this work, an alternative method, called direct liquid reactor-injector (DLRI) of nanoparticles, is applied. It allows to synthesize nanoparticles prior to their injection in the plasma in a pulsed injection regime[7].

In a low-pressure RF plasma coupled with DLRI of ZnO nanoparticles, it enables to form nanocomposite thin films with really small (<10 nm in diameter) and highly dispersed nanoparticles embedded in a matrix[7] that exhibits the classical optical properties of ZnO (absorbance at their band-gap - 3.37 eV and fluorescence when illuminated by ultraviolet light - 320-360 nm[8–10]). However, the volume fraction of nanoparticles embedded in the matrix is 5 times lower than expected. Indeed, in-situ optical emission spectroscopy (OES) of the plasma presents the characteristic luminescence of ZnO nanoparticles suggesting that nanoparticles are efficiently confined in the plasma volume during the process and does not participate to the nanocomposite formation.

To estimate the number of nanoparticles confined in the plasma volume and the global process balance of matter, one must establish the relation between the absorption / fluorescence and the number of nanoparticles. Here, we report an abacus obtained with ZnO nanoparticles synthesized by an organometallic approach: it shows that the optical characteristics of the ZnO nanoparticles follow the classical Beer-Lambert and luminescence laws, a useful tool for in-situ analyses. It also enables to determine the absorptivity and the quantum yield of the ZnO nanoparticles produced.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-2-WeA

New Horizons in Boron-Containing Coatings II

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Helmut Riedl**, TU Wien, Austria, **Johanna Rosén**, Linköping University, Sweden

2:00pm **F4-2-WeA-1 Understanding and Optimizing the Properties of Superhard Metal Borides***, **Sarah Tolbert (tolbert@chem.ucla.edu)**,* University of California, Los Angeles, USA **INVITED**

In this talk, we will examine a family of super-hard materials based on late transition metal borides.These materials are exciting because, unlike diamond, they can be synthesized at atmospheric pressure.The materials were initially constructed using three very simple design rules:1) use late transition metals to create high electron density so that the materials are incompressible; 2) add boron to build strong covalent bond to prevent slip and generate hard materials; 3) use solid-solution effects to further tune materials properties.While these ideas is incredibly simple, they have also proven to be very effective.In this talk, we will thus use a combination of materials synthesis, indentation measurements, and high-pressure diffraction to gain an understanding of how the hardness in this family of materials can be tuned based on chemical composition and bonding motifs.We will specifically take advantage of non-hydrostatic high pressure X-ray diffraction methods to directly probe both elastic lattice deformations and the onset of plastic deformation in a wide range of materials in a lattice specific manner.To gain a global understanding of the family of materials we will move from metal (M) rich MB phases, to more conventional MB_2 and MB_4 type materials, and finally to very high boron content MB_{12} type materials.In all cases, the goal will be to correlate structure and bonding with hardness.Finally, we will end with some new studies on nanoscale versions of these materials, where nanoscale architecture is combined with bonding constraints to further improve hardness.

2:40pm **F4-2-WeA-3 Si alloyed Transition Metal Diborides - A Novel Class of Oxidation Resistant Coating Materials***, T. Glechner, L. Zauner, R. Hahn, A. Bahr, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Surface Solutions AG, Liechtenstein*; 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

Surface protection of highly stressed components used in aviation or energy production is of great interest, especially to extend the operation ranges in oxidative high-temperature environments. Here, transition metal (TM) ceramics are a suitable class to resist such conditions. However, studies on a drastic improvement of the oxidation resistance of TM-diborides based coatings are relatively rare, as up to now many studies focus on the synthesis and mechanical properties of such films.

Therefore, within this study we suggest the combination of TM-boride based coating materials – as a high temperature stable ceramic – with the excellent oxide former Si, resulting in coatings with outstanding oxidation resistance, tested up to 1500 °C. Various $\text{TM-Si-B}_{2\pm z}$ (TM=Ti, Cr, Hf, Ta, W) films have been sputter deposited and subsequently oxidized in a DTA/TG setup to study their oxidation kinetics. Above certain Si contents, $\text{Ti-Si-B}_{2\pm z}$, $\text{Cr-Si-B}_{2\pm z}$, and $\text{Hf-Si-B}_{2\pm z}$ coatings exhibit strongly retarded oxidation kinetics obtaining k_p values below 10^{-11} $kg^2m^{-4}s^{-1}$ at 1100 °C. Long term oxidation tests at 1200 °C (up to 60 h in ambient air on hard substrates) confirmed the superior protective capability of these coatings, with i.e. $Hf_{0.20}Si_{0.23}B_{0.57}$ possessing an oxide scale thickness of only 1.5 µm after 60 h. Along with a broad set of high-resolution characterization techniques (i.e. HR-TEM, APT) the study introduces this new class of hard coatings for oxidation protection at ultra-high temperatures.

Keywords: Oxidation Resistance; Transition Metal Ceramics; Thin Films; Borides; UHTC;

3:00pm **F4-2-WeA-4 High-Power Impulse Magnetron Sputter Deposition of TiB_x Thin Films: Effect of Pulse Length and Peak Current*, Niklas Hellgren (nhellgren@messiah.edu),*** Messiah University, USA*; I. Zhirkov,* Linköping University, IFM, Thin Film Physics Division, Sweden*; M. Sortica,* Uppsala University, Sweden*; A. Petruhins, G. Greczynski,* Linköping University, IFM, Thin Film Physics Division, Sweden*; I. Petrov,* University of Illinois at Urbana-Champaign, USA*; L. Hultman, J. Rosen,* Linköping University, IFM, Thin Film Physics Division, Sweden

We report on titanium boride, TiB_x, thin films grown by high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target. Commonly HiPIMS studies are conducted in constant power mode, so when the pulse length in changed, so is the peak current and/or frequency. Here we independently vary pulse length (t_{on} = 50 – 200 µs) and peak current density (J_{peak} = 0.5 – 2 A/cm^2), while keeping the pulse frequency constant at f = 100 Hz. Thus, the total power vary depending on deposition condition. All other parameters were kept constant; substrate-target distance d = 6.5 cm, Ar pressure p_{Ar} = 10 mTorr, substrate temperature T_s = 500 °C, and substrate bias V_s = - 60 V.

The resulting films are all under-stoichiometric with B/Ti ranging from 1.3 to 1.9, as determined by ToF-ERDA and RBS. For any given t_{on}, the B/Ti ratio increases monotonically as J_{peak} increase from 0.5 to 2 A/cm^2. The trend is more complex as a function of t_{on}; in most cases, the highest B/Ti is observed for t_{on} = 100 µs, and decreases for both higher and lower t_{on}. The exception is for J_{peak} = 2 A/cm^2, where B/Ti increased slightly when increasing t_{on}.

The trends are discussed in terms of variations in both the total atom deposition flux, as determined from ERDA and RBS, and B^+, Ti^+ and Ar^+ ion flux measured by time- and energy-integrated mass spectrometry. Especially the Ti and Ti^+ fluxes saturate for the highest values of t_{on} and J_{peak}, which explains the highest film B/Ti ratios. This is also accompanied by a transition from strongly 001-textured films to predominantly 101-texture.

3:20pm **F4-2-WeA-5 Effect of Ar Particles on the Growth and Mechanical Properties of ZrB_{2+x} Films*, Tomas Fiantok (tomas.fiantok@fmph.uniba.sk),*** *T. Roch,* Comenius University, Bratislava, Slovakia*; P. Svec,* Academy of Science, Bratislava, Slovakia*; M. Truchly, V. Sroba, M. Mikula,* Comenius University, Bratislava, Slovakia

Highly demanding aerospace applications create an opportunity to exploit the promising potential of transition metal diboride based thin films (TMB_2, where TM = Ti, Zr, Nb, Ta, Mo, W) due to their high hardness and wear resistance. But their real use is still limited by brittle character and low oxidation resistance at elevated temperatures. TMB_2 films are most often prepared by physical vapor deposition (PVD) methods such as magnetron sputtering from stoichiometric compound targets in an inert argon atmosphere. The deposition processes are accompanied by (i) different angular distribution of sputtered boron, and metals, respectively, leading to the growth of overstoichiometric TMB_{2+x} films; (ii) the energy of reflected Ar neutrals causing resputtering and lead to grow a substoichiometric vacancy-containing TMB_{2-x} films. Here, we would like to demonstrate the effect of Ar particles on the structure, mechanical properties, and oxidation resistance of ZrB_{2+x} films. The films were deposited by high target utilization sputtering (HiTUS) technology where it is possible to independently change the kinetic energy of the argon ions accelerated toward the target (steering of target voltage) while maintaining the same amount (constant target current). Therefore, we have grown nanocrystalline ZrB_{2+x} films over a wide concentration range (x ~ 0.02 ÷ 2.1) with hardness values in range of 45.5GPa ± 1.2 GPa ÷ 8.3 GPa ± 0.3GPa. The films have a brittle character, expressed by Young's moduli, with the highest value of 480.9 GPa ± 8.8 GPa for $ZrB_{2.11}$. X-ray diffraction analysis confirmed the presence of hexagonal ZrB_2 phase with different preferred orientations depending on stoichiometry of the films. The highest oxidation resistance exhibited $ZrB_{2.27}$ films with onset temperature of ~ 750°C. Due to better understanding of the obtained results a deeper insight into nanostructure via transmission electron microscopy was performed. Mechanical behavior of ZrB_{2+x} was explained by density functional theory calculations.

Authors acknowledge funding from Operational Program Integrated Infrastructure [project /ITMS2014+/:313011AUH4] and Operational Program Research and Development [project ITMS 26210120010]

3:40pm **F4-2-WeA-6 Accurate Composition Depth Profiling of Light Elements in Thin Films Using Ion Beams - What Can Be Achieved?*, Daniel Primetzhofer (daniel.primetzhofer@physics.uu.se),*** Uppsala University, Sweden **INVITED**

For compound materials, subtle differences in stoichiometry often significantly alter the material properties of interest. This fact becomes particular important for compound systems for which a wide range of different compositions is accessible during synthesis as exemplified by transition metal carbides and borides. However, while accurate data on the composition on such compound samples containing light chemical species is thus of critical relevance, only very few methods can accurately provide the information requested. Ion beam-based analysis offers a unique toolbox to access the sample chemistry of such systems by a number of different non-destructive composition depth profiling techniques.

In this contribution we will illustrate the potential of ion beam analytical techniques in the characterization of light species ranging from hydrogen to oxygen while simultaneously providing reliable concentration depth profiles of the heavier constituents. Particular emphasis will be given to boron containing systems of different nature, i.e. thin films as well as multilayered or ion-implanted systems. At first, the underlying principles of ion-beam based analysis will be reviewed, illustrating the general characteristics and advantages of the methodology. These include amongst others minimum sample-preparation, non-destructive analysis, as well as typically fast measurements and analysis.

Subsequently, we will present a number of different ion-beam based methods by showcasing how they can answer specific scientific questions ranging from lattice location of hydrogen interstitials in energy storage materials to accurate measurements of the stoichiometry of borides as used for hard coatings. The methods presented will include tools capable of high-resolution depth profiling of specific isotopes as in nuclear resonance analysis or elastic backscattering spectrometry as well as methods providing composition depth profiles of the whole sample inventory on nanometer depth scales as enabled by Time-of-Flight Elastic Recoil Detection Analysis. We will discuss the achievable accuracy as well as limitations of the techniques also in comparison to other analytical approaches. Finally, we will also discuss, how a combination of methods can be employed to further increase the accuracy of analysis.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-3-ThM

New Horizons in Boron-Containing Coatings III

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Helmut Riedl**, TU Wien, Austria, **Johanna Rosén**, Linköping University, Sweden

8:40am **F4-3-ThM-3 Synthesis of MoAlB Thin Films ContainingMoB MBene Regions**, *R. Sahu,* Max-Planck-Institut für Eisenforschung GmbH, RWTH Aachen University, Germany*; D. Bogdanovski, S. Evertz, P. Pöllmann, D. Holzapfel, E. Mayer, J. Achenbach,* RWTH Aachen University, Germany*; S. Zhang,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; C. Scheu,* Max-Planck-Institut für Eisenforschung GmbH, RWTH Aachen University, Germany*; **Jochen M. Schneider (schneider@mch.rwth-aachen.de)**,* Materials Chemistry, RWTH Aachen University, Germany

Two-dimensional (2D) inorganic transition metal boride nanosheets are emerging as promising post-graphene materials in energy research due to their unique properties. State-of-the-art processing strategies are based on chemical etching of bulk material synthesized *via* solid-state reaction at temperatures above 1000 °C. Here, we report the direct formation of MoB MBene domains in an MoAlB thin film by Al deintercalation from MoAlB in the vicinity of AlO$_x$ regions. Hence, based on these results a straightforward processing pathway for the direct formation of MoB MBene-AlO$_x$-heterostructures without employing chemical etching is proposed here.

Furthermore, the nanolaminated ternary boride MoAlB exhibits a promising high-temperature oxidation resistance due to the formation of a dense alumina scale. While bulk synthesis of MoAlB requires temperatures larger than 1000 °C with up to 40% of excess Al in the feedstock, here we report the temperature range for the formation of single phase, orthorhombic MoAlB synthesized by magnetron sputtering from a stoichiometric target is 450 – 650 °C. Lower synthesis temperatures yield the formation of amorphous films, while at 700 °C, impurity phases form in addition to orthorhombic MoAlB. Amorphous MoAlB films were observed by in-situ X-ray diffraction to crystallize between 545 and 575 °C. Hence, we infer that the formation of orthorhombic MoAlB thin films issurface diffusion mediated below 545 °C. As bulk diffusion is activated between 545 and 575 °C the synthesis of fully dense MoAlB films with a maximum hardness of 15 ± 2 GPa and a Young's modulus of 379 ± 30 GPa at 600 °C is surface and bulk diffusion mediated.

9:00am **F4-3-ThM-4 On the Surpassing Fracture Toughness of TiB$_2$±$_z$ Thin Films**, ***Christoph Fuger (christoph.fuger@tuwien.ac.at)**, A. Hirle, R. Hahn, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG , Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Their unique material characteristics make transition metal diboride-based thin films to perfect candidates for replacing state of the art protective and functional coatings. Not only machining tools but also high-precision components (e.g. turbine blades) within aircrafts and turbines used for energy production demand for surface improving materials. Mechanical properties like hardness, Young's modulus and fracture toughness of the thin films are essential to protect the components from impacting mechanical stresses, especially against sudden impacts at high stress levels. Well-known for their superior hardness, various TMB$_2$ exhibit enhanced resistance against fracture exceeding K$_{IC}$ values of well-established nitride-based coating materials (e.g. TiN or Ti$_{1-x}$Al$_x$N) and are therefore perfect aspirants for various industrial applications.

Here, we focus on magnetron sputtered non-stoichiometric TiB$_{2\pm z}$ exhibiting outstanding mechanical properties. Beside super hardness of 45.90 ± 1.20 GPa and Young's modulus of 524.27 ± 14.10 GPa the coatings exhibit a fracture toughness of K$_{IC}$ = 4.79 ± 0.57 MPa√m – tested via different micro-mechanical testing procedures. Detailed TEM and TEM-EELS investigations elucidate, that the distinct excess of boron predominates the constitution of the precipitating tissue phases around the columnar growth morphology. Due to covalently bonded boron-boron bonds the cohesive grain boundary strength is enhanced, impeding severe intercolumnar crack growth. The study highlights the great potential of TiB$_{2\pm z}$ for new applications in the field of high-performance components and reveal the importance of a detailed understanding of the grain boundary strength for fracture tough thin films.

Keywords: Fracture Toughness; Transition Metal Diborides; TiB$_2$; Tissue Phase; Micro-mechanical Testing;

9:20am **F4-3-ThM-5 Revealing the Beauty of Imperfection in Novel Diboride Coatings by Transmission Electron Microscopy**, ***Justinas Palisaitis (justinas.palisaitis@liu.se)**,* Linköping Univ., IFM, Thin Film Physics Div., Sweden **INVITED**

Transition metal diborides (TMB$_2$) are considered as an extremely hard ceramics owning to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes TMB$_2$ coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1,2].Currently, magnetron sputtering is the primary technique for obtaining TMB$_2$ coatings. Typically obtained TMB$_2$ coatings are overstoichiometric in boron (B/TM>2) [3]. Recent addition of novel understoichometic variants of TMB$_2$ coatings (B/TM<2) have greatly widened their compositional range [3-8]. As the field of non-stoichiometric TMB$_2$ coatings is starting to open, this work offers the first systematic investigation into the different types of extended planar defects presented in the TMB$_2$ coatings throughout the wide compositional and elemental range. Atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects. Distinct types of planar defects residing on the {1-100} planes have been identified that are accompanied with or without local compositional changes. The characteristic atomic structures and factors leading to the formation of these planar defects in TMB$_2$ coatings will be presented.

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10:00am **F4-3-ThM-7 Thermally Induced Structure Evolution and Improved Oxidation Behavior of Ternary Ta$_{1-x}$Al$_x$B$_{2+\Delta}$ Hard Thin Films**, ***Viktor Šroba (viktor.sroba@fmph.uniba.sk)**,* Comenius University, Bratislava, Slovakia*; T. Fiantok,* Comenius University in Bratislava, Slovakia*; M. Truchlý, T. Roch, B. Grančič,* Comenius University, Bratislava, Slovakia*; P. Švec,Jr.,* Institute of Physics, Slovak Academy of Sciences, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics SAS, Slovakia*; V. Izai,* Comenius University, Bratislava, Slovakia*; T. Glechner,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, Austria*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria*; P. Kúš, M. Mikula,* Comenius University, Bratislava, Slovakia

Diborides of transition metals (TMB$_2$) from IIIB to VIB group are due to their excellent mechanical properties and thermal stability promising materials for hard thin films used in extreme environments. Notable example being overstoichiometric TiB$_{2+\Delta}$ with value of hardness up to 60 GPa. However, formation of volatile boric acid (H$_3$BO$_3$) at elevated temperatures in air (450 °C for TiB$_{2+\Delta}$) and low fracture toughness expressed by high values of elastic modulus (500-600 GPa for TiB$_{2+\Delta}$) significantly reduce application potential of binary diboride coatings [1]. Alloying with aluminum to form ternary systems is well-proven method leading to improved oxidation resistance and higher hardness due to age hardening as a result of spinodal decomposition. This effect was theoretically predicted in TiAlB$_2$ by Alling et al. [2] and experimentally confirmed by Mockute et al. [3] in which decomposition of TiAlB$_{2+\Delta}$ films during annealing at 1000 °C led to increase in hardness from 32 to 37 GPa.

Here, we present structural evolution and oxidation behavior of ternary Ta$_{1-x}$Al$_x$B$_{2\pm\Delta}$ films. Experimental results obtained on magnetron co-sputtered Ta$_{1-x}$Al$_x$B$_{2\pm\Delta-}$ films were supported by density functional theory (DFT) calculations on TaAlB$_2$ system. Addition of aluminum resulted in decrease of hardness from ~34 GPa for amorphous TaB$_{1.21}$ films to ~29 GPa for Ta$_{0.75}$Al$_{0.25}$B$_{2.14}$ films with typical 0001 texture of hexagonal α-AlB$_2$ type structure. Positive effect of aluminum alloying in improvement of oxidation behavior was observed during thermogravimetric analysis (TGA) with onset oxidation temperature of approx. 700 °C for Ta$_{0.75}$Al$_{0.25}$B$_{2.14}$ films compared to 600 °C for TaB$_{1.21}$ films.

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10:20am **F4-3-ThM-8 Mapping the X-B-C Systems: Search for the Elusive X_2BC Phase**

***Pavel Soucek (soucek@physics.muni.cz)**, S. Debnarova, M. Alishahi, S. Mirzaei, M. Kroker, L. Zabransky, V. Bursikova,* Masaryk University, Czechia*; Z. Czigany, K. Balazsi,* Centre for Energy Research, Hungary*; M. Hans, D. Holzapfel, S. Mraz, J. Schneider,* RWTH Aachen, Germany*; P. Vasina,* Masaryk University, Czechia **INVITED**

Binary borides and binary carbides have been known for many decades. Their outstanding mechanical, electrical and thermal properties made them indispensable in the industry, either in bulk or as thin films. The idea of combining these systems into a ternary X-B-C system naturally evolved. Such systems in the form of bulk have been investigated since the 1950s. The X has been from all of the s, p d and f blocks of the periodic table of the elements. Different structures were found. The orthorhombic Mo_2BC phase, being the first with the X_2BC stoichiometry, was described by Jeitschko in 1963 [1]. This structure attracted interest for its superconducting properties. Sixty years later, this is still the only synthesised X_2BC phase.

An interest in the X-B-C thin films can be traced to the mid-1980s, with experimental work accelerating in the 1990s. The focus was on the Ti-B-C system in the form of multilayers or in the form of a crystalline-crystalline nanocomposite. Superior mechanical properties of this system were described. A renaissance of the X_2BC phases, this time in the form of the thin films, has begun in 2009 when the Mo_2BC phase was prepared by direct current magnetron sputtering [2]. This phase was no longer studied for its superconducting properties, in which other materials superseded it, but for its highly unusual combination of high hardness and moderate ductility. Theoretical studies describing other crystalline ternary X_2BC phases predicting the thermodynamic possibility of their preparation together with even better mechanical properties followed [3]. Since then, several different systems from these predictions have been studied, including W-B-C, Nb-B-C and Ta-B-C. No definitive proof of the existence of any X_2BC phase apart from the original Mo_2BC phase was found. This contribution will cruise through the ups and downs of this research in the last decade. It will be shown that thin films from these systems can have interesting mechanical and thermal properties even without the formation of the desired and elusive X_2BC phase. It will be discussed why these phases won't form even under energetically very harsh conditions such as HiPIMS. We will also sketch the possibilities for the future directions of the studies of the X_2BCs.

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11:00am **F4-3-ThM-10 Industrial Deposition of W-B-C Coatings: Properties and Process Modelling**

***Michael Kroker (kroker@physics.muni.cz)**, P. Souček, L. Zábranský, V. Buršíková,* Masaryk University, Czechia*; V. Sochora, M. Jílek,* SHM s.r.o., Czechia*; P. Vašina,* Masaryk University, Czechia

W-B-C coatings have the potential to replace current state-of-the-art hard protective coatings in the industry owing to their unprecedented combination of high hardness and increased fracture resistance, as the brittle fracture is the most limiting shortcoming of the traditional hard protective coatings based on ceramics such as TiN, CrN, AlN, and their combinations. So far, only a few studies have dealt with industrial deposition of the W-B-C coatings.

This study shows the properties of W-B-C coatings industrially deposited by non-reactive magnetron sputtering using a system provided by SHM, Czech Republic. The system utilizes a single cylindrical sputter source fitted with a segmented target composed of tungsten, boron carbide, and graphite segments. The segmented target provides for the adaptation of the coatings' chemical composition by rearranging the position of individual segments. As an industrial standard, the planetary table capable of multi-axis rotation of substrates was used to simulate batch coating of the tools. The depositions were carried out in both stationary and single-axis rotation regimes to understand the differences between laboratory-like and industrial preparation of the coatings.

W-B-C coatings were studied over a broad range of chemical compositions. Although the coatings were mostly amorphous, they still exhibited high hardness (up to 29 GPa) and elastic modulus (up to 440 GPa). Detailed analyses of their mechanical properties proved their superior fracture resistance compared to current ceramic-based protective coatings. The comparison of the fracture resistance was possible using the instrumental indentation technique and indentation tip with a very small curvature radius (cube-corner diamond tip) and very thick coatings. This method induced cracking in the coating without the significant influence of the substrate.

To further ease the industrial utilization of these coatings, a simple yet powerful model was developed to predict the influence of the target setup and the influence of movement and placement of the substrates in the chamber. The modelling procedure was based on freeware SDTrimSP for the sputtering processes and SiMTra for the particle transport. The results showed very good agreement in terms of chemical composition as well as the relative thickness of the coatings. They were able to identify the crucial difference between the laboratory-like and industrial preparation of the W-B-C coatings.

11:20am **F4-3-ThM-11 Magnetron Sputter Deposition of Boron Carbide Films on Tilted Substrates**

***Swanee Shin (shin5@llnl.gov)**, L. Bayu Aji,* Lawrence Livermore National Laboratory, USA*; J. Bae,* General Atomics, USA*; A. Engwall, M. Nielsen, J. Hammons,* Lawrence Livermore National Laboratory, USA*; X. Zuo, B. Lee,* Argonne National Laboratory, USA*; X. Lepro Chavez, P. Mirkarimi, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Many applications of boron carbide films call for deposition onto non-planar substrates in the regime when the substrate normal is tilted away from the main deposition flux direction. Properties of boron carbide films deposited on such tilted substrates have not been previously studied, and the underlying physics of boron carbide film growth in the oblique angle deposition regime remains poorly understood. Here, we present results of our systematic study of the effect of substrate tilt on properties of boron carbide films deposited by direct current magnetron sputtering. The influence of the working gas (Ar vs Ne) on the deposition rate and film properties will also be discussed.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

New Horizons in Coatings and Thin Films
Room Golden State Ballroom - Session FP-ThP

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

FP-ThP-1 Analysis of (Al,Cr,Nb,Ta,Ti)-Nitride and Oxynitride Diffusion Barriers in Cu-Si Interconnects by 3D-Secondary Ion Mass Spectrometry*, Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at),* TU Wien, Institute of Materials Science and Technology, Austria*; F. Bohrn, H. Hutter,* TU Wien, Institute of Chemical Technologies and Analytics, Austria*; E. Pitthan, D. Primetzhofer,* Uppsala University, Department of Physics and Astronomy, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

A number of different high-entropy sublattice nitrides have been investigated in the past as diffusion barriers between Cu and Si. These investigations were performed by depositing several nanometer thin barriers on single crystalline Si substrates, followed by a thick Cu layer on top, and subsequent vacuum annealing. In this work we report on the barrier performance of a nitride, and also three oxynitrides of the high-entropy alloy Al-Cr-Nb-Ta-Ti by depositing a reversed stacking sequence. 10 nm of (Al,Cr,Nb,Ta,Ti)-O-N (between 0.5 and 63.7 at% O, obtained by Elastic Recoil Detection Analysis) were deposited on polished polycrystalline Cu substrates by magnetron sputtering at room temperature with -100 V bias, followed by deposition of 200 nm Si. The samples were then vacuum annealed at 600, 700, 800 and 900 °C for 30 min. All four investigated coatings perform similar. While Secondary Ion Mass Spectrometry depth profiling in high-current-bunched (HCBU) mode with a high mass resolution (of >12.000 amu, lateral resolution ≈1 µm) shows breakthrough of Si even at 600 °C, 3D constructed images with Burst Alignment (BA, lateral resolution of ≈2 nm) depth profiles reveal that this failure is a highly localized phenomenon. The failure is likely related to recrystallization effects at the Cu grain boundaries, leading to punctuation of the diffusion barrier, as the diffusing Si stays confined in columnar regions within the Cu. Aside from this penetration, the majority of the area of each barrier coating retains its function. This in-depth analysis shows that the barrier function of the nitride and oxynitride coatings essentially stays intact up to 800 °C and fails completely at 900 °C.

FP-ThP-2 Maximum Achievable N Content in Amorphous Nitrides*, Jiri Houska (jhouska@kfy.zcu.cz),* University of West Bohemia, Czechia

The contribution reports the latest results concerning the maximum achievable N content in amorphous nitrides prepared by atom-by-atom growth. Structures of amorphous CN_x, Si-C-N, B-C-N and Si-B-C-N are predicted by extensive ab-initio molecular-dynamics simulations (over 15 000 trajectories) in a wide range of compositions and densities [1-3]. When and only when the structures are allowed to include unbonded N_2 molecules, the predicted lowest-energy densities are in agreement with the experiment. The main attention is paid to the N_2 formation, with the aim to predict and explain the relationships between [Si]/[B]/[C] ratios and the maximum achievable content of N bonded in stable amorphous networks ($[N]_{network}$). The results reveal that N_2-free networks are characterized by maximum $[N]_{network}$ between 34% (CN_x) and 57% (SiN_x). Networks formed in parallel to the formation of unbonded N_2 molecules (which subsequently either diffuse out or stay trapped in the material) are characterized by maximum $[N]_{network}$ between 42% (CN_x) and 57% (SiN_x). The measured N contents in (Si)-(B)-C-N films prepared in our laboratory by reactive magnetron sputtering are in an excellent agreement with the prediction. Further analysis shows that while the N_2 formation takes place at a packing factor below the critical value of 0.28 which is valid in a wide range of compositions, the lowest-energy packing factor (sometimes below 0.28, sometimes above 0.28) depends on the composition. The presented methodology constitutes a new way how to support the experiment by ab-initio simulations. The results are important for the design of amorphous nitrides for various technological applications, prediction of their stability, design of pathways for their preparation, and identification of what may or may not be achieved in this field.

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FP-ThP-3 Bulk Diffusion of Impurities in TiN: An Ab Initio Study*, Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at),* Montanuniversität Leoben, Austria*; M. Popov,* Material Center Leoben, Austria*; D. Holec,* Montanuniversität Leoben, Austria

TiN-based materials are widely established as protective coatings for cutting tools. Grain interiors (single crystal regions) could serve as reservoirs for functional species, e.g. Al or V, which provide effective lubrication and wear protection at high temperatures by diffusing to the coating surface where they form a protective oxide scale (Al) or a lubricious oxide to reduce friction (V).

In this contribution, we will report on our recent work in addressing issues related to the atomistic modeling of mass transport. To do so we employ complementary computational investigations to determine elementary point-defect migration mechanisms in crystalline materials and subsequently their relative rates. The density functional theory (DFT) is used to describe interatomic forces, is the most reliable computational tool to calculate atomic jump rates as a function of temperature. Since TiN is a harmonic crystal it gives us access to temperature-based properties derived from the lattice vibration with harmonic and quasi-harmonic approximation. We will present the DFT-based “5-frequency model” allowing us to calculate the diffusion coefficient in the crystalline material. Moreover, the influence of TiN stoichiometry on its diffusion properties is taken into account through the change in the concentrations of the intrinsic point defects as a function of composition. These concentrations are obtained via a thermodynamic formalism based on the dilute solution model. We find that in stoichiometric TiN the vanadium impurity diffusion proceeds via the vacancy mechanism on the Ti sublattice. Furthermore, we also demonstrate that pressure has a notable impact on the diffusivity of V, Al, and Ti in TiN.

FP-ThP-5 Data-Driven Design Guidelines for Ceramic Superlattices With Enhanced Fracture Resistance*, Nikola Koutná (nikola.koutna@tuwien.ac.at),* *A. Brenner,* TU Wien, Austria*; D. Holec,* Montanuniversitat Leoben, Austria*; P. Mayrhofer,* TU Wien, Austria

Superlattices—alternating coherently grown materials of nm thicknesses—showed a great potential for enhancing typically antagonistic properties of ceramics: strength and toughness. Selection of layer components, however, is far from trivial, as nanolaminated films do not combine mechanical properties of the layer materials in a simple manner. In this work, we employ high-throughput density functional theory calculations to develop design guidelines for superlattices based on cubic transition metal nitride and/or carbide ceramics. Out of 153 MX/M*X* superlattices (M, M* = Al, Ti, Zr, Hf, Nb, V, Ta, Mo, W, and X, X* = C, N) 145 are chemically and mechanically stable and most often contain vacancies on the non-metallic sublattice. Superior ductility together with moderate-to-high fracture toughness and interface strength (above that of the cubic TiN) narrow the set of the most perspective candidates. Key ingredients promoting the interface-induced enhancement of hardness and/or fracture toughness are lattices parameter and shear modulus mismatch of the layer constituents. Adding the requirement of phonon stability yields MoN/M*N, M*=Nb, Ta,Ti; TiN/WN (nitrides); HfC/M*N, M*=Mo, W; NbC/M*N, M* = Mo, W; TaC/M*N, M* = Mo,W; VC/M*N, M* = Hf, Ta, Zr (carbonitrides); as the top candidates for novel superlattice films.

FP-ThP-6 Preparation of Single and Multilayer Films of Boron Carbide, Titanium Diboride and Hexagonal Boron Nitride Using Pulsed Laser Deposition*, Falko Jahn (jahn@hs-mittweida.de),* *S. Weißmantel,* Laserinstitut Hochschule Mittweida, Germany

Boron containing film materials provide outstanding mechanical, thermal and chemical properties which leads to growing interest in applying these materials in wear resistance coatings. Boron carbide, the third hardest known material after diamond and cubic boron nitride, shows indentation hardness values up to 49 GPa and a very high chemical and thermal stability. Titanium diboride’s thermal properties exceed even those of boron carbide with a melting point over 3200°C and exceptional hardness at high temperatures (> 2000°C). Both materials are very well suited as wear resistance coatings, especially in very corrosive or hot environments. However, the brittleness of both materials may restrict their use regarding applicable loads

The presented approach to overcome these restrictions is to combine the material properties of boron carbide and titanium diboride with the properties of a less brittle but also very hard material by forming multilayer structures. Since this material should provide a similar thermal and chemical stability, we chose hexagonal boron nitride whose hardness can be varied between 10 GPa and 25 GPa depending on the process parameters.

The presented results contain both the produced single and multilayers using the pulsed laser deposition technology. The mechanical properties of the produced films of boron carbide, titanium diboride and hexagonal boron nitride are investigated in dependence of the process parameters such as ablation fluence and substrate temperature.

The obtained mechanical material properties are applied to simulations of various multilayer designs under certain load conditions in order to find suited multilayer parameter combinations such as thickness or mechanical property of the sublayers. Promising multilayer designs are produced and characterized. The mechanical properties of the presented thin films are measured using nanoindentation. The surface quality is characterized by scanning electron microscopy and the sublayer adhesion is estimated using instrumented scratch testing and a calotte-grinding method.

FP-ThP-7 Anisotropic Super-hardness of Hexagonal WB$_{2-z}$ Thin Films*, **Christoph Fuger (christoph.fuger@tuwien.ac.at)**, R. Hahn, L. Zauner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; M. Weiss, A. Limbeck,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Physical vapor deposited transition metal borides are an emerging class of materials. Their inherent promising properties range from ultra-low compressibility, highest thermal stability to chemical inertness, allowing an application as protective coating in quite harsh environments. Our recent ab initio calculations suggest an attractive combination of Poisson’s ratio, bulk-, and shear modulus for α-structured WB$_{2-z}$ (space group 191, AlB$_2$-prototype, P6/mmm). This leads to an interesting combination of high hardness while maintaining a sufficient fracture toughness. The stabilization of the α-structure over the intrinsically favored ω-structure (space group 194, W$_2$B$_5$-prototype, P6$_3$/mmc) is based on omnipresent growth defects (e.g. various types of 0-dimensional vacancies) throughout the PVD deposition. However, next to the stabilized phases (hence prevalent bonding nature) also the morphology, especially column size and grain boundary interior, has a huge impact on the mechanical response.

Here, we focus on the binary WB$_2$ material system in terms of its phase formation using DFT and further illustrate the impact of prevalent lattice orientations on the mechanical properties. We show, that the α-WB$_{2-z}$ structure is preferentially stabilized by B vacancies, exhibiting its energetic minima at sub-stoichiometric compositions of about WB$_{1.5}$ – being also experimentally underlined.The mechanical properties show that α-WB$_{2-z}$ coatings in 0001 orientation reveal super-hardness (H > 40 GPa) compared to their 10-11 oriented α-WB$_{2-z}$ counterparts (H ~ 30 GPa). This is attributed to differences in the generalized stacking fault energies (GSFE) of basal and pyramidal slip systems in hexagonal diboride crystals. Our results show that the mechanical properties, in particular H, of PVD α -WB$_{2-z}$ coatings can change significantly due to the crystallographic orientation, highlighting the feasibility of tuning mechanical properties by crystallographic orientation relations.

Keywords: WB$_2$; Physical Vapour Deposition; DFT; Structural defects; Anisotropy;

FP-ThP-10 Characterization of a Novel Ionic Liquid-Based Chromium Plating Formulation*, **Cameron Longo (cameron.m.longo.civ@army.mil)**, D. Sconyers,* US Army - DEVCOM AC - Benet Laboratories, USA*; M. Quiroz-Guzman, D. Morrison, T. Bush, M. Arsenault,* Trion Coatings, LLC, USA*; J. Maurer,* US Army - DEVCOM AC - Benet Laboratories, USA

Hexavalent chromium electroplating has come under severe scrutiny, with increasingly strict regulations and plans for complete removal from operations within the US within the next 10 years. Hexavalent chromium poses large risks, as it is a known carcinogen and presents severe occupational and environmental hazards in its use. However, chromium coatings offer many benefits, including excellent wear and corrosion resistance, and has good hardness and adhesion properties. As such, an effective chromium plating alternative for hexavalent-based processes is sorely needed.

Several systems which utilize trivalent chromium have been proposed, which offer highly reduced health and environmental risks, and could serve as appropriate replacements. An ionic liquid-based trivalent chromium process, dubbed SAFE Chrome, has been developed as an alternative to aqueous chemistries, and utilizes a charged organic species to bind to chromium ions to facilitate deposition. The analysis of weakly-bound organometallic complexes holds many unique challenges, the most salient of which is the desire to characterize the complex as it exists in solution. Mass spectrometry techniques are some of the most attractive options, as they afford highly robust and sensitive means of characterization. Traditional techniques, such as electrospray ionization (ESI) or matrix-assisted laser desorption/ionization (MALDI), have great potential to perform structural characterization of the components of these complexes using varying ionization approaches and tandem MS analyses, while more novel technique such as liquid injection field desorption/ionization (LIFDI) may offer unique insights into the bound form of the complex. Techniques such as infrared (IR) and ultraviolet-visible (UV-VIS) spectroscopy, as well as X-ray techniques like small-angle X-ray scattering (SAXS) can also offer insights into the structure or binding of the complex, while electrochemical analyses can inform on the electron transfer processes and valence of the metals. These data together help to form a deeper understanding of the chemistry occurring in solution during plating, and enable more intelligent design and better control of these emerging plating technologies.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F3-FrM

2D Materials: Synthesis, Characterization, and Applications

Moderator: Suneel Kodambaka, University of California Los Angeles, USA

8:00am **F3-FrM-1 Tackling Scalability in the Synthesis of Two Dimensional Chalcogenide Semiconductors and their Heterostructures***, **Nicholas Glavin (nicholas.glavin.1@us.af.mil)**,* Air Force Research Laboratory, USA **INVITED**

The rapid development of 5G communications, wearables, sensors, and internet of things have pushed forward the need for all types of electronics and sensors requiring the exceptional properties of two-dimensional (2D) nanomaterials. Graphene and other 2D materials have become an increasingly interesting candidate in these systems due to the mechanical strength and flexibility at the ultimate materials scaling limit, unique transport characteristics, tunable optical properties, controllable surface sites and the potential for facile device fabrication. In this talk, challenges and opportunities to address scalability in 2D material transition metal dichalcogenides is presented. These techniques include low cost and customizable laser-manufacturing approaches and a two-step metal conversion process for direct synthesis of superlattices to allow material properties by design.

8:40am **F3-FrM-3 2D Nanosheets Exfoliation and Functionalization from Hexagonal Boron Nitride in Aqueous Phase for Ultrafast Solvent Transport of Molecular Solute Screening Film***, **Degu Lere Keshebo (keshebos@gmail.com)**, C. HU, J. Lai,* National Taiwan University of Science and Technology, Taiwan

Currently hexagonal boron nitride is promising materials for its solidity in different working conditions but preparation based on environmental friendly technique is challenging. In this study, aqueous phase exfoliation using tannic acid has demonstrated an easy, novel, green method used to prepare functionalized boron nitride nanosheets. Both microscopic techniques (TEM, SEM AFM) and spectroscopic techniques (XRD, XPS, FTIR, and Raman) were used to characterize the exfoliated nanosheets and synthesized membrane. Tannic acid is adsorbed on hexagonal boron nitride surface and gradually exfoliating in the form of a few layers of functionalized boron nitride nanosheets, it behaves as a green surfactant by weakening the interlayer interaction. Ultimately, the functionalized exfoliated nanosheets used to prepare membrane for environmental applications. Fascinatingly, the prepared membrane is an exceedingly stable in water and other organic solvents and shows good efficiency in transporting solvents with excellent screening of solutes with long-term antifouling. The synthesized membrane's rapid transport rate of solvents and good separation efficiency of solutes can be due to robust nanochannel and thin laminar networks of nanosheets, which afford beneficial properties for the membrane effective separation and purification processes.

Keywords: hexagonal boron nitride, 2D nanosheets, tannic acid, noncovalent functionalization, antifouling, molecular sieving

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