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).

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