Atom Probe Tomography Focus Topic
Room: 211D - Session AP+AS-TuM

New Applications of Atom Probe Tomography

Moderator: Arun Devaraj, Pacific Northwest National Laboratory

8:00am **AP+AS-TuM1 Development of Atom Probe Tomography for Studying Nuclear Corrosion Issues**, ***Daniel Schreiber***, Pacific Northwest National Laboratory **INVITED**

Material degradation and corrosion create significant challenges to nuclear energy production, both in terms of the structural integrity of plant components and also in the long-term disposal of high-level radioactive waste. For structural materials, stress corrosion cracking (SCC) continues to be a prominent issue for Ni-base alloys in the high temperature (~320 °C in pressurized water reactors) corrosive reactor environment. Despite decades of research, there has yet to be a consensus on the fundamental mechanisms that control SCC response. On the other hand, the long-term disposition of high-level nuclear waste generated by nuclear energy production continues to be an open question. Vitrification of high-level waste into a relatively stable form (e.g. borosilicate glass) is being actively pursued. However, disagreement exists about the long-term stability of the glass if/when exposed to ground water in a geologic repository due to an ill-defined rate-limiting process controlling glass dissolution. In both cases, high-resolution microscopy techniques including atom probe tomography (APT) provide unique opportunities to test various mechanistic theories with unprecedented spatial resolution and chemical sensitivity. Such studies have only recently been made possible through the advancement of site-specific focused ion beam (FIB) sample preparation methods and pulsed-laser APT systems, creating a unique environment for revolutionary discoveries.

In this talk, I will discuss the development of APT methods for characterizing SCC microstructures in select model and commercial alloys and also for characterizing the dissolution of model vitrified nuclear waste glasses. The corrosion of metals and the dissolution of glass present unique but overlapping challenges in sample preparation, data acquisition and data interpretation that will be discussed in detail. Highlights will be presented in both cases on how APT is changing the way we view the fundamental mechanisms dictating SCC of metals and glass alteration.

8:40am **AP+AS-TuM3 Using Aqueous Solutions by Cryo-Fixation As a Matrix for Analyzing Materials in APT**, ***Stephan Gerstl***, *B. Scherrer*, ETH Zürich, Switzerland, *J.M. Cairney*, University of Sydney, Australia, *R. Spolenak*, *R. Wepf*, ETH Zürich, Switzerland **INVITED**

Atom probe tomography has progressively engaged the world of materials characterization with 3-dimensional nanometer-level maps of various dense materials. These atom maps have been the attraction of the technique because they enable new perspectives and analysis of solid materials literally atom by atom. The analysis of soft organic materials, even aqueous solutions, has however been a long-standing issue as it is impaired by contamination, uncertain phase formation, and questionable observed states. These outcomes have been interrogated, retested, and re-analyzed to better understand the artifacts involved. Here we present the development steps achieved together with the APT results obtained of three aqueous based solutions: a water-based citrate solution, a 1:1 water-ethanol mixture, and a commercially available marginally alcoholic beverage. These aqueous solutions were chosen so as to exhibit differences in their mass-spectrum response due to their dissimilarities. The methodologies enabling these analyses require arresting the liquids so they are stable in vacuum environments, sharpening them to a needle geometry, and transporting them between chambers whilst not altering their structural integrity; all steps being done close to LN_2 temperatures. The main challenge was with contamination, which needs to be minimized and separated from the material of interest in the analysis. The cryo-fixation method involves plunge freezing the region of interest (ROI) in cryogenic liquids, sharpening the ROI in a FIB fitted with a cryogenically cooled stage, and field evaporating it in a retrofitted cryo-transfer enabled LEAP 4000X-HR.

All aqueous specimens could be analyzed successfully; with the resulting amounts of ROI analyzed being small (only a thin film is probed due to sample geometry), trends and fluctuations in ion concentrations have been interrogated and will be presented.

The application space of this technique will be considered in terms of using fluids as matrices and designing the experiments to increase the volume of soft materials analyzed.

11:00am **AP+AS-TuM10 Atom Probe Tomography Investigation of TiSiN Thin Films Made Possible by ^{15}N Isotopic Substitution**, ***David Engberg***, Linköping University, Sweden, *L.J.S. Johnson*, Sandvik Coromant, Sweden, *M.P. Johansson-Jöesaar*, SECO Tools AB, Sweden, *M. Odén*, Linköping University, Sweden, *M. Thuvander*, Chalmers University of Technology, Sweden, *L. Hultman*, Linköping University, Sweden

TiSiN is one of the most important materials for commercial wear resistant coatings on cutting tools. Understanding of the growth and structure of these coatings has become increasingly important for optimizing their performance. Yet knowledge regarding the solid solubility, distribution, and stoichiometry of SiN_y has been lacking in the complex metastable TiN-SiN structure. Atom probe tomography (APT) in combination with analytical electron microscopy provides a way to attain compositional information in 3D on the nanometer scale. However, mass spectrum overlaps of N and Si ions have so far prevented such APT analyses. By growing TiSiN coatings with ^{15}N using cathodic arc deposition, we show that the mass spectrum overlaps of Si and N can be largely avoided. $TiSi^{15}N$ films of two compositions, $Ti_{0.81}Si_{0.19}{}^{15}N$ and $Ti_{0.92}Si_{0.08}{}^{15}N$ in a predominantly cubic structure, have been studied using APT. We find evidence of Si-Si clustering on the nanometer scale, while there are no indications of overstoichiometric SiN_y ($y \approx 1$).

11:20am **AP+AS-TuM11 Investigating the Alternating Cation/Anion Compositions in a High-Voltage Li-Mn-Rich Oxide Electrode during First Charge-Discharge Cycle using Atom Probe tomography**, ***Baishakhi Mazumder***, *D. Mohanty*, *C. Daniel*, *D. Wood III*, Oak Ridge National Laboratory

High-voltage layered lithium and manganese-rich (LMR) oxides are potential cathodes for high-energy-density lithium-ion batteries for electric vehicles1. Unfortunately, structural transformation during charging and discharging in these oxides2 leads to undesired phenomena, such as voltage fade during subsequent cycles and lower columbic efficiency in the first cycle, that remain stumbling blocks for practical usage. Understanding the micro-structural changes during the first cycle is critical to obtaining fundamental insight regarding the activation mechanism(s) related to the first cycle capacity loss. In this work, Atom Probe Tomography (APT) has been employed to obtain the 3D microstructural and sub-nm-level compositional information of LMR oxides during the first cycle to resolve the activation mechanism(s) that lead to structural transformation.

The greatest challenge for APT analysis from the actual electrode materials is the complexity in creating needle-shaped specimens. Owing to the discontinuous geometry of the electrode, which is characterized by non-uniform interconnected channels, it is extremely difficult to make a structurally stable needle for controlled field evaporation. Micro-fractures and irregular evaporation due to differences in evaporation fields between the composite elements during APT analysis is also challenging. Additionally, experimental parameters, including tip temperature, laser energy, and detection rate, all strongly impact the field-evaporation and subsequent data analysis. By overcoming these challenges, reliable and reproducible data has been obtained after optimizing the experimental parameters and developing a reliable procedure to prepare stable samples. Mass spectra reveal molecular complexes MxOy for M=Ni,Mn,Co, while the Li appears predominantly as elemental ions. The 3D distributions as well as the compositions of each element were obtained for each sample at different states of charge during the first cycle. These data provides insight towards understanding the structural rearrangements during the first charge-discharge cycle that correlates with the first cycle irreversible capacity loss.

1) M.M. Thackeray, et al., J. Mat. Chem.17 3112 (2007)

2) D. Mohanty, et al., Chem. Mat. 26 6272 (2014)

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