Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM1-1-TuM

Spatially-resolved and in situ Characterization of Thin Films, Coating and Engineered Surfaces I

Moderators: Damien Faurie, Université Sorbonne Paris Nord, France, **Naureen Ghafoor**, Linköping University, Sweden, **Aparna Saksena**, Max Planck Institute for Sustainable Materials, Germany

8:00am **CM1-1-TuM-1** ***Accelerated Atomic-Scale Exploration of Phase Evolution in Compositionally Complex Solid Solution Using Combinatorial Processing Platforms (CPP), Yujiao Li [yujiao.li@rub.de],*** Ruhr University Bochum, Germany **INVITED**

Combining microtip arrays with combinatorial thin film deposition and processing, along with direct atomic-scale characterization, we recently developed a new approach-combinatorial processing platform (CPP), which enables accelerated exploration of temperature- and environment-dependent phase evolution by (1) simultaneous synthesis of 36 identical volumes of nanocrystalline thin films on commercially-available Si tips; (2) rapid phase evolution upon successive thermal treatments; (3) direct near-atomic-scale analysis by atom probe tomography (APT), complemented by transmission electron microscopy (TEM).

Traditional methods of studying phase stability, evolving time-consuming material production process, long-term annealing for phase evolution, and sample preparation for microscopy, often take months or even years [1]. In contrast, our accelerated CPP approach dramatically reduces investigation time from months or years to several days.

In this talk, I will present the application of the CPP approach to study the phase stability of compositionally complex solid solution (CCSS) with a focus on the Cantor alloy (CrMnFeCoNi) [2] and CrCoNi alloy [3]. While these alloys are known for their unusual mechanical properties, they are susceptible to phase decomposition under elevated temperatures or reactive conditions. This can alter their superior properties and lead to potential failure. Therefore, understanding and controlling phase stability is crucial to optimizing their performance in real applications. We also extend this approach to investigate the oxidation [4] and electrochemical reactions [5] of CCSS. The results of these studies will also be presented.

[1] F. Otto, A. Dlouhý, K. G. Pradeep, M. Kubenova, D. Raabe, G. Eggeler and E. P. George, Acta Mater., 2016, 112, 40–52.

[2] Y. J. Li, A. Savan, A. Kostka, H. S. Stein and A. Ludwig, Accelerated atomic-scale exploration of phase evolution in compositionally complex materials, Mater. Horiz., 2018, 5,86–92.

[3] Y. J. Li, A. Kostka, A. Savan and A. Ludwig, Phase decomposition in a nanocrystalline CrCoNi alloy, Scr. Mater., 2018, 766, 1080–1085.

[4] Y. J. Li, A. Kostka, A. Savan and A. Ludwig, Atomic-scale investigation of fast oxidation kinetics of nanocrystalline CrMnFeCoNi thin films, J. Alloys Compd., 2018, 766, 1080–1085.

[5] V. Strotkötter, Y. Li, A. Kostka, F. Lourens, T. Löffler, W. Schuhmann and A. Ludwig, Self-formation of compositionally complexsurface oxides on high entropy alloys observed by accelerated atom probe tomography: a route to sustainable catalysts, Mater. Horiz., 2024, 11, 4932-4941 [tel:4932-4941] .

8:40am **CM1-1-TuM-3 Advanced Thin Film Characterization Through the Combination of New GD-OES System and Raman Analysis*, Kayvon Savadkouei [Kayvon.savadkouei@horiba.com]*,** Horiba, USA*; Suyeon Lee, Patrick Chapon, Lionel Garrido,* Horiba Europe Research Center, France

Surface and interface studies require the use of complementary analytical techniques, as each instrumentation provides only partial information based on the interaction between the probing medium and the investigated material [1]. Here, we introduce a novel coupling of **Glow Discharge Optical Emission Spectroscopy (GD-OES)** with **Raman spectroscopy** for element-specific thin film characterization.

By combining GD-OES depth profiling with Raman spectroscopy, both elemental and molecular information of multilayers at different depths can be obtained [2]. This integrated approach provides a unique correlation between compositional and structural changes, enabling in-depth investigations of multi-layer thin films, conversion coatings, and organic coating systems. Representative results from multi-layered paint coatings for automobile applications demonstrate how the coupling of these two techniques enhances the understanding of complementary information from each layer.

Recent developments in GD-OES instrumentation, particularly the introduction of a new *Echelle* spectrometer and complementary metal-oxide-semiconductor (CMOS) camera detection system, have significantly expanded analytical possibilities. The *Echelle* system enables ultra-fast, simultaneous and automatic detection of all elements from hydrogen (and deuterium) to uranium at high acquisition rates, which is crucial for capturing transient phenomena and resolving nanometric interfacial layers. These improvements allow for more precise, comprehensive, and time-efficient investigations when GD-OES is coupled with Raman spectroscopy, ultimately enhancing the overall analytical performance of this hybrid approach.

These **hybrid analytical strategies**, coupling GD-OES with Raman spectroscopy, enable **quantitative, depth-, and time-resolved** characterization of complex materials.

[1] Compendium of Surface & Interface Analysis, Springer Raman and glow discharge optical emission spectroscopy studies on structure and anion incorporation properties of a hydrated alumina film on aluminum. Applied Surface Science 592 (2022) 153321.

[2] Advances in RF Glow Discharge Optical Emission Spectrometry Characterization of Intrinsic and Boron-Doped Diamond Coatings. *ACS Appl. Mater. Interfaces* 14, 5 (2022) 7405–7416.

9:00am **CM1-1-TuM-4 *In Situ* Micromechanical Characterization of Nanocrystalline Materials Coupled with X-Ray Nanodiffraction*, Michael Meindlhumer [michael.meindlhumer@unileoben.ac.at]*,** Technical University of Leoben, Austria*; Juraj Todt,* Technical Univeristy of Leoben, Austria*; Manfred Burghammer, Martin Rosenthal, Asma A. Medjahed,* ESRF, Grenoble, France*; Noel Sheshi,* University of Udine, Italy*; Michal Zitek, Anton Hohenwarter,* Technical University of Leoben, Austria*; Enrico Salvati,* University of Udine, Italy*; Doris Steinmüller-Nethl,* CarbonCompetence GmbH, Austria*; Daniel Kiener, Jozef Keckes, Markus Alfreider,* Technical University of Leoben, Austria **INVITED**

In order to improve our understanding of the mechanical behavior of nanocrystalline materials, it is essential to elucidate the multiaxial stress and strain fields throughout their irreversible deformation, especially in the regime where simplified homogeneous linear elastic assumptions are not valid anymore. Here, *in situ* micromechanical testing coupled with cross-sectional X-ray nanodiffraction (CSnanoXRD) with a spatial resolution down to 80 nm was used to resolve the individual multi-axial stress and strain fields throughout deformation history in two unique model experiments.

First, the capabilities of *in situ* CSnanoXRD will be showcased for monolithic ZrN and multi-layered ZrN-CuZr indented by a diamond wedge indenter tip coated with nanocrystalline (nc) diamond. Therefore, a diamond wedge indenter tip was coated with a nc diamond thin film, which was subsequently removed at the edges of the wedge using focused ion beam milling to ensure uniform signal during the CSnanoXRD experiment. Additionally, wedge samples for indentation were prepared from monolithic ZrN and a CuZr-ZrN multilayer thin films. This new kind of indentation experiment allows for tor the first time to directly assess the multi-axial stress distributions across the contact area for both the indenter tip and tested volume, thus, extending the classical single degree-of-freedom and single contact load-displacement response into a locally resolved a three-dimensional high-resolution probe.

In the second part of the contribution, we extend the CSnanoXRD capabilities further by nanoscale strain-mapping surrounding a growing crack tip in fracture specimens fabricated from a nc FeCrMnNiCo HEA. Thereby, one of two identical cantilevers was deformed *in situ* in a scanning electron microscope using the sequential loading-unloading approach to evaluate the incremental *J*-integral. Additionally, a point pattern was added on the surface of this cantilever allowing for the detailed analysis of the complete 2D surface strain components. CSnanoXRD was used to uncover the multi-axial stress fields associated with crack growth in the second HEA cantilever. This correlative approach for obtaining stress and strain data could be used for the first time to evaluate the *J*-integral around the crack tip in its original analytical form.

Altogheter, the quantitative experimental multi-axial strain and stress results give unprecedented insight into nanoscale deformation under severe loading conditions, which has significant implications in the development and assessment of modern damage-tolerant (thin film) materials and microstructures.

9:40am **CM1-1-TuM-6 Nanoscale Mapping of Electrical Breakdown in Polycrystalline Thin Films Using High-Voltage Conductive AFM**, ***Zakhar Kudrynskyi [Zakhar.Kudrynskyi@nottingham.ac.uk]**, Timothy Cooper,* The University of Nottingham, UK*; James Kerfoot,* Park Systems UK Limited, UK*; Xiang Zheng,* University of Bristol, UK*; Vladimir Korolkov,* Park Systems UK Limited, UK*; Martin Kuball,* University of Bristol, UK*; David Grant,* The University of Nottingham, UK

Understanding dielectric breakdown at the nanoscale is essential for developing reliable insulating coatings for high-power electronic systems. However, direct observation of breakdown initiation and defect evolution under realistic high-field conditions remains a major experimental challenge. Here, we introduce a high-voltage conductive atomic force microscopy (HV-C-AFM) methodology capable of probing local electrical failure mechanisms in thin dielectric films with nanometer spatial precision.The HV-C-AFM setup integrates a conductive probe with an external high-voltage amplifier (up to 200 V at the tip–sample junction) and a low-noise current detection system, enabling controlled, spatially resolved I–V spectroscopy and in situ electrical stressing of targeted nanoscale regions. This configuration allows direct visualization of defect generation and local dielectric breakdown processes in polycrystalline aluminium nitride (AlN) thin films deposited by reactive DC magnetron sputtering. The films, exhibiting dense hexagonal microstructure and excellent adhesion to metallic substrates, were mapped over multiple areas to construct local breakdown field distributions.Nanoscale electrical mapping revealed record dielectric field strengths up to 1.6 $kV \cdot \mu m^{-1}$ for ~30 nm films, decreasing to ~1.0 $kV \cdot \mu m^{-1}$ for thicker (>90 nm) coatings. Post-breakdown imaging captured the formation of nanometer-scale craters associated with localized thermal and structural degradation. Weibull statistical analysis across hundreds of sites demonstrated a narrow dispersion, confirming exceptional uniformity and reliability of the sputtered films. The combination of high spatial resolution, controlled high-field stressing, and correlative topographical imaging distinguishes this HV-C-AFM approach from conventional macroscale breakdown testing.Complementary nanosecond transient thermoreflectance (TTR) measurements provided in situ thermal transport data, revealing very high through-plane thermal conductivity (κ = 290 ± 5 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature, remaining ~160 $W \cdot m^{-1} \cdot K^{-1}$ at 300 °C).Together, the HV-C-AFM and TTR analyses deliver a multimodal, spatially resolved framework for correlating nanoscale defect dynamics with macroscopic dielectric and thermal performance. This novel high-voltage AFM methodology opens new routes for in situ reliability assessment of dielectric thin films and underpins the development of next-generation electrical insulation materials.

10:00am **CM1-1-TuM-7 High Spatial Resolution Electrical Characterization of Crystal Defects in Metals and Alloys**, ***Hanna Bishara [hbishara@tauex.tau.ac.il]**,* Tel Aviv University, Israel

Microstructural defects such as Grain boundaries (GBs) and dislocations significantly affect the electrical properties of metallic materials. Generally, the GB interfacial resistivity or dislocation specific resistivity are captured as an accumulative property of all the defects within the material. However, for example, it is evident that different boundary types exhibit distinct structural and chemical characteristics. Therefore, the GB electrical properties are expected to span over a spectrum of values. Yet, the relationship between the boundary's characteristics and their electron transport properties is not well-understood. This research employs SEM in-situ local electrical measurements to study on the impact of GB (and dislocations) structure, chemistry and precipitates on its resistivity.

The talk initially introduces an experimental procedure to measure the local electrical resistivity of GB segments with high sensitivity and spatial resolution *in-situ* scanning electron microscopy (SEM). The local electrical properties are correlated with microstructural characters resolved by electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and atom probe tomography (APT), in addition to molecular dynamics (MD) simulations. Multiple materials system will be addressed, namely, pure Cu, dilute Cu alloys, aluminum alloys, and Half Huesler alloys. In addition the disolcation-dislocation interaction on resistivity will be demonstrated for Full-Heusler alloy.

The talk provides insights to the high-resolution methodology of assessing local electrical resistivity of well-defined complexions. The directly-measured interfacial resistivity are discussed in means of thermodynamic excess properties, segregation, and material type.The novel results contribute to a better understanding of the defects' resistivity, and opens new horizons in in knowledge-based defect engineering of smart materials. The present research is promising to be applied on phase boundaries and internal interfaces.

10:20am **CM1-1-TuM-8 Nanoscale 3D Tomography Verifying Corrosion Barrier Healing in Steels**, ***Robert Ulfig [robert.ulfig@ametek.com]**,* CAMECA Instruments Inc., USA **INVITED**

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