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],*** *Juraj Todt,* Technical University 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.

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

Stainless steels exposed to high temperatures undergo sensitization, a process that significantly reduces corrosion resistance due to chromium carbide precipitation along grain boundaries [1]. This precipitation depletes chromium in the surrounding matrix below the threshold required for passivity, creating galvanically active regions prone to intergranular corrosion [2].

This study demonstrates the use of Ultrasonic Nanocrystalline Surface Modification (UNSM)—a high strain-rate surface peening technique—to rapidly desensitize sensitized AISI 304H austenitic stainless steel. High-resolution transmission electron microscopy and selected area electron diffraction confirmed that UNSM-induced localized strain and strain rate promote nanoscale deformation twinning in the austenite matrix.

Atom probe tomography (APT) revealed that deformation twinning facilitates nanoscale chromium homogenization near sensitization-induced grain boundary carbides. The minimum chromium content in the matrix increased from 7 at.% in the sensitized condition to ~12 at.% after UNSM treatment, surpassing the 11–12 at.% threshold for passivation. Crystallographic analysis of chromium distribution and carbide morphology suggests atomic transport during twin thickening as the underlying mechanism. These findings were enabled by recent advances in APT such as improved signal-to-noise ratio and a wide field-of-view. These capabilities will be discussed in relation to their impact on corrosion barrier characterization [4].

References:

1. ASM Handbook, Vol. 13B: Corrosion: Materials. ASM International, 2005.

2. E.L. Hall and C.L. Briant, Metall. Trans. A, 1984, vol. 15, pp. 793–811.

3. Ulfig, R. et al. LEAP 6000XR, New Applications, New Performance. Microscopy and Microanalysis 2022 vol. 28, pp. 3190–3191.

4. Sasidhar, K. N. et al. Understanding the protective ability of the native oxide on an Fe-13 at% Cr alloy at the atomic scale: A combined atom probe and electron microscopy study. Corrosion Science 2023 Vol. 211, pp. 110848.

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