Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session H1
Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces

H1-1 INVITED TALK: Multimodal and *in situ* Electron Microscopy to Understand Local Deformation Mechanics*, Josh Kacher (josh.kacher@mse.gatech.edu),* 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 also necessitated the increased integration of data analytics based analysis of results as data acquisition rates now exceed what can be manually processed and understood.

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 mechanical testing platforms. I will discuss these advances in terms of two materials applications: 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.

H1-3 Development of In-situ Liquid Cell Transmission Electron Microscopy for Quantifying Temperature-Dependent Thin Film and Nanostructure Processing*, Serin Lee (serinlee@mit.edu),* Massachusetts Institute of Technology, USA*; N. Schneider,* Renata Global, USA*; J. Park,* Princeton University, USA*; S. Tan, F. Ross,* Massachusetts Institute of Technology, USA

Over the last several years, the technique of liquid cell TEM(LC-TEM) has been developed for imaging liquid samples in TEM with good spatial and temporal resolution. LC-TEM enables us to complete the triangle of structure-properties-processing of materials under controlled conditions of temperature, biasing, and liquid composition. Temperature control is particularly important as it is a key parameter in the operation of battery materials and the kinetics of electrochemical processes such as corrosion and etching, as well as being a useful variable in understanding the physics of nanostructure evolution. Here, we will discuss the effect of temperature on the evolution of dendrite formation from metal ions in solution, because this is a widely found morphology that has significant relevance to battery electrode stability and materials synthesis. First, we build a robust model to calculate the equilibrium concentration of chemical species in the liquid medium under electron beam irradiation as a function of temperature. The model includes the complete radiolysis reaction set for the full sent of chemical species in the initial solution. The model also includes the temperature-dependent radiolysis reaction parameters. We use Arrhenius behavior for the reaction rates and G values (rates of generation of the primary products due to beam irradiation). We use this model to predict how temperature affects the radiolysis-driven equilibrium concentrations of the species. Next, we expand the model so that it can be applied to understand temperature-dependent kinetics of nanostructure evolution, by considering the diffusion and depletion of precursors. This involves modification of the Stokes-Einstein equation with temperature-dependent viscosity to calculate the diffusion length. This complete model provides an opportunity to understand how radiolysis species behave at different temperatures under the combined effect of parameters such as the important experimentally controllable variables for liquid cell experiments: dose rate, initial concentration of the solution, pH, and aeration. We will show the results of testing this model by comparison of calculated results with experimental observations on nanoparticle generation from silver nitrate solution, dendrite growth trajectories, and the beam-induced etching and growth of metal thin films at different temperatures. We are excited by the opportunities presented by LC-TEM to develop and test a robust model that enables the temperature to be used quantitatively to probe the physics of nanostructure evolution and for a range of practical processing applications in energy storage, corrosion, and catalyst synthesis.

H1-4 UHV Specimen Transfer Systems for Analysis of Reactive Materials with Atom Probe Tomography*, Robert Ulfig (robert.ulfig@ametek.com),* *K. Rice, T. Prosa, D. Reinhard, J. Shepard,* CAMECA Instruments Inc., USA*; U. Maier,* Ferrovac GmbH, Switzerland

Atom Probe Tomography is the highest sensitivity 3D analytical technique with nanoscale spatial resolution and has been used to study a wide variety of materials. APT however analyzes small volumes and requires specialized specimen preparation resulting in very high surface to volume ratios. For a wide variety of microscopies and associated applications, changes related to exposed surfaces, or the bulk temperature history have little or no effect on the goal of the analysis, e.g. characterization of stainless steel grain size. For other studies, especially when using atom probe tomography, a carefully controlled environment (temperature, pressure, atmosphere, etc.) may be critical. For example:

– Rapid oxidizers (e.g. uranium, lithium)

– Surface contamination (e.g. catalysts)

– Characterization of hydrogen content in steels, semiconductors, etc.

– Analysis of “soft” materials potentially encased in vitreous ice (e.g. biological)

– Transport between various microscopic analysis/treatments (e.g. FIB-SEM, reaction chambers)

Due to growing interest in the above applications that require this capability, a UHV/Cryogenic transfer system has been developed based on a collaboration between the Max Plank Institute for Steel Research in Germany, CAMECA in the United States, and Ferrovac in Switzerland. The transfer design is based on the mobile UHV Suitcase from Ferrovac, customized to transfer samples held in a standard LEAP specimen carrier. This system can be fully integrated to a specially modified LEAP 5000 system’s hardware and software. Transfer can be completed in less than 1 minute to the LEAP or any system with a standard vacuum connection. This talk will describe the existing system and a new version of VCTM to FIB transfer system developed with cooperation from ThermoFisher Scientific for fast and easy transfer in/out of a standard FIB-SEM, to the LEAP, and to other systems such as reaction chambers.

H1-5 Cold Sprayed Cr-coating on Optimized ZIRLO™ Claddings: An Atom Probe Tomography Study of the Cr/Zr Interface and its Microstructural and Chemical Evolution after Autoclave Corrosion Testing*, Andrea Fazi (fazi@chalmers.se),* *H. Aboulfadl, H. Andrén, M. Thuvander,* Chalmers University of Technology, Gothenburg, Sweden

As-produced Cr-coated Optimized ZIRLO™ cladding material fabricated with the cold-spray deposition process is studied. Atom probe tomography is used to investigate the nature of the cold sprayed Cr-coating/Optimized ZIRLO™ bonding interface and the heat affected zone produced by the coating deposition on the Zr-substrate. A 10–20 nm thick intermixed bonding region is observed at the interface between coating and substrate. The chemical composition of this region suggests that this layer originated from a localized melting of a thin volume of the outermost former surface of the substrate. Chromium, diffusing from the coating into the Optimized ZIRLO™ substrate during the deposition process, is found segregating at grain boundaries at up to a few hundred nanometres distance from the interface. The same material is also analysed after autoclave corrosion testing to examine the microstructural and chemical evolution of the previously mentioned intermixed bonding region. Nucleation of $ZrCr_2$ intermetallic phase is discovered at the interface, inside the intermixed layer. Cr-rich regions are observed penetrating a few hundreds nanometres beyond the interface into the substrate, possibly along grain boundaries or sub-grain boundaries.

H1-6 INVITED TALK: Multicracking of Thin Films and Nanostructures on Stretchable Substrates; Impact on Magnetic Properties*, Damien Faurie* ***(faurie@univ-paris13.fr)****, F. Zighem, S. Merabtine,* LSPM-CNRS, Université Paris13, France*; P. Lupo, A. Adeyeye,* National University of Singapore **INVITED**

Nanoscale systems fabricated on flexible or stretchable substrates are being studied more and more because of their ability to adapt to non-planar surfaces, particularly in confined environments. In addition, these systems have the advantage of being lighter and less expensive than their counterparts deposited on more conventional rigid substrates. In recent years, many magneto-electronic devices have been made on different polymer substrates. The ability of these magnetic thin films on polymer substrates to be folded or stretched is essential, but their use is still delicate, which is a brake on the industrialization of these systems.

The main issues are to understand how the applied strains to the flexible magnetic systems impact their magnetic properties. Obviously, when a thin film is deposited on a flexible substrate, it is usually submitted to high stresses due to the stretching or the curvature of the whole system and to the mechanical contrast between the film and the substrate. These stresses may have an important effect on the static and dynamic magnetic properties of thin films, especially on the resulting magnetic anisotropy. In particular, it is important that the large strains to which they are subject are not harmful to their functional properties. In fact, beyond the classical magnetoelastic effects observable at small strains, the phenomenon of multi-cracking and associated localized buckling observed for inorganic thin films on organic substrates tensily stressed lead to heterogenous strains must have effects on the magnetic properties. However, these are rarely discussed in the case of flexible magnetic systems, and have never been studied in depth.

In this work, we focused on experimentally identifying the cracking mechanisms for different magnetic alloys ($Co_{40}Fe_{40}B_{20}$, $Ni_{80}Fe_{20}$) deposited on Kapton® substrate. The phenomena of multicracking but also buckling of thin films have been studied. Thin films surface was probed by atomic force microscopy during *in situ* tensile tests to clearly identify these mechanisms. Subsequently, we have identified the effects of these irreversible phenomena on the magnetic properties of thin films (anisotropy and Gilbert damping coefficient).

References :

[1] S Merabtine, F Zighem, D Faurie, A Garcia-Sanchez, P Lupo, AO Adeyeye, Nano letters 18 (5), 3199-3202 (2018).

[2] S Merabtine, F Zighem, A Garcia-Sanchez, V Gunasekaran, M Belmeguenai, X Zhou, P Lupo, AO Adeyeye, D Faurie, Scientific reports 8 (1), 13695 (2018).

[3] D Faurie, F Zighem, P Godard, G Parry, T Sadat, D Thiaudière, P-O Renault, Acta Materialia 165, 177 (2019)

H1-9 Nano-scale Residual Stress Profiling in Ultra-thin Si_3N_4/ZnO Multilayer Stacks using FIB-DIC Method*, Marco Sebastiani* ***(seba@uniroma3.it)****,* Roma TRE University, Italy

Silicon nitride (Si_3N_4) is commonly used in many optical applications because of its transparency over a wide spectral range from near-ultraviolet (UV) to the infrared (IR) region. One example is the low emissivity (Low-E) coatings, which are applied to large area architectural glazing to reduce heat losses from buildings. They combine high visible transparency with high reflectance in the far-infrared region. To achieve such combination of properties, Low-E coatings generally consist of dielectric/Ag/dielectric multi-layers stacks, where the thin (~ 10 nm) Ag layer reflects long wavelength IR back into the building while the dielectric layers both protect the Ag and act as an anti-reflective layer.

The architecture of the multi-layer stack influences its mechanical properties and it is strongly dependent on the residual stress distribution in the stack. Residual stress measurement by micro-ring core focused ion beam (FIB) milling at the surface offers lateral resolution better than 1 mm and provides information about the residual stress depth profiling with a resolution better than 50 nm. The method is suitable for both equi-biaxial and non-biaxial stress distribution and hence covers a large number of material systems. In this work, thin Si_3N_4/ZnO/Si_3N_4 stacks with varying thickness (100, 160 and 200 nm) were deposited by magnetron sputtering onto glass substrate and post deposition annealed at 650 ^oC for 12 minutes. Residual stress measurement by FIB-DIC revealed that the individual Si_3N_4 layers in the multi-layer stack are under different amount of compressive stresses. The magnitude of these stresses changes after the heat treatment cycle and provides useful insight into the multi-layer architecture. The results show that FIB-DIC is a reliable method for accurately probing the residual stresses with nanoscale resolution.

Author Index

Bold page numbers indicate presenter