Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-1-MoM

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

Moderators: Dr. Damien Faurie, Université Sorbonne Paris Nord, France, **Dr. Michael Tkadletz**, Montanuniversität Leoben, Austria

10:00am **H1-1-MoM-1 In-situ Imaging of Au Bicrystals and Hydrogen Charged Iron***, **Wendy Gu,*** Stanford University, USA*; M. Kiani,* Cornell University, USA*; A. Lee, A. Parakh,* Stanford University, USA **INVITED**

High resolution in-situ imaging is useful for understanding deformation, plasticity and fracture at internal microstructural features and under complex environmental conditions. Here, I will describe in-situ transmission electron microscopy (TEM) tension testing of Au bicrystal thin films that each contain a single grain boundary. This allows us to correlate the stress-strain curve and failure mode (e.g. twinning mediated fracture) to the grain boundary misorientation angle and grain boundary energy. Then, I will describe synchrotron transmission X-ray microscopy (TXM) of hydrogen charged iron thin films. This investigation is meaningful for understanding hydrogen degradation of metals, which is highly relevant to the green hydrogen economy. Home-built in-situ tension stages are used to test single edge notched samples. TXM is used to detect the formation of voids of ~100 nm to microns in size at the crack tip while simultaneously performing electrochemical hydrogen charging. We find that voids are elongated perpendicular to the loading direction, and highly localized at the crack tip during hydrogen charging in intergranular failure. Dynamic (time-dependent) TXM imaging enables the observation of void-mediated crack growth, as well as the coalescence of the primary crack with secondary cracks. Cracks and additional plasticity occur at grain boundaries during transgranular failure. These observations are discussed in the context of the predominant hydrogen embrittlement mechanisms.

10:40am **H1-1-MoM-3 High-Throughput Surface Analysis for Accelerated Thin Film Materials Development***, S. Zhuk, A. Wieczorek, K. Thorwarth, J. Patidar, **Sebastian Siol,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

New functional coatings are instrumental for the advancement of many sustainable technologies. As demands for functional properties are increasing, the materials and associated parameter spaces are becoming more complex. Combinatorial physical vapor deposition coupled with automated characterization and data analysis is routinely used to accelerate the development of new multi-functional thin films. Surface analysis using X-ray photoelectron spectroscopy (XPS) plays an important role in conventional thin film materials development. However, in combinatorial materials science methodology XPS analysis is much less common. In this presentation, we will show how spatially-resolved, automated XPS mapping can complement other high-throughput characterization techniques and provide unique insights in complex phase-spaces. Different use cases for high-throughput surface analysis will be presented, from the development of corrosion-resistant thin films [1] over phase-analysis in nano-crystalline materials [2] to combinatorial interface studies.[3] We will present results on the development of different inorganic thin films, including conductive ceramics, as well as semiconducting oxides and nitrides. In particular, we will introduce and discuss how measurements of the Auger parameter can augment standard XPS analysis for a robust and meaningful high-throughput analysis of air-sensitive and semiconducting samples.[2,4] Such studies can give insight not only into the chemical state of the constituent elements, but also their coordination and consequently the structure of the investigated materials. Finally, we will highlight how combinatorial XPS, coupled with clean inert-gas or UHV transfers can help to not only characterize light element contamination, but also oxidation resistance in air-sensitive coatings.

The concepts presented here are easily transferable to other material systems and can be adapted in standard measurement equipment.

[1] Siol et al., Acta Materialia, 2020, **186**, 95-104

[2] S. Zhuk et al. Appl. Surf. Sci., 2022, **601**, 154172

[3]S. Siol et al. Advanced Materials Interfaces, 2016, **3**, 24, 1600755

[4] A. Wieczorek et al. 2022, arXiv:2207.14123

11:00am **H1-1-MoM-4 Advanced Experimental Techniques Quantifying Thin Film Delamination at the Nano-Scale***, **Alice Lassnig**, C. Gammer, S. Zak, M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Interface stability between thin films and substrates is a prerequisite to ensure overall reliability of multi-component structures since such interfaces are known to be mechanically weak. Thus, a deep understanding of the mechanisms involved in the delamination process throughout their length scales is crucial and allowing to improve their reliability. Previously [1] we could demonstrate by means of a FIB-based characterization technique that intrinsic film properties can significantly influence interface adhesion and that plastic deformation occurring during delamination of the films can be understood as a toughening mechanism preventing delamination, as confirmed by finite element modelling [2].

To understand the mechanisms involved during thin film delamination, dedicated fracture experiments were designed to study the fracture behavior of ductile thin films using bending beam and push to pull geometries in situ under the transmission electron microscope. Particular focus is set on the thin film- interface delamination interaction to study the influence of thin film deformation behavior. On selected thin film systems strain mappings are conducted to quantify the thin film deformation during delamination within the transmission electron microscope.

[1]A. Lassnig, V.L. Terziyska, J. Zálešák, T. Jörg, D.M. Többens, T. Griesser, C. Mitterer, R. Pippan, M.J. Cordill, E. Al., Microstructural Effects on the Interfacial Adhesion of Nanometer-Thick Cu Films on Glass Substrates: Implications for Microelectronic Devices, ACS Appl. Nano Mater. 4 (1) (2021) 61–70. https://doi.org/10.1021/acsanm.0c02182.

[2]S. Žák, A. Lassnig, M.J. Cordill, R. Pippan, Finite element-based analysis of buckling-induced plastic deformation, J. Mech. Phys. Solids. 157 (2021). https://doi.org/10.1016/j.jmps.2021.104631.

11:20am **H1-1-MoM-5 New Generation In Situ Process Control of Chemical Composition of Compound Materials and Superalloys During PVD Process***, **George Atanasoff,*** AccuStrata, Inc., USA

Multiple challenges associated with thin film deposition accuracy, and especially the challenge of real-time control of chemical composition for compound films and superalloys, spread over the entire contemporary thin film vacuum coating industry. These challenges predominantly affect the new-generation thin films such as high entropy superalloys (HESA), wide band semiconductors (WBS), Extreme UV and X-Ray coatings and others. Traditional in situ process control technologies are not adequate to the challenge: they monitor either the attained optical thickness of the film on the substrate, or the mass of the deposited material. In rare cases plasma optical emission or X-Ray fluorescence are used, but they both do not offer sufficient accuracy to meet the requirements for real time in situ monitoring.

A novel *in situ* PVD process control system for the manufacturing of high-precision thin films, based on simultaneous atomic absorption and optical emission spectrometry in the vicinity of the substrate (AtOMS), is presented. By simultaneous monitoring the atomic concentration of up to 6 metals in the deposition plum under the substrate together with the optical emission of a variety of particles and radicals, the method provides accurate deposition rate and film composition control during deposition, as well as control of extremely thin films and pre-engineered interface layers. The presented technology is viewed as an enabling technology for real time composition control of HESA and WBS for thermal barrier and bond coatings, anticorrosion, stimuli-response and other advanced coatings. Being agnostic to the type or the motion of the substrate, AtOMS technology is suitable for control of alloys and WBS deposited on complex substrates and composite materials. AtOMS provides real time deposition rate and film composition measurements utilized for dynamic feedback process control. The fiber optics design of the system allows flexibility and reconfigurability for fast and seamless installation in almost all legacy PVD equipment.

We present our most recent experimental results from *in situ* monitoring of variety of thin films such as Si, Mo, Al, In, Ti, Co, Cu, Au, B and compound thin films (MoSix, AlSix, WSix, ITO, NiCr) deposited by a magnetron sputtering, MBE and E-Beam evaporation. Results for the achieved accuracy, stability and repeatability under various equipment configurations and monitored materials in manufacturing environment are also presented. The results validate the applicability and practicality of combined atomic absorption/ optical emission spectroscopy in the deposition of WBS and superalloys as well as for combinatorial discovery of new HESA and WBS.

11:40am **H1-1-MoM-6 Influence of Al Incorporation and N Stoichiometry on the Thermal Stability of (Ti,V,Zr,Nb,Hf,Ta)N Thin Films**, ***Deborah Neuß***, *M. Hans, G. Fidanboy, H. Lasfargues, C. Azina, S. Mráz,* RWTH Aachen University, Germany*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; J. Schneider,* RWTH Aachen University, Germany

Recently, the concept of high entropy alloys has been transferred to ceramic thin films such as transition metal aluminum nitrides. In the present work $(Ti,V,Zr,Nb,Hf,Ta)_{1-y}N_y$ (TMN) and $((Ti,V,Zr,Nb,Hf,Ta)_{1-x}Al_x)_{1-y}N_y$ (TM,AlN) films were grown by reactive sputtering using a hybrid co-deposition geometry. The thermal stability was studied through vacuum annealing in a temperature range from 700 to 1300 °C and subsequently the films were analyzed regarding chemical composition, phase formation as well as mechanical properties.Configurational entropy contributions on the metal sublattice exceed 1.5R for all configurations, increasing in TMN as well as (TM,Al)N from overstoichiometric to understoichiometric compositions: from 1.57R up to 1.79R in case of TMN films as well as from 1.69R to 1.86R for (TM,Al)N films. Spatially-resolved compositional analysis at the nanometer scale has been carried out using atom probe tomography (APT). In case of (TM,Al)N films a dual-phase structure is readily observed in the as deposited state as aluminum decorates the grain boundaries and the formation of Al-rich regions is enhanced after vacuum annealing at 700 °C. Thus, surface diffusion, as driving force for Al segregation dominates the phase formation regardless of the higher configurational entropy compared to TMN. Contrary, in the as deposited state of TMN, all metals are equally distributed and no segregation is observed. The onset of thermal decomposition for TMN films occurs after annealing at 1100 °C independent of the N content and the formation of V-rich clusters is observed. Thus, it is noteworthy that despite the similar values computed for the metal sublattice configurational entropy for TMN and TMAlN films significant differences in decomposition behavior and hence thermal stability are observed. Nanoindentation of as deposited TMN revealed the elastic modulus increasing with N-content from 329 ± 10 GPa (41 at.% N) to 420 ± 9 GPa (56 at.% N). Despite the presence of a secondary Al-rich phase at the grain boundaries, the elastic modulus of (TM,Al)N films increases from 354 ± 21 GPa (45at.% N) to 395 ± 8 GPa (56 at.% N).

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-2-MoA

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

Moderators: Dr. Damien Faurie, Université Sorbonne Paris Nord, France, **Dr. Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **H1-2-MoA-1 Multimodal and *in Situ* Electron Microscopy to Understand Local Deformation Mechanics*, Josh Kacher,*** Georgia Institute of Technology, USA **INVITED**

Understanding dislocation generation mechanisms and interactions with obstacles such as grain boundaries and other dislocations is central to understanding the mechanical behavior of metals and alloys, including thin films. This has motivated decades of research into the unit processes governing dislocation interactions by *in situ* transmission electron microscopy (TEM) mechanical testing, resulting in the establishment of basic rules that govern how these interactions occur. However, much of this research has been largely observation based with direct quantification of the interactions in terms of the local and global stress state limited. With the advent of high speed electron detectors and the continued improvement of quantitative *in situ* mechanical testing platforms, it is now possible to extract accurate information on the material stress state associated with dislocation generation and their interactions with surrounding microstructural features, spurring renewed interest into these fundamental dislocation interactions. These advances have necessitated the increased integration of data analytics based analysis of results as data acquisition rates now exceed what can be manually processed and understood. They also open new spaces for integration with computational simulations, beyond simple visual comparisons that are prone to human bias.

In this talk, I will discuss the development of advanced *in situ* TEM testing techniques, including local stress mapping and multimodal imaging via scanning nanobeam diffraction as well as quantification of the global sample stress state using MEMS-based nanomechanical testing platforms. I will discuss these advances in terms of two materials systems: understanding transgranular and intergranular dislocation mechanisms in ultrafine grained thin films and understanding the influence of the deformation-induced grain boundary state on dislocation/grain boundary interactions in coarse-grained thin films. For both of these systems, I will also discuss how irradiation induced defects affect local strain accommodation and active deformation mechanisms.

2:20pm **H1-2-MoA-3 Nanomechanical Characterization and Residual Stress Analysis in Thin ALD Coatings on 3D Printed Nano-Ceramics*, Marco Sebastiani,*** Università degli studi Roma Tre, Rome, Italy

Recently, Nano-Architected Mechanical Metamaterials (NAMM) have been proposed as a novel class of lightweight and sustainable materials, where a unique combination between high strength and low density is achieved. Such materials are usually produced by Two-Photon Lithography (TPL) Direct Laser Writing (DLW) method, which allows for fast 3D printing with nanoscale spatial resolution.

Unfortunately, the improvement of strength is usually not accompanied by a similar improvement of toughness and ductility, because of the effects of imperfections and flaws on structural reliability.

In this work, we explore the effects of this ALD coatings, by different materials, on the strength and toughness of NAMM.

In particular, we present a detailed study on the effect of the coatings' residual stress on the apparent fracture toughness, showing that a significant change in the crack propagation mechanisms for different residual stress states in the thin film.

The residual stress in the films with thickness below 50 nm is measured by an improved FIB-DIC method, which was specifically optimized to achieve sub-micrometer lateral and depth resolution.

This study demonstrated that fracture toughness in additively manufactured nano-ceramics is, in contrast to macroscopic ceramics, is a surface dominated characteristic, where surface residual stress states can have a paramount effect on reliability and durability

2:40pm **H1-2-MoA-4 *In-Situ* Monitoring of Stress Evolution in Hipims-Deposited Ti-Al-N Films: Effect of Substrate Bias and Temperature*, Pedro Renato Tavares Avila,*** *O. Zabeida, L. Varela Jiménez, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

The origin of stress during film deposition is a topic of interest in the surface engineering community and requires appropriate investigation tools to explain the different mechanisms acting on the evolution of stress, and how they relate to process conditions and materials characteristics. The use of a single stress analysis methodology relying on *ex-situ* results cannot provide a complete insight into stress formation and makes the distinction among the different stress contributors difficult.

In the present work, we used *in-situ* curvature stress probing combined with *ex-situ* techniques such as $Sin^2\psi$ in depositions of TiAlN films, to understand the mechanisms underlying stress evolution. Films were prepared at room temperature (RT) and 300 °C, and four bias strategies, namely two conditions with constant values of 0 V and -75 V, and two conditions with a superposition of layers with alternating high and no bias have been applied.

At RT, the bias increase changed the stress from slightly tensile to compressive, with a small rise in hardness (H), while at 300°C, the use of higher bias increased the compressive intrinsic stress by 3 GPa along with H from 14 to 30 GPa. The combined stress analysis revealed three mechanisms acting in the evolution of intrinsic stress: 1) grain boundary (GB) closing (tensile), dominating at conditions of low adatom mobility and low ion energy bombardment; 2) atom insertion in GB (compressive), dominating at high mobility and low energy of bombardment, and 3) defect generation (compressive), dominating at highly energetic bombardment and low temperature.

In-situ stress probing allowed direct calculation of thermal stress (TS) and determination of the Coefficient of Thermal Expansion (CTE) and Poisson's ratio (v) of TiAlN. CTE increased from 6.6 to 12.4 x 10^{-6} K^{-1} for higher bias, while v was found to be 0.22.

The use of alternating bias showed a dependence of the structure and stress on the conditions of previous layers. When growing dense on porous films, the porous surface is initially filled, stopping the propagation of the less dense structure, resulting in an intermediate morphology between the conditions of 0 V and -75 V. In contrast, when growing porous on dense film, less structural change is observed, and the film resembles a dense layer deposited at a single high bias condition. Films with alternating -75/0/-75 V bias sequence presented the same H as films deposited at a single -75 V condition, but with stress 20% lower. Based on the above-described results, we will discuss the overall strategies to tailor the film stress level with respect to the specific applications and coating durability.

3:00pm **H1-2-MoA-5 High Strength and Deformability in 3D Interface Cu/Nb Nanolaminates Under Multiple Loading Orientations*, Justin Y. Cheng,*** University of Minnesota, USA*; S. Xu,* University of Oklahoma, USA*; J. Baldwin,* Los Alamos National Laboratory, USA*; M. De Leo,* University of Minnesota, USA*; I. Beyerlein,* University of California Santa Barbara, USA*; N. Mara,* University of Minnesota, USA

Bimetallic nanolamellar composites have been studied extensively to probe the influence of interface structure on mechanical properties in nanocrystalline alloys. Previously, we have shown that Cu/Nb nanolaminates incorporating 3D interfaces (3D Cu/Nb) containing chemical, crystallographic, and structural nanoscale heterogeneities in all spatial dimensions have remarkable strength and deformability compared to 2D interface counterparts (2D Cu/Nb) under *in situ* micropillar compression normal to interface planes. This work also demonstrated the role of 3D interface thickness relative to layer thickness in optimizing mechanical behavior. However, a detailed investigation of post-deformation microstructures was not completed. In this work, present *in situ* micropillar compression results on 3D Cu/Nb at normal and 45° inclination to interfaces to show that 3D Cu/Nb behaves more isotropically than 2D Cu/Nb and that 3D interfacial shear strength exceeds that of 2D interfaces. *Post mortem* TEM characterization of deformed 3D Cu/Nb microstructures provides insight on the effect that 3D interfaces have on energetically favored slip pathways in different loading conditions. Experimental results reveal key microstructural features indicating delayed shear instability, providing insight on possible methods for increasing strength and deformability in nanostructured alloys by controlling interface structure.

3:20pm **H1-2-MoA-6 Multiaxial Stress-Strain Transfer Across Indenter-Sample Interface During *in Situ* Indentation of Nanocrystalline Thin Films**, ***Michael Meindlhumer**, J. Todt,* Montanuniversität Leoben, Leoben, Austria*; A. Medjahed,* ESRF, The European Synchrotron, Grenoble, France*; M. Burghammer,* ESRF, The European Synchrotron, France*; M. Zitek, R. Daniel,* Montanuniversität Leoben, Leoben, Austria*; D. Steinmüller-Nethl,* CarbonCompetence GmbH, Wattens, Austria*; J. Keckes,* Montanuniversität Leoben, Leoben, Austria

Nanoindentation is routinely used to determine local mechanical properties of materials such as hardness and Young's modulus. Especially for the testing of thin films, the versatile nanoindentation method is used also on materials approaching a stiffness and hardness regime close to diamond, typically the indenter tip's material. Yet, up to now, the stress-strain response in the indenter tip remained unknown during testing of materials of extremely high hardness.

Contrary, in recent years, *in situ* cross-sectional X-ray nanodiffraction coupled with an indenter system has given new insights into the elasto-plastic deformation of thin films during indentation with a resolution down of 500 nm. In this work, the *in situ* indentation setup developed for the ID13 beamline at the ESRF was used for the first time to determine experimentally the multi-axial stress distributions across both the indenter and the tested material with a resolution below ~100 nm.

For this purpose, a 75 µm wide diamond wedge indenter tip with an opening angle of 60 deg and a tip radius of 2 µm, was coated using chemical vapour deposition with a nanocrystalline diamond thin film of 4 µm thickness. In order to test the mechanical response of the indenter-sample system, wedge samples with a thickness of ~70 µm were prepared by means of consecutive mechanical polishing, femtosecond laser ablation and focused ion beam milling steps from nanocomposite AlCrSiN, a biomimetic CuZr-ZrN multilayer and a nanocrystalline diamond thin films.

Prior to the *in situ* cross-sectional X-ray nanodiffraction experiment, the coated indenter tip is aligned parallel to the incident beam and perpendicular to the smaple using small-angle X-ray scattering microscopy. The samples of highly different elasto-plastic behaviour are loaded to the same indentation depths, which depending on the stiffness yields highly different loads. Therefore, unique multiaxial stress-strain transfer across the indenter tip-sample interface was evaluated for each sample system depending on the Young's modulus, hardness and the ability for plastic deformation of the indented material.

This new kind of indentation experiment allows for tor the first time to directly assess the multi-axial stress distributions in the contact area for both tip and tested volume. The thereby gathered results give unprecedented insights into the deformation of both indenter and tested (thin film) material.

3:40pm **H1-2-MoA-7 Film Thickness Effect on Stress Sign Transition in ITO Thin Films**, ***Jianhui Liang**, J. Zhang, K. Rubin, W. Johnson,* KLA Corporation, USA*; R. Schelwald,* KLA Corporation, Germany*; O. Amster,* KLA Corporation, USA*; B. Cuénod, R. Juttin,* EPFL, Switzerland

Indium tin oxide (ITO) is widely used as a transparent conductive thin film in the production of semiconductor devices including solar cells, liquid crystal displays (LCDs), light emitting diodes (LEDs), and sensors. However, various stress configurations are usually generated during ITO film growth, which can impact device performance. Stress-induced wafer bow changes the device planarity, impacting subsequent production processes. Stress can dramatically change the physical properties of the ITO film, potentially causing a failure of the ITO device. Quantitatively determining the stress generated during the ITO film formation and investigating the origin of the stress from a micro perspective provide tools to improve the quality of the ITO films and devices.

In this work, we report on the results of a quantitative study on the stress of ITO films with various thicknesses. ITO films were deposited on glass wafers by standard radio frequency sputtering at room temperature. The film thickness was characterized using optical reflectometry and the stress was characterized by high-precision stylus profilometry. A stress-type transition from tensile to compressive was observed with increased ITO film thickness. The highest tensile stress was 1.9GPa for the 13.7nm thick ITO film, and the highest compressive stress of -0.4GPa was found in ITO films thicker than 300nm.

A separate investigation of the surface morphology of the ITO suggests that the film follows Volmer-Weber growth, and the tensile stress originates from the impingement and coalescence of the newly-deposited film islands [1]. With the continuous deposition of the film, the grain size becomes larger and the structure transitions to a nanorod shape - fewer new islands emerge, thus decreasing the tensile stress. Compressive stress dominates and stabilizes at -0.4GPa for thicker ITO films. The origin of the post-coalescence compressive stress is consistent with the incorporation of excess material in the grain boundaries. This study reveals the thickness effect on the ITO film stress evolution, which can be a reference for the ITO film stress monitor and modulation during production process control.

1. Brian W. Sheldon, K. H. A. Lau, and Ashok Rajamani, Intrinsic stress, island coalescence, and surface roughness during the growth of polycrystalline films, Journal of Applied Physics 90, 5097 (2001).

4:00pm **H1-2-MoA-8 Reactions of Metal-Tmhd Compounds in the Gas-Phase: Insights from Microreactor Studies Using Synchrotron Radiation**, ***Sebastian Grimm**,* Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Germany*; P. Hemberger,* Paul Scherrer Institute, Switzerland*; B. Atakan,* Institute for Combustion and Gas Dynamics and CENIDE, University of Duisburg-Essen, Germany

In CVD deposition processes gas-phase reactions are often the inital steps, but gaseous intermediates can lead to unwanted film morphology, unsatisfactory purity or a depletion of the precursor, and consequently a reduction in growth rate. Understanding the decomposition mechanisms, especially the sequence of bond dissociation steps, is important for improving and modelling such processes.

Consequently, the analysis of the inital stages of growth is important and requires analytical techniques with sufficiently low detection limits for elusive gas-phase species. Because of limitations in various experimental techniques, it was until recently not possible to detect most of the postulated intermediate species and their temperatue-depdenent kinetics often remained unknown.1

We have overcome some of these challenges and demonstrated for various metal-organic precursors that by using a microreactor coupled to a very mild ionization source, we can detect and characterize elusive species, especially metal-containing intermediates, with short liftetimes below 50 µs.2,3

Here, the vacuum pyrolysis of aluminium and zirconium 2,2,6,6-tetramethyl-3,5-heptanedionate, Al(tmhd)3 and Zr(tmhd)4, is investigated. In brief, the precursor is sublimed, subsequently transported by helium carrier gas and expanded through a pinhole into a resistively heated 1 mm inner diameter SiC-microreactor of 10 mm length. Species leaving the reactor are ionized by tuneable vacuum ultraviolet (VUV) synchrotron radiation, and characterized by imaging photoelectron photoion coincidence spectroscopy (i2PEPICO) and mass spectrometry at the Swiss Light Source.

In the experiments, hydrocarbons, oxygenated and metal-containing species were detected and characterized unambigously in the gas-phase at temperature from 450-950 K, which provides insights in the underlying decomposition mechanisms. Most importantly, we detected and characterized metal-bis(diketo)acetylacetonate-H, M(C11H19O2)(C11H18O2) as major inital decomposition product in the gas-phase at temperatures above 650 K, which subsequently forms M(C11H19O2)(C10H15O2) by a methyl loss. The temperature-dependent formation mechanisms of the assigned species will be discussed and compared to previous results on M(acac)x precursors.

References:

1. Y. Jiang, M. Liu, Y. Wang, H. Song, J. Gao and G. Meng, J. Phys. Chem. A, 2006, 110(50), 13479.

2. S. Grimm, S.-J. Baik, P. Hemberger, A. Bodi, A. M. Kempf, T. Kasper and B. Atakan, Phys. Chem. Chem. Phys., 20221, 23(28), 15059

3. S. Grimm, S.-J. Baik, P. Hemberger, T. Kasper, A.M. Kempf and B. Atakan, J. Mat. Research, 2022, 37(9), 1558.

4:20pm **H1-2-MoA-9 How to Simultaneously Determine Absolute Thickness, Chemistry, and Other Properties of Crystalline Layers Using XRD**, ***Thomas Degen**, M. Sadki, N. Norberg,* Malvern Panalytical, Netherlands*; N. Shin,* Deep Solution Inc., Korea (Democratic People's Republic of)

For the in-line absolute thickness analysis of FeZn layers on galvanized steel, we developed a Rietveld [1] based, full-pattern fitting method that fits a general layered structural model to a measured XRD Scan. The fitted model then delivers both the absolute layer thicknesses as well as the chemical composition of the layers and other key information like unit cell sizes, size/strain, and texture-related information for all phases of the model. The method is implemented in the Malvern Panalytical software package HighScore Plus [2] V5.1.

The layer thickness modeling is based on the variable and increasing absorption of X-rays in the layers with different chemistry and thickness. Basically, by integrating over all beam paths, we accumulate the reduction in the intensity of the total beam. Each layer adds a new absorption term with its own linear absorption coefficient. The method is theoretically correct, still, in practice, we need to know the packing factor and density of each layer. To solve that, we introduced an instrument-dependent (alignment, tube aging, etc) calibration factor for each layer. These calibration factors are determined from a dedicated data set, where many samples are characterized using multiple methods like SEM, wet analysis, etc.

The initial fit model comprises:

1. Initial/expected thickness values, for all the phases
2. Calibration factors for all phases determined based on analyzed knowns
3. Intensity calibration factor to counteract tube aging
4. Atomic phase models, typically taken from structural databases

Output after fit:

1. Absolute thickness for all as layer-marked phases
2. All other fit model parameters, like unit cells, size/strain information, texture index, and more, including estimated standard deviations
3. Quality of fit indicators, Chi-Square, R_{wp} etc.

[1] H.M. Rietveld, *A profile refinement method for nuclear and magnetic structures*, J. Appl. Cryst. (1969), **2**, 65-71.

[2] *T. Degen, M. Sadki, E. Bron, U. König & G. Nénert*, *The HighScore Suite*, *Powder Diffr*. Vol. **29**, (2014), 13-18.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-1-TuM

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

Moderator: Prof. Olivier Pierron, Georgia Institute of Technology, USA

8:40am **H2-1-TuM-3 Multifunctional Characterization of Nanomultilayers**, ***Andrea Maria Hodge***, University of Southern California, USA **INVITED**

Nano multilayers (NMs) films consist of alternating layers of materials with thicknesses on the order of nanometers and typically display many attractive properties which are attributed to the fact that, as the layer thicknesses decrease, the individual layer behavior changes and the interface volume increases. In this presentation, I will discuss how to synthesize and characterize systems of nanostructured multilayers, leveraging nanoscale features to enhance properties and function. To address this, samples with a wide range of composition and layer thicknesses were synthesized via DC/RF and reactive magnetron sputtering. Multilayer configurations of metal/metal, ceramic/metal and ceramic/ceramic systems were designed as model systems for either optical optimization or thermal studies. A comprehensive microstructural and mechanical evaluation of selected metal and ceramic multilayers are presented in order to elucidate on the role of their interfaces for properties and function.Several NMs configurations including SiO_2/TiO_2, AlN/SiO_2, AlN/Ag, Fe/W, and Mo/Au be discussed. The role of bilayer thickness and composition are evaluated and related to final microstructure and behavior.

9:20am **H2-1-TuM-5 Effects of Radiation Damage on the Critical Resolved Shear Stresses in Zirconium Alloys for Nuclear Applications**, ***James Gibson***, *C. Grovenor, A. Wilkinson,* Oxford University, UK

Nuclear power provides 10% of the world's electricity and is likely to expand as countries seek to provide low-carbon energy in the future. Of the current operating 442 commercial nuclear reactors, 96% are water cooled and thus have their uranium oxide fuel contained within a zirconium alloy cladding. This cladding limits fission product release into the primary water loop, as well as acting as the main transport medium for neutrons and heat.

Under irradiation, like most metals, these zirconium alloys exhibit strong hardening effects. Typically, the yield stress of Zr-alloys doubles during the early stage of irradiation while a dramatic loss of strain-to-failure is observed. Irradiation hardening is currently qualitatively described by <a> loops being barriers for dislocations during mechanical loading. This hardening is also supplemented by irradiation-induced precipitates, but their effect on irradiation hardening in Zr-alloys is currently unknown.

Like most of other hexagonal close packed (HCP) materials, zirconium deforms anisotropically via plastic slip on the basal, prismatic and pyramidal planes. As loop formation is also crystallographically influenced, a full picture of the radiation damage effects in zirconium must be gathered on a piece-by-piece basis, with the influence of damage levels, strain rate and temperature being determined on each slip system.

We present here the first steps towards painting this picture of radiation damage effects in zirconium. Nano-indentation testing using spherical and Berkovich tips correlated with indented grain orientations from EBSD has been used for initial rapid screening of irradiation hardening and strain softening effects, as required by complementary CP-FEM models. Subsequently identified "interesting" samples have been selected for more quantitative micro-mechanical investigation to determine critical resolved shear stresses on specific slip systems.

9:40am **H2-1-TuM-6 Link between Cracking Mechanisms of Trilayer Films on Flexible Substrates and Electro-Mechanical Reliability Under Biaxial Loading**, ***Shuhel Altaf Husain***, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; P. Kreiml,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; P. Renault,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; C. Mitterer,* Montanuniversität Leoben, Leoben, Austria*; M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; D. Faurie,* CNRS, France

Flexible electronics is a technological innovation that involves the use of flexible polymer substrates as the basis structure for the assembly of electronic circuits [1–3]. Currently, flexible electronic devices have new emerging applications, especially for foldable displays and even in biology for integration on skin [4,5]. Flexible polymeric substrates show the advantages of low cost, light weight, mechanical compliance and bendability [6]. Nonetheless, these systems suffer from limited durability, both mechanically and electrically due to the multi-cracking phenomenon during loading [7]. Many works have studied the mechanical behavior of multilayers in order to profit from interfaces and mechanical contrasts (ductile/brittle, stiffness) between each layer to improve the durability [8].

In this work, the propagation of cracks from a top layer in trilayer systems (Cr/Cu/Mo) on a polyimide substrate is studied experimentally by in situ synchrotron X-ray diffraction under equi-biaxial loading (see figure 1). The results show that depending on the thickness of the ductile Cu middle layer (100 nm or 500 nm), the propagation can be a direct vertical path through all layers or a more complex path. These effects are analyzed by monitoring the individual stresses of each layer along with electrical resistance and resulting crack patterns. Cracks starting from the upper Cr layer propagate instantaneously through the whole system for a 100 nm Cu layer, but are strongly deflected in a 500 nm Cu layer, thus delaying the global fracture of the system measured by the increase of electrical resistance. Mechanisms are proposed and allow to anticipate the electro-mechanical performances of stretchable systems constructed of several layers.

[1] S. Yuvaraja, A. Nawaz, Q. Liu, D. Dubal, S.G. Surya, K.N. Salama, P. Sonar, Chem. Soc. Rev. 49 (2020) 3423–3460.

[2] S. Kim, H.Y. Jeong, S.K. Kim, S.Y. Choi, K.J. Lee, Nano Lett. 11 (2011) 5438–5442.

[3] H. Li, Q. Zhan, Y. Liu, L. Liu, H. Yang, Z. Zuo, T. Shang, B. Wang, R.W. Li, ACS Nano 10 (2016) 4403–4409.

[4] D. Makarov, Nat. Mater. 20 (2021) 1589–1590.

[5] Y. Zhou, X. Zhao, J. Xu, Y. Fang, G. Chen, Y. Song, S. Li, J. Chen, Nat. Mater. 20 (2021).

[6] M.J. Cordill, O. Glushko, B. Putz, Front. Mater. 3 (2016) 1–11.

[7] S. Merabtine, F. Zighem, D. Faurie, A. Garcia-Sanchez, P. Lupo, A.O. Adeyeye, Nano Lett. 18 (2018) 3199–3202.

[8] M.J. Cordill, P. Kreiml, B. Putz, C. Mitterer, D. Thiaudière, C. Mocuta, P.-O. Renault, D. Faurie, Scr. Mater. 194 (2021) 113656.

10:00am **H2-1-TuM-7 Effect of Nanometric Stacking on the Magneto-Mechanical Properties of Thin Films on Flexible Substrate**, *H. Ben Mahmoud,* ***Damien Faurie***, CNRS-LSPM, France*; P. Renault,* CNRS-Pprime, France*; F. Zighem,* CNRS-LSPM, France

Flexible or stretchable magnetic systems are of growing interest in the scientific community, on the one hand for the fundamental aspects of magnetomechanical couplings in low dimensional objects and on the other hand for the numerous applications they can generate (magnetoelectric deformable devices for media, textiles or the human body, etc). Thus, it is important for the community to acquire numerical and experimental means to better understand the evolution of the physical properties (magnetic and electrical) of these flexible systems when they are subjected to deformations [1-2].

Regarding the experimental means, it is essential to be able to evaluate the evolution of the magnetization curves at strain levels comparable to those of a real use (a few ten of percent). Indeed, these strains applied at the macroscopic scale can have repercussions at the microscopic level on the organization of the material (in this case magnetic) and affect the functional properties. In the case of nanometer-thick films on deformable substrates (such as polymers), this can in most cases be characterized by cracks that multiply during the mechanical test. This multi-cracking phenomenon can be complex and involves, by the creation of new surfaces, a strong heterogeneity of stress (and strain) at the scale of the inter-crack fragments, but with a rather weak evolution of the stress averaged on the whole thin film.

However, the links between these mechanical phenomena and magnetic properties have been little explored. Currently, the most ambitious in situ developments have been either at small strains (piezoactuation or bending, up to 1-2%), or at large strains for the properties of giant magnetoresistance. Actually, there is a lack of measurements of magnetization curves at large strains.

In this presentation, we present in situ magneto-mechanical experiments carried on 50 nm Co and NiFe thin films deposited on a polyimide substrate in order to highlight links between damaging of these nanometric films and their magnetic properties. Moreover we will show that the addition of

weak layer (W) in the systems affects on the one hand the pattern of cracks and consequently the magnetomechanical properties (evolution of coercive and saturation field, magnetic anisotropy and remanent magnetization).

[1] F. Zighem & D. Faurie, « A review on nanostructured thin films on flexible substrates: links between strains and magnetic properties », Journal of Physics: Condensed Matter 33, 233002 (2021)

[2] D. Faurie, A. O. Adeyeye, F. Zighem, « Prospects towards stretchable and flexible magnonic systems», Journal of Applied Physics 130, 150901 (2021)

10:20am **H2-1-TuM-8 Influence of the Aspect Ratio of the Micro-Cantilever on the Determined Young's Modulus Using the Euler-Bernoulli Equation**, *F. Konstantiniuk,* Montanuniversität Leoben, Austria*; M. Krobath, W. Ecker,* Materials Center Leoben Forschungs GmbH, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; **Nina Schalk,*** Montanuniversität Leoben, Austria*; M. Tkadletz,* Montanuniversitat Leoben, Austria

Micro-cantilever bending experiments can be used to determine fundamental material properties, such as fracture stress and fracture toughness. Furthermore, the Young's modulus can be calculated from the slope of the load-displacement curve using the classical Euler-Bernoulli equation. However, in literature it can be frequently found that applying this technique, the Young's modulus is significantly underestimated, especially when using micro-cantilevers with aspect ratios (bending length/width) < 6. In order to investigate the influence of the aspect ratio on the determination of the Young's modulus, SiO_2 and single crystalline α-Al_2O_3 micro-cantilevers with aspect ratios ranging from ~3.5 to 6.5 were fabricated using focused ion beam milling and subsequently tested with a nanoindenter system. In addition to the quasi-static tests, dynamic micro-cantilever bending tests were performed by using an excitation frequency on top of a quasi-static loading and the results of both techniques were compared to each other. Finally, finite element analysis was used to simulate the static-micro-cantilever bending experiments and investigate the influence of shear deformation, flexing of the support and the geometry of the micro-cantilever on the load-displacement curves.

10:40am **H2-1-TuM-9 Engineering Metal-MAX Phase Multilayered Nanolaminates for Tunable Strength and Toughness**, ***Skye Supakul,*** *S. Pathak,* Iowa State University, USA*; K. Yaddanapudi,* University of California at Davis, USA

Metal-Ceramic nanocomposites have long been of interest to combine the high strength of ceramics with the toughness in metals. To achieve this combination, metal-ceramic multilayers have relied on significantly reduced bilayer thickness (few nm's) and crystalline components, leveraging improved plastic co-deformation for the improved mechanical properties. Here, we discuss the process of designing metal-MAX phase multilayered nanolaminates (MMN) which leverages the unique combination of metallic, covalent, and ionic bonding in MAX phases to enhance the threshold thickness for improved plastic co-deformation and enhanced toughness. Furthermore, with the atomically layered structure of MAX phase coupled with the metal and MAX phase layers, we engineer a hierarchical layered microstructure – where the metal and MAX phase layers are in direct competition with the internal interfaces within the MAX layers and atomically layered structure – taking advantage of the mechanisms of confined layer slip, Hall-Petch strengthening, and the competing deformation mechanisms to improve the strength of the system. By adjusting the combination of individual layer thicknesses, we can tune the mechanical properties of the metal-MAX phase multilayered nanolaminate system.

We begin by discussing the challenges associated with synthesizing MAX phase, followed by preliminary depositions on a Nb and Ti2AlC metal-MAX phase system which prefaced the overarching challenge of diffusion in the metal-MAX phase multilayered nanolaminates. To investigate and understand the diffusion, the next set of depositions focus on Ti and Ti2AlC metal-MAX phase multilayered nanolaminates to simplify the material system, as well as improve the plastic co-deformation between the metal and MAX phase systems. We utilize conventional direct current (DC) magnetron sputtering physical vapor deposition as well as a unique twin chamber deposition system, capable of automated atomic layer deposition and direct current magnetron sputtering physical vapor deposition without breaking chamber vacuum. We implement high temperature deposition, mixed low and high temperature deposition, as well as combined ALD-PVD depositions with amorphous Al2O3 layers to investigate the pathways to fabricate continuous metal-MAX phase multilayered nanolaminates. The multilayered depositions are characterized with XRD and TEM, and their mechanical properties are evaluated using nanoindentation and micropillar compression.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Town & Country A - Session H3-1-TuA

Characterization of Coatings and Small Volumes in Extreme and Cyclic Conditions I

Moderators: Prof. Dr. Peter Hosemann, University of California, Berkeley, USA, **Prof. Dr. Barbara Putz**, Montanuniversität Leoben, Austria

1:40pm **H3-1-TuA-1 Local Deformation Mechanisms under Ambient and Non-Ambient Conditions Tested via Advanced Nanoindentation***, Verena Maier-Kiener,* Montanuniversität Leoben, Leoben, Austria **INVITED**

Nanoindentation over the recent years established itself as a versatile tool for probing local mechanical properties beyond hardness and modulus. By adapting and improving standard nanoindentation testing methods, reliable protocols capable of probing thermally activated deformation processes can be accomplished. Abrupt strain-rate changes within individual indentations allow determining the strain-rate dependency of hardness at various indentation depths. For probing lower strain-rates and excluding thermal drift influences, long-term creep experiments can be performed by using the dynamic contact stiffness for determining the true contact area. From both procedures hardness and strain-rate, and consequently quantities such as strain-rate sensitivity, activation volume and activation energy can be reliably deducted within individual indentation tests, permitting information on the locally operating thermally activated deformation mechanism.

This presentation will first discuss various testing protocols including possible challenges and improvements, with particular emphasis towards testing at higher temperatures and under hydrogen atmosphere. Second, it will showcase different examples highlighting the direct influence exerted by microstructure, phase transformations and environmental conditions on the underlying deformation behavior in pure and highly alloyed material systems.

2:20pm **H3-1-TuA-3 Extracting High-Temperature Stress-Strain Curves and Assessing Transformation Pressures: The Spherical Indentation of Silicon***, Gerald Schaffar,* Montanuniversität Leoben, Austria*; D. Tscharnuter,* KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Austria*; V. Maier-Kiener,* Montanuniversität Leoben, Austria

In the past nanoindentation with spherical tips has already been extensively employed to characterize the mechanical properties of silicon. This work aims to combine advances in spherical indentation testing [1], [2] with the idea of using continuous stiffness measurement (CSM) during the unloading of silicon [3]. Combining both advanced methods allows directly the calculation of the compression flow behavior, including the acquirement of the pressure-induced phase transformations in silicon. Therefore, the use of CSM during the indentation unloading process permits the measurement of the phase transformations during unloading. These transformations can, at room temperature, be seen as “elbows”, “pop-ins” or mixes thereof in the load-displacement curve [4]. In the current work, this combined approach is applied to both room-temperature and high-temperature indentations up to 950°C. Subsequently, confocal Raman spectroscopy is used to identify the phase transformations occurring at lower testing temperatures. Further, confocal laser scanning microscopy is used to check the remaining indentations for irregularities, such as pronounced pile-up behavior. Indentation tests using self-similar Berkovich tips, performed beforehand across this entire temperature range, revealed that the plastic deformation behavior is controlled by phase transformations up to ~ 400 °C. At even higher temperatures dislocation plasticity dominates the plastic deformation underneath the indenter. This transition between phase transformations and dislocations as the main mechanism of plasticity when indenting silicon is in good agreement with previous observations from high-temperature indentation testing [5].

[1]S. Pathak and S. R. Kalidindi, *Mater. Sci. Eng. R Reports*, vol. 91, pp. 1–36, 2015.

[2]A. Leitner, V. Maier-Kiener, and D. Kiener, *Mater. Des.*, vol. 146, pp. 69–80, 2018.

[3]G. J. K. Schaffar, J. Kappacher, D. Tscharnuter, and V. Maier-Kiener, *Jom*, vol. 74, no. 6, pp. 2220–2230, Jun. 2022.

[4]V. Domnich, Y. Gogotsi, and S. Dub, *Appl. Phys. Lett.*, vol. 76, no. 16, pp. 2214–2216, 2000.

[5]V. Domnich, Y. Aratyn, W. M. Kriven, and Y. Gogotsi, *Rev. Adv. Mater. Sci.*, vol. 17, no. 1–2, pp. 33–41, 2008.

2:40pm **H3-1-TuA-4 Micro-Impact Tests of Novel Thermal Barrier Coating Systems and >1000C Nanoindentation on Ni-Base Superalloy***, Ben Beake,* Micro Materials Ltd, UK*; C. Chalk,* Cranfield University, UK*; S. Goodes, A. Harris,* Micro Materials Ltd, UK*; L. Isern, J. Nicholls,* Cranfield University, UK

Thermal barrier coatings (TBCs) with improved erosion resistance are needed to increase the efficiency of gas turbines in aero-engines by enabling them to operate at higher temperatures. Rare earth zirconate (REZ) TBCs have potential as low-conductivity TBCs permitting higher temperature operation by more effectively thermally shielding the Ni-base superalloy turbine blade material. Although they have much lower thermal conductivity than current yttria-stabilised zirconia (YSZ) TBCs they have lower toughness making them susceptible to erosion. Nanomechanical tests are used to streamline the development of advanced multilayered TBC systems that can combine optimum thermal and mechanical properties.

The micro-scale impact test capability in the NanoTest has been modified to closely simulate real erosion conditions. The resistance of single-layered YSZ coatings and bilayer TBC coatings comprising a top layer of the REZ $Gd_2Zr_2O_7$ and YSZ sub-layer of similar total thickness to repetitive high strain rate contacts has been studied in detail. YSZ showed almost identical impact behaviour in 75 and 90 degree impact tests but in contrast the REZ coating was more resistant in angled impact than normal impact. The performance of the coatings in the novel micro-impact tests correlated with that in conventional erosion tests.

The nanomechanical behaviour of the Ni-base superalloy substrate (Nimonic 75) has been assessed at temperatures above 1000 °C for the first time. The critical role of the nanoindentation load-time profile to mitigate the enhanced creep at these temperatures and obtain more accurate measurements of hardness and elastic modulus is investigated.

Funding support from Innovate UK is acknowledged ("High temperature tools for designing sustainable erosion resistant coatings" Project#10020751).

3:00pm **H3-1-TuA-5 Influence of Si on the Mechanical Properties and High-temperature Fracture Toughness of Cr-Si-$B_{2\pm z}$ Coatings***, L. Zauner, Rainer Hahn,* CDL-SEC at TU Wien, Austria*; O. Hunold, J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvari, P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* CDL-SEC at TU Wien, Austria

Si-alloyed diboride systems show outstanding oxidation resistance compared to their unalloyed binary or ternary counterparts. This allows operating temperatures up to 1200 °C, further extending the possible applications of such systems, such as protective coatings in turbines. In addition to the necessary oxidation resistance, adequate mechanical protection is also of great interest. This work investigates the impact of Si segregates on the structural and mechanical properties of Cr-Si-$B_{2\pm z}$ thin films from ambient to elevated temperatures. Overstoichiometric, AlB_2-structured Cr-Si-$B_{2\pm z}$ thin films with Si-content up to 15 at.% were synthesized on Ti-6Al-4V substrate by magnetron sputtering using a substrate bias of -120 V.

Enhanced surface diffusion of film constituents promotes the growth of mechanically superior, (001)-oriented coatings with a hardness of H~30 GPa up to a Si content of 3 at.%. Higher Si concentrations result in a significant hardness loss to H~20 GPa related to a bias-independent solubility limit in the CrB_2 structure, causing the formation of mechanically weak Si grain-boundary segregations. The as-deposited hardness of all Cr-Si-$B_{2\pm z}$ compositions is maintained after annealing up to 800 °C despite the initiation of material recovery. In addition, minimum interdiffusion and excellent adhesion are observed on the Ti-6Al-4V-alloy.

In line with the room temperature hardness, an increasing Si content is accompanied by a decreasing fracture toughness, reducing from K_{IC}~2.9 ($Cr_{0.28}B_{0.72}$) to ~1.7 MPa√m ($Cr_{0.24}Si_{0.10}B_{0.66}$), respectively. High-temperature cantilever bending up to 800 °C revealed a brittle-to-ductile-like transition for $Cr_{0.28}B_{0.72}$, resulting in a fracture toughness increase to K_{IC}~3.3 MPa√m. Similar behavior is observed for Si-alloyed coatings up to 400 °C, whereas beyond this temperature, Si-segregates enable high-temperature plasticity and, thus, a significantly increased damage tolerance.

4:00pm **H3-1-TuA-8 Nanoindentation Measurements at Combined High Sustained Strain Rates and Elevated Temperatures***, **Benoit Merle**,* University of Kassel, Germany **INVITED**

Constant strain rate nanoindentation is a versatile method well suited for measuring the microscopic mechanical properties of materials within a wide range of temperatures. Recent developments have focused on increasing the permissible strain rates beside the typical ~0.1/s threshold present in most commercial systems. The current limitation primarily derives from the plasticity error of the continuous stiffness measurements (CSM) and has recently been overcome with a custom evaluation method avoiding the need for a measurement of the contact stiffness. With this improvement, the experimental upper strain rate limit is only limited by the hardware time constants of the system.

Based on a study of an intermetallic alloy, the presentation will demonstrate that nanoindentation is a potent technique for systematic investigations of changes in mechanical properties as a function of the testing temperature and deformation rate.

Refs:

1. B. Merle, V. Maier-Kiener, G. M. Pharr. Influence of modulus-to-hardness ratio and harmonic parameters on continuous stiffness measurement during nanoindentation (2017) Acta Materialia, 134, pp.167-176.
2. B. Merle, W.H. Higgins, G.M. Pharr. Critical issues in conducting constant strain rate nanoindentation tests at higher strain rates (2019) Journal of Materials Research, 34(20), pp. 3495-3503.
3. B. Merle, W.H. Higgins, G.M. Pharr. Extending the range of constant strain rate nanoindentation testing (2020) Journal of Materials Research, 35(4), pp. 343-352.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-2-WeM

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

Moderator: Dr. James Gibson, University of Oxford, UK

8:40am **H2-2-WeM-3 The Nature of Defects and their Dynamics Characterized using Scanning Electron Microscopy Approaches***, **Dan S. Gianola,*** University of California Santa Barbara, USA **INVITED**

The past several years has witnessed a surging popularity of two techniques for defect characterization in crystalline materials: (*i*) scanning transmission electron microscopy (STEM) using diffraction contrast imaging, and (*ii*) electron back-scattered diffraction (EBSD) mapping.Here, we link these capabilities by employing a field emission SEM equipped with a transmission detector for defect characterization – termed transmission SEM (TSEM).Imaging modes that are similar to conventional CTEM bright field (BF) and dark field (DF) and STEM are explored, and some of the differences due to the varying accelerating voltages highlighted.We further demonstrate how the richness of information encoded in EBSD patterns is amplified by a new generation of direct electron detectors that enable high speed mapping and acquisition of high-fidelity patterns that can be used for statistically-meaningful defect analyses.Using this new system, we quantify the sharpness of EBSD patterns obtained from several additively manufactured metallic alloys, which reveals sub-grain dislocation structures with high fidelity.Our results demonstrate that the dislocation cell walls produced during fast solidification do not always possess measurable misorientations, and thus do not reflect a geometrically necessary defect organization.Finally, we will show how these techniques can be employed for *in situ* tensile experiments to study the nature of dislocations dynamics in several structural alloys.

9:20am **H2-2-WeM-5 Measurement of Hardness and Elastic Modulus by Depth Sensing Indentation: Improvements to the Technique Based on Continuous Stiffness Measurement***, **Warren Oliver,*** KLA-Tencor, USA*; P. Sudharshan,* ARCI, India*; G. Pharr,* Texas A&M University, USA

The method to measure hardness and elastic modulus of small volumes of material by instrumented indentation presented in the seminal works of Oliver and Pharr in 1992 and 2004, has revolutionized the field of small scale nanomechanical testing. Several recent advances in measurement electronics have enabled testing over a wider range of test conditions (speeds) using methodologies that were developed earlier, which requires a critical assessment. In the backdrop of the latest developments in instrumentation and test methodologies, an overview of the various factors affecting the precision and accuracy of the nanoindentation test results at different test conditions with specific focus on Continuous Stiffness Measurement (CSM) technique will be presented. The CSM technique has also been used to explore the time dependence of material properties.In particular, the stiffness of the contact together with the modulus of the material being characterized gives a direct way of calculating the contact area at any instant that is relatively insensitive to thermally driven displacement drift rates.One of the parameters used to calculate the hardness being measured in such experiments is the load being exerted on the sample by the indenter.The CSM technique requires that the load on the sample be modulated to some degree at a specific frequency.The question arises what value of the load should be used to calculate the hardness when the load is being modulated.Results indicating how the load could be chosen will be presented.

9:40am **H2-2-WeM-6 Ultrasonically Induced Nanofatigue During Nanoindentation***, **Antanas Daugela,*** Nanometronix LLC, USA*; J. Daugela,* Johns Hopkins University, USA

In the era of fast product development thin film developers are looking for quick and efficient methods of characterization.This is especialy true in a semi-conductor industry where advanced multilayered chip/MEMS develpment process needs advanced characterization techniques. Nanoindentation based multi-cycle loading is offering insides into the real-time contact fracture dynamics [1]. A nanofatigue phenomenon can be observed on thin sub-micrometer films by monitoring the resulting multi-cycle nanoindentation loading-unloading curves where post-test imaging helps in identifying materials' behavior [2, 3].In addition, clasical Mason-Coffin and racheting fatigue models derived for the nanoscale contact can be utilized in the predictions and correlate reasonably well with nanofatigue cycles obtained experimentally.

A newly developed ultrasonic nanoindentation tip operates at hundreds of kHz, therefore, inducing milions of load cycles within seconds.The resulting nanofatigue induces different thin film fracture modes such as radial, sink-in and produce unique acoustic signatures.The ultrasonic nanoindentation tip monitors associated waveforms, which can provide additional inside into nanofatigue process dynamics via advanced acoustic waveform analysis.Following our previous study [4], acoustic waveforms were processed using a combination of wavelet based signal decomposition and Deep Learning. The proposed Deep Learning technique yields a reliable classification of acoustic signatures obtained during fracturing ofsub-micrometer thick coatings.

References:

1. B. D. Beake et al, *Materials Science & Engineering A*, 7**80** 139159 (2020)

2. H. Kutomi et al, *Tribology International*, **36**, p.255-259 (2003)

3. Y. Matsuda et al, Wear, **259**, p. 1497–1501 (2005)

4. A Daugela et al, *Materials Science & Engineering A*, **800** 140273 (2021)

11:00am **H2-2-WeM-10 Comparison of Electrical and Image-Based Sensing for Quantitative in Situ TEM Nanomechanical Testing***, S. Stangebye, L. Daza, X. Liu, J. Kacher, **Olivier Pierron,*** Georgia Tech, USA

This presentation describes a microelectromechanical system (MEMS) based, quantitative in situ TEM nanomechanical testing technique to measure the mechanical properties of thin film specimens and characterize their plastic flow kinetics, while observing their deformation mechanisms. The MEMS is comprised of a thermal actuator and load sensor. Two types of sensing techniques, electrical (capacitive) and image-based, are compared in term of their accuracy and precision. The advantages and drawback of each sensing technique are also discussed. The mechanical properties of Al and Au thin films, with a range of thickness (from 25 to 200 nm) and average grain size (from ~50 to 350 nm), and their deformation mechanisms are characterized, and the associated size effects are investigated.

11:20am **H2-2-WeM-11 Understanding the Interface Strain Induced hcp-to-bcc Phase Transformation in Nanolaminate Mg***, K. Jacob,* Iowa State University, USA*; K. Yaddanapudi,* University of California, Davis, USA*; M. Jain,* University of Nevada, Sandia National Laboratory, USA*; J. Michler,* EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; **Sid Pathak,*** Iowa State University, USA

In this work, we strive to answer fundamental questions related to the hcp-to-bcc pseudomorphic phase transformation of Mg in Nb/Mg nanolaminates. Mg and its alloys attract immense attention for being one of the most promising lightweight structural materials, and are of growing interest to automobile and aircraft industries due to their low density, being 35% lighter than aluminum and 78% lighter than steel . The constituent Mg phase is plastically anisotropic and not ductile due to its inherent hexagonal closed pack (hcp) structure. However, by encouraging a pseudomorphic phase transformation of Mg within the Mg/Nb multilayers, the hcp structure of Mg was transformed to a less anisotropic and more ductile body center cubic (bcc) structure at ambient pressures. The critical layer thickness for stabilizing the pseudomorphic bcc Mg phase (above which the metal reverts back to its traditional hcp structure under ambient conditions) was found to be around 7-8 nm from experimental observations. However this value is significantly larger than the critical layer thickness of 4.2 nm for Mg predicted using an analytical model with density functional theory (DFT) information, or 5 nm from direct thermodynamic calculations. This large discrepancy between experimental and theoretical values clearly indicates that a complete understanding of the underlying mechanisms involved during the phase transformations is still lacking.

This work aims to investigate the following questions: (a) What are the operative mechanisms that control the critical layer thickness of pseudomorphic bcc Mg in a Nb/Mg nanolaminate? In particular, can the discrepancy mentioned above between the experimental and theory/modeling results be explained by considering the effects of the bottom (substrate) vs. top Nb layers separately in a Nb/Mg multilayered structure? (b) What would be the effects of the Nb volume fraction on the resultant structure?

We utilize a novel deposition strategy where bi-layers of Nb/Mg will be terminated/protected by an amorphous coating before further deposition in order to isolate the effects of the bottom (substrate) vs. top Nb layers on the pseudomorphic phase transformation of Mg. We also use micro pillar compression tests to investigate the effects of layer thickness vs. crystal structure (Mg bcc vs. hcp) on these fine-tuned microstructures.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Town & Country A - Session H3-2-WeM

Characterization of Coatings and Small Volumes in Extreme and Cyclic Conditions II

Moderators: Prof. Dr. Peter Hosemann, University of California, Berkeley, USA, **Prof. Dr. Barbara Putz**, Montanuniversität Leoben, Austria

8:00am **H3-2-WeM-1 Characterizing Interfacial Straining Mechanisms Using High Temperature *in situ* Tem*, Shen Dillon,*** University of California Irvine, USA **INVITED**

Thin film stress relaxation can depend strongly on interfacial strain mechanisms, particularly at grain boundaries within the film and at the film-substrate interface. Diffusion dependent strain, i.e that requiring atomic fluxes, is typically assumed to be diffusion rate limited, and in some cases, rate limited by the emission and absorption of point defects at sources and sinks. The process could also be rate limited by the nucleation of interfacial line defects that mediate climb during the atomic flux. This latter process has largely been ignored within the literature, since it is assumed to require large stresses. The nucleation rate limited kinetic mechanism can stabilize large stresses and exhibits discontinuous stress relaxation. The other mechanisms, diffusion and point defect emission/absorption limited, relax stress continuously. Appropriately identifying the correct mechanism is, therefore, of significant importance for understanding stress evolution in thin films. The work presented in this talk demonstrates the use of high temperature *in situ* transmission electron microscopy (TEM) based mechanical testing applied to characterizing the strain mechanisms active at bicrystal grain and phase boundaries. These experiments indicate that interfacial strain kinetics are nucleation rate limited up to large stresses, and that creep at low stresses in polycrystals results from stress concentration effects. Models for bulk and local interfacial creep are discussed. The strain behavior at and around metal-oxide interfaces is discussed as an example relevant to many thin film applications. These systems are interesting because metal-oxide tensile strain is extremely unfavorably, while interfacial sliding is facile. Such factors must be accounted for to understand microstructural changes occurring during interfacial stress relaxation.

8:40am **H3-2-WeM-3 Quantitative in Situ TEM Observations of a Grain-Boundary-Migration-Assisted, Radiation-Damage Healing Mechanism in Ultrafine Grained Au Thin Films*, Lina Daza,*** *S. Stangebye, K. Ding, X. Liu, T. Zhu, J. Kacher, O. Pierron,* Georgia Tech, USA

The plastic deformation mechanisms of ultrafine grained gold thin films (average grain size of 150 nm) irradiated with 2.8 MeV Au+ ions at three different levels (0.1, 1 and 5 dpa) have been studied using quantitative *in-situ* transmission electron microscopy (TEM) nanomechanical testing. This technique allows for the simultaneous observation and comparison of the active deformation mechanisms, measurement of mechanical properties and true activation volume.Some of the observed deformation mechanisms include dislocation nucleation at grain boundaries (GB), dislocation pinning/de-pinning at irradiation induced defects, and stress-induced GB migration. During the early stages of deformation, dislocation nucleation and GB migration occur simultaneously. However, the dense populations of irradiation-induced defects prevent transgranular dislocation motion. As the deformation levels increase, GB migration leads to defect-free zones which then provide avenues for unimpeded dislocation glide. The true activation volume increases from ~$10b^3$ in unirradiated specimens, to ~$22b^3$ in irradiated specimens at 1dpa, for flow stresses ranging from 400 to 550 MPa.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Golden State Ballroom - Session HP-ThP

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

HP-ThP-1 Femtosecond Laser Ablation (FESLA) XPS – A Novel XPS Depth Profiling Technique for Thin Films, Coatings and Multi-Layered Structures, ***Mark Baker**, S. Bacon, S. Sweeney,* University of Surrey, UK*; A. Bushell, T. Nunney, R. White,* ThermoFisher Scientific, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers through the use of argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. A prototype XPS depth profiling instrument has been constructed which employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (10s - 100s microns) and is much faster than sputter XPS sputter depth profiling. FESLA XPS results will be shown for selected bulk, thin films and oxidised surfaces and the outlook for this new technique discussed.

HP-ThP-3 *in Situ* and Real-Time Measurements in Metallic Thin Film Research and Applications: The MISSTIC Experimental Setup, ***Ramiro Zapata**,* Laboratoire Surface du Verre et Interfaces UMR 125 / Institut des Nanosciences de Paris UMR 7588, France*; R. Lazzari,* Institut des Nanosciences de Paris UMR 7588, France*; H. Montigaud, M. Balestrieri, I. Gozhyk,* Laboratoire Surface du Verre et Interfaces UMR 125, France

Magnetron sputtering deposition is one of the main PVD deposition techniques, for a wide range of materials ranging from metals to semiconductors and insulators. Current research efforts in thin film growth and characterization are often hindered by extraneous interferences and impurities, stemming from film surface contact with the atmosphere between the film elaboration and *ex situ* characterization steps.

In order to overcome these challenges, the **MISSTIC** (Multilayers and Interfaces Sputtered-deposition on STructured substrates and In-situ Characterization) vacuum experimental setup was developed. This setup (Fig-A) is composed of a deposition chamber and an analysis chamber, connected via a load-lock mechanism through which samples can be transferred under vacuum conditions. This internal sample transfer between chambers avoids contact with the atmosphere, thereby avoiding interfering phenomena such as film ageing and adsorbed species from air. As such, by eliminating the need for capping (protective) layers on top of the deposited metallic films, *in situ* X-Ray Photoemission Spectroscopy (XPS) in the analysis chamber can characterize the deposited film surface chemistry, without any depth profiling necessary. Sample annealing under vacuum, with an electron beam setup located in the same chamber, can even be used for studying elemental diffusion in thin film stacks. Finally, surface characterizationusing *in situ* Low Energy Electron Diffraction (LEED) is used for the study of crystallized surfaces, and for studying thin film epitaxial growth – such as for the case of Ag film sputtering on ZnO underlayers.

Real-time characterization techniques are another kind of measurement, present in the **MISSTIC** deposition chamber. These measurements are carried out during film deposition, and allow for the detection of different stages of film growth: they include Surface Differential Reflectance Spectroscopy (SDRS), film electrical resistance, and a new method for film mechanical stress measurements (PReMC, Refs[1,2]. For the study of Ag film growth on silica substrates during magnetron sputtering deposition, real-time measurements allow for the detection of the nucleation, growth, coalescence, percolation, and continuous film formation threshold thicknesses. Combinations of these techniques are used for studying the effects of different parameters of the sputtering deposition process, on the Ag thin film growth mechanism.

Ref1: Sergey Grachev et al 2022 Nanotechnology 33 185701

Ref2: Quentin Hérault et al. Acta Materialia 221 (2021) 117385

HP-ThP-4 Ultrasonic Contact Impedance Measurements at Nanometer Scale, ***Jurgis Daugela**,* Johns Hopkins University, USA*; A. Daugela,* Nanometronix LLC, USA

Active ultrasonic microhardness aka Ultrasonic Contact Impedance (UCI) testers have been around since 1970s.While UCI microhardness testers relied on microscale contact elastic deformation, this technique, *at the nanoscale*, has a new application in the area of multi-cycling nanofatigue monitoring [1, 2]. A theoretical contact mechanical impedance model was explored during design stage in order to match impedances of ultrasonic tip/resonator and contacting surface.The contacting surface impedance consists of the contact compliance term since reactive terms are insignificant at the nano scale. The resulting operational mechanical impedance functions were employed in design optimization of the ultrasonic tip.

With the newly developed instrumentation such as the ultrasonic nanoindentation tip integrated into a nanoindentor that localizes nanonometer range displacements, millions of precisely placed loading cycles can be delivered within seconds.Thin film interface breakthrough induced nanoindentation displacement excursion and simultaneously monitored ultrasonic signals indicate fatigue failure and provide the number of failure cycles.

An experimental ultrasonic nanoindentation tip operated at 272kHz is delivering approximately 4.5 million cycles till 80nm thick SiC film interface fracture.It had to be pointed out that ultrasonically induced nanofatigue cycles reasonably agree with Ratcheting and Mason-Coffin fatigue models.

References:

1. H. Kutomi et al, *Tribology International*, **36**, p.255-259 (2003)

2. Y. Matsuda et al, Wear, **259**, p. 1497–1501 (2005)

HP-ThP-5 A Direct Correlation between Structural and Morphological Defects of Tio_2 Thin Films on Fto Substrates and Photovoltaic Performance of Planar Perovskite Solar Cells, ***Mario Alejandro Millan Franco**,* IER-UNAM, Mexico

Titanium oxide (TiO2) is often deposited on conductive fluorine doped tin oxide (FTO), followed by a thermal annealing to obtain anatase phase for planar perovskite solar cells (p-PSCs). Although high annealing temperature is desirable to increase the crystallinity of TiO2, morphological changes are induced in both TiO2 and FTO. In this work, structural and morphological changes in thermally annealed (400 - 550°C) FTO, TiO2 and TiO2/FTO system are identified and semi-quantified by X-ray diffraction, scanning electron and atomic force microscopy. 400 °C annealed TiO2 show the lowest crystallinity and the highest dislocation density, resulting in the lowest efficient p-PSCs. Conversely, 550 °C annealed TiO2 exhibits the highest crystallinity and lowest dislocation density, but the FTO film undergo an increase of surface roughness by more than 25%. Additionally, the 550 °C annealed TiO2 coatings on FTO show the highest concentration of surface ruptures and the largest exposed FTO substrate area. Such morphological defect concentration originates a larger direct contact of FTO and the perovskite film. TiO2 thin films annealed at 450 or 500 °C show a compromising between the crystalline structure and defect density, giving a better photovoltaic performance of p-PSCs prepared under ambient conditions with a conversion efficiency of 16.3%.

HP-ThP-6 In-Situ Stress Evolution in Sputtered Metal Alloy Films, ***Vania Jiao**, C. Appleget, C. Panetta, K. Folgner, J. Barrie,* The Aerospace Corporation, USA

Space-based optical glass sensors are sensitive to the harsh radiation of Earth's Van Allen belts, and one approach to protect these sensors is by using thick optical coatings. However, thick films of radiation absorbing materials, such as silver or gold, often exhibit increased surface roughness compared to the thin films used for high reflectivity mirrors. This surface roughness degrades the desired reflectivity and increases the optical scatter as film thickness increases. Alloying Ag with Al is an approach towards improving the surface roughness of these thick optical films, but alloying can lead to high residual stresses. These residual stresses are compositionally dependent and can be detrimental to surface figure and film adhesion. In this work, in-situ stress of sputtered AgAl alloy thick optical films (≈1 µm thickness) was monitored to better understand stress evolution. Films of varying composition were deposited on pre-

characterized Si substrates via RF magnetron sputtering to investigate the interplay of alloy content on microstructure, stress, and optical performance. For the AgAl alloys, the focus was on compositions within the intermetallic region, as this has been shown to yield films with greatly improved optical properties. All AgAl thick films showed improved surface roughness and scatter performance compared to their thick undoped Ag counterparts. In-situ stress measurements for all compositions revealed compressive films, developing into a more compressive state with increasing thickness. However, ex-situ stress measurements revealed films with tensile residual stresses. Monitoring the film stress post-deposition and during venting showed that the films underwent a stress reversal as they cooled. Various venting conditions were explored to further investigate this phenomenon.

HP-ThP-7 Characterising Thin Films Using Hard X-Ray Angle Resolved XPS, ***T Swift***, Kratos Analytical Inc, USA*; J. Counsell, S. Coultas,* Kratos Analytical Ltd, UK*; C. Tupei, Y. Li,* Nanyang Technological University, Singapore

High-energy X-ray photoelectron spectroscopy has been used to determine the structure and chemical nature of HfOx thin-films deposited on Alumina substrates.

Shrinking device dimensions has increased the use of atomic layer deposition (ALD) due to the need for increased uniformity and control of layer thickness. The ability to deposit high dielectric constant (high-k) films via ALD has allowed for their widespread use in a swath of optical, optoelectronic, and electronic devices.

Using standard Al Kα excited XPS allowed determination of film thicknesses up to 7nm however beyond this it was not possible to accurately quantify the Si 2p peak from the substrate. Ag Lα excitation results in electrons of higher KE for the same photoemission peak. This increases the over-layer effective attenuation length which in real terms means the sampling depth increases by approximately a factor of two.

Here we use high-energy Ag XPS (Ag Lα radiation - 2984eV) in a conventional angle-resolved XPS (ARXPS) experiment. The ARXPS data is analysed using algorithms linked with physical data parameters based on thermodynamic models, maximising the entropy to find a solution of best fit [1] and generate a reconstructed depth profile over the greater sampling depth provided by the higher energy excitation source.This approach allows the non-destructive elucidation of the structure of ALD thin films of hafnia, alumina and a combination of the two not possible with the conventional Al Kα excitation source. The use of the higher photon energy excitation source mitigates the need for destructive depth profiling using Ar-ion beams to remove material with the risk of ion beam induced chemical changes.

We conclude with calculation of film thickness, the chemistry at the interfaces and the usefulness of Ag Lα excited XPS for such applications.

[1] K. Macak, SIA 43(13) 2011

HP-ThP-8 The Anisotropic Behavior of Super-Hard TiB_2 Films Studied by Synchrotron Nano-Diffraction, ***Anna Hirle***, *C. Fuger, R. Hahn, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; M. Weiss,* Institute of Chemical Technologies and Analytics, TU Wien, A-1060 Vienna, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; S. Kolozsvari, P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; Institute of Materials Science and Technology, TU Wien, A-1060 Wien, Austria

For hexagonal structured materials, anisotropic properties are well known due to their specific lattice distortion with respect to basal and prismatic planes. In the case of magnetron sputtered transition metal diborides direction-dependent hardness was reported for WB_{2-z}, ZrB_2, as well as for TiB_2 [1-3]. In more detail, the anisotropic behaviour of hexagonal AlB_2 structured diborides is explained by a more difficult dislocation movement due to energetically less preferred slip systems. For TiB_{2+z} it was shown that a preferred crystal growth in 0001 direction predominates super-hardness (> 40 GPa) over any stoichiometry variations [3,4]. Furthermore, the growth orientation of TiB_{2+z} is highly dependent on process parameters, especially the pressure, which was suggested by Neidhardt et al. [5] and experimentally confirmed in a recent publication [3].

For state-of-the art protective coatings not only a high hardness is beneficial, but also specifically low residual stress states are preferred. By varying the pressure during the growth of TiB_{2+x} coatings, the mechanical properties have been tailored by structural adaptions throughout the film cross-section. In addition, the incorporation of metallic Ti interlayers is an interesting tool for stress management within these films. To study the progression of the stress sates as well as orientation relations throughout the film cross-section, X-ray nano-diffraction synchrotron experiments (beamline P03 at PETRA III) have been performed. Furthermore, the structure-mechanical properties were described by a broad set of characterization techniques such as SEM, Nanoindentation, or micro-mechanical testing techniques.

Keywords: Transition Metal Diborides, Anisotropy, Residual Stresses, Synchrotron Investigations, PVD

[1]B. Hunter et al., Investigations into the slip behavior of zirconium diboride, J. Mater. Res. 31 (2016) 2749–2756.

[2]C. Fuger et al., Influence of Tantalum on phase stability and mechanical properties of WB2, MRS Communications. 9 (2019) 375–380.

[3]C. Fuger et al., Revisiting the origins of super-hardness in TiB2+z thin films – Impact of growth conditions and anisotropy, Surf. Coat. Technol. 446 (2022) 128806.

[4]P.H. Mayrhofer et al., Self-organized nanocolumnar structure in superhard TiB2 thin films, Appl. Phys. Lett. 86 (2005) 131909.

[5]J. Neidhardt et al., Experiment and simulation of the compositional evolution of Ti–B thin films deposited by sputtering of a compound target, J. Appl. Phys. 104 (2008) 063304.

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