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Correlative Studies on a Subnanoscale Utilizing Atom-Probe Tomography and Transmission Electron Microscopies

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Atom-probe tomography (APT) is in the midst of a dynamic renaissance as a result of the development of a well-engineered commercial instrument that is robust and ergonomic and capable of collecting large data sets, hundreds of millions of atoms, in short time periods compared to earlier instruments. An APT is a field-ion microscope coupled directly to a special time-of-flight (TOF) mass spectrometer that permits one to determine the mass-to-charge state of individual field-evaporated ions plus their x-, y-, and z-coordinates in a specimen in direct space with subnanoscale resolution. The three-dimensional (3D) data sets acquired are analyzed using increasingly sophisticated software programs that utilize high-end workstations, which permit one to handle increasingly large data sets. APT has the unique ability to dissect a lattice, with subnanometer-scale spatial resolution, using either voltage or laser pulses, on an atom-by-atom and atomic plane-by-plane basis and to reconstruct it in 3D with the chemical identity of each detected atom identified by TOF mass spectrometry. Employing femto- or pico-second laser pulses using visible (green or blue light) to ultraviolet light (355 nm wavelength) makes the analysis of metallic, semiconducting, ceramic, and organic materials practical to different degrees of success. The utilization of dual-beam focused ion-beam microscopy [1] for the preparation of microtip specimens from multilayer structures and surface films, semiconductor devices, and for producing site-specific specimens extends enormously the capabilities of APT to a wider range of scientific and technologically important problems than could be previously studied for a range of materials: metals, semiconductors, ceramics, biominerals, and organics.

The advent of aberration-corrected scanning transmission electron microscopy (STEM) coupled with an electron-energy loss (EELS) equipped, which is equipped with a LN_2 double-tilt cooling-stage, operating between 94 to 300 K, makes it possible to utilize annular bright-field (ABF) imaging of atoms as light as hydrogen. And the presence of H in an ABF image is proven to be real by recording EELS H K-edge spectra from the same specimen. STEMs are also equipped with a high-angle annular dark-field (HAADF) detector, which provides Z (atomic number) contrast from individual columns of atoms.

Dual-beam focused ion-beam (FIB) microscopy has become an extremely important tool for preparing both APT and STEM specimens from samples with a planar geometry where one wants to study internal interfaces that are parallel to the surface of a sample. Additionally, dual-beam FIB microscopy plays an important role in performing site specific specimen preparation. For example, for studying solute-atom segregation at a grain boundary or a heterophase interface in a specimen by APT, TEM, EELS and energy dispersive x-ray spectroscopy.

In my talk I will focus on several recent examples utilizing correlative techniques to analyze the same sample, to obtain information that would be impossible to obtain using only one

instrument. The specific problems are as follows: (1) Using APT and STEM sequentially, on the same microtip sample, we characterized the evolution of Nb-oxide and Nb-hydride phases using APT. We detected NbO_2, NbO, Nb_2O_5, Nb, H, and NbH using Three different Nb oxides are formed at the top-most surface of the SRF Nb material within ~5 nm. Nb, H, and NbH atoms are detected below the niobium-oxide layer. Each dot is a single atom, not to scale. We find agreement of the stacking sequence of the 5 nm thick Nb-oxide surface layer determined by EELS: NbO_2, Nb_2O_5 and NbO on top of Nb. Below the surface we find an ~40 nm thick region with a high H concentration, which in some regions form an ordered β-NbH phase at room temperature (RT) [2]. Identifying the exact Nb-oxide stacking sequence on the Nb surface, and the presence of Nb-hydride phases in bulk Nb grains are of tremendous value to the superconducting radio frequency cavity community, as it will enable tailoring of specific pinning centers and the reduction of surface losses during the production process of cavities; (2) APT is utilized to obtain three-dimensional chemical information concerning grain boundary (GB) segregation in a Ni-Cr-Fe alloy 600 with atomic spatial resolution. The detailed crystallography of GBs is determined using a combined approach of electron backscatter diffraction and FIB to establish a GB's five macroscopic degrees of freedom, followed by an APT GB composition analysis. Characterizations of GB microstructure and microchemistry are performed to improve our understanding of mechanisms controlling intergranular attack and stress-corrosion cracking [3]; and (3) Complex thermally grown oxides (TGO) are formed on a single-crystal Ni-based superalloy due to a large fraction of alloying elements. Combining APT and TEM analyses the 3D elemental distributions of metal oxides are quantified in the spinel and refractory metal-oxide regions [4]. A spinel-type oxide, $Ni(Cr,Al)_2O_4$, is formed with a crystallographic orientation relationship with the Ni-based superalloy substrate, which decomposes into other oxides. The sequence of oxides observed in the TGO are $NiO \rightarrow Cr_2O_3 \rightarrow Ta_2O_5 \rightarrow NiTaO_4$, $NiTa_2O_6 \rightarrow Ni(Cr,Al)_2O_4 \rightarrow Al_2O_3$, which is made possible by APT [5].

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