



Introduction

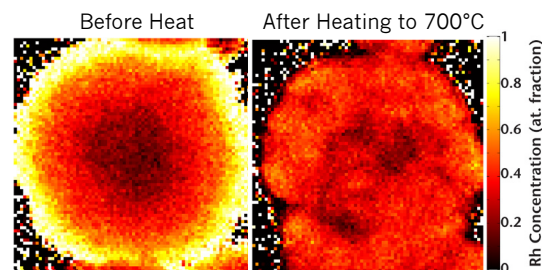
Energy dispersive x-ray spectroscopy (EDS) is an important technique in the microscopist's materials analysis toolbox. Most EDS systems use silicon-based detectors to detect characteristic x-rays generated by interactions between the primary electron beam and the sample. EDS can identify trace quantities of elements within a material using elemental mapping in the SEM and EDS spectrum imaging (EDSSI) in the TEM. Modern software packages make it relatively straightforward to obtain EDS spectra and maps. It is a tool both the beginner and advanced EM operator can use to obtain compositional information of a sample, with results that are usually easy to interpret.

Recent advances in EDS detectors and systems include silicon drift detectors (SDD) with a large detection area (large solid angle) and multiple detectors in a single system. These advances have enabled TEMs with Cs aberration correctors on the probe forming optics to analyze atoms one by one. Atomic resolution EDSSI is now possible.

To fully utilize new and existing EDS systems, compatible sample holders must be used. An EDS detector in a TEM is usually situated at an angle of $\sim 10\text{-}20^\circ$ with respect to the sample. Since EDS systems detect photons (x-rays), they require direct line of sight from the sample to the detector. The design of bulk type heating holders, for example, is not compatible with EDS systems. The furnace surrounds the sample with no direct line of sight from the sample to the EDS detector, limiting the functionality of the TEM for in situ analysis.

The Aduro system uses a flat ceramic membrane that acts as both the heating element and the sample support. By design, the system is compatible with EDS. In fact Aduro does not limit capabilities of your EM and is compatible with most tools and techniques, including EELS, diffraction and STEM. Compatibility with these tools makes Aduro an exceptionally versatile and powerful platform for in situ science.

High temperature EDS with Aduro is possible with detectors that have an opaque window. For systems that have a thin transparent window or no window EDS spectra can easily be acquired by taking advantage of the rapid heating and cooling rates of Aduro (up to $1,000^\circ\text{C/ms}$). If EDS is required, first quench the sample to room temperature (RT), which takes about 1 ms. Second, acquire the spectrum. Third, heat back to the temperature of interest, which also takes about 1 ms. Repeat the process as needed. The high stability and low drift keeps the area of interest within the field of view, and the drift subsides after at most a few minutes depending on magnification.



TEM EDS Spectrum Images of Core/Shell Pd/Rh Alloy Particles

Experiment

EDS spectra in the SEM and TEM are shown in the top and bottom figures on the previous page. In both experiments particles were deposited via solvent suspension dispersion onto an Aduro Thermal E-chip™. TEM EDSSI spectra of Pd/Rh particles are shown in the top figures, and were collected with a JEOL 2010F in STEM mode. In the top figure Cu and Ag SEM EDS element maps were collected with a JEOL JEM-7600F on Cu/Ag particles. The sample was subjected to multiple heat cycles and returned to RT for additional SEM imaging and collection of EDS elemental maps.

The figure on the bottom left, current page is an EDS spectrum of the carbon-coated ceramic membrane on a thermal E-chip. This was collected on a JEOL 2010F to show the E-chip background or baseline spectrum.

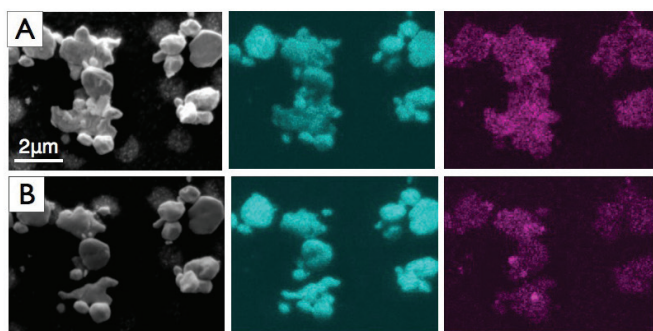
Discussion

The figures at the bottom of the previous page show quantitative TEM EDS spectrum images of Pd/Rh particles. These images show the spatial distribution of Rh within the particle, and the color bar indicates the concentration. The evolution and rearrangement of Rh throughout the particle can be seen by comparing the images before and after heating to 700°C . The particle starts as a core/shell of Pd/Rh and after heating the Pd and Rh mix and become more evenly distributed throughout the particle. These particles are being studied for hydrogen storage applications, and Rh in this case is used to increase the particle thermal stability. It is important to understand the evolution of Rh as a function



of temperature, because Rh has a higher melting point and its distribution is critical to thermal performance.

The SEM elemental maps at the top of the previous page shows Cu/Ag particles at RT in figure A, and the particles after heating in sequence to 800 °C for 60 s and then to 900 °C for 20 s in figure B. Upon heating the outer shell of Ag undergoes a distinct transformation as shown in the figures. After further heating the Ag evaporates and also begins to alloy with Cu creating a CuAg intermetallic compound. This behavior follows the basic bulk CuAg phase diagram, especially in the regime where the percentage of Ag is relatively small. At high temperatures the Ag evaporation and alloying process occur quickly. Bulk heating holders heat and cool too slowly to capture this reaction.

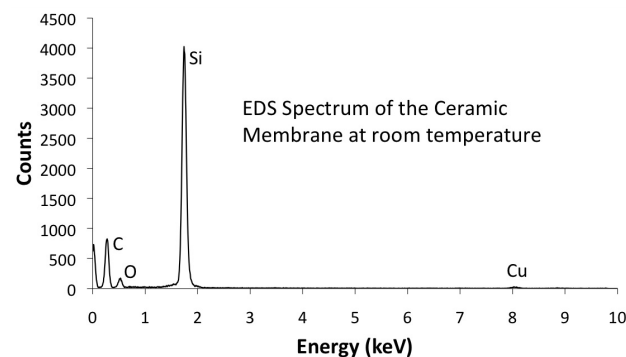


In the above figure an EDS spectrum of the ceramic membrane with a thin carbon overlay collected in the TEM. Silicon and oxygen from the E-chip is detected along with carbon from the thin overlay. Copper is a component in the four contact pins on the

holder. Beryllium is also present in the contact pins, but is too light to reliably detect with the EDS systems used here. Titanium or zinc may also appear which originate from the holder tip materials. When analyzing samples, the presence of these materials should be taken into account. If a sample contains silicon, for example, it cannot be analyzed with EDS using E-chip. However, EELS could be used to detect silicon instead.

(particularly in particles 3 and 5), which significantly shrank in size. These particles may also have been in better contact with the

heating membrane. LAST has poor thermal conductivity and heat transfer to particle 4 may not have been as efficient. It should be noted that not all EDS systems can take spectra at high temperatures.



Applications

DS is an important and versatile tool for materials characterization in the EM. New types of detectors and software continue to improve data quality and ease of use. In the past many in situ characterization instruments were not compatible with such analysis tools. Bulk heating holders, for example, are not usually compatible with EDS systems, and their heating/cooling rates are not fast enough to capture many dynamic reactions. The design of the Aduro™ holder ensures full compatibility with all EDS systems. The materials that make up the holder and E-chips limit analysis of these elements, but the vast majority of elements can be detected and analyzed.

Contact us to discuss the full range of capabilities of the Aduro system with the heating and electrical biasing E-chip sample supports for your applications. We can be reached at (919) 341-2612 or contact@protochips.com.

SEM Experiments: N. Erdman, T. Laudate, S. Mick, *Micros. Microanal.*, vol. 17, pp. 514-515. The TEM EDS measurements were done at Sandia National Laboratories in Livermore, CA.