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Aberration-Corrected Four-Detector STEM-EDS Analysis of Embedded Nanoclusters

Chad M. Parish and Michael K. Miller

Physical Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Examining small particles embedded in a specimen foil is a challenging application for analytical STEM methods. When the particles are ~2 nm or smaller and the foils must be prepared by FIB (which results in thicker foils and more surface damage), the challenges increase. Here we report the use of aberration-corrected STEM, equipped with high-detection-efficiency EDS systems, and multivariate statistical analysis (MVSA) post-treatment analysis of the data, to analyze such particles.

Nanostructured ferritic alloys (NFAs) require advanced analytical STEM methods. NFAs are Fe-Cr-based steels that contain high densities ($>10^{23}/m^3$) of small (<2 nm) oxygen- and vacancy-enriched precipitates, referred to as nanoclusters (NCs) [1]. In alloy 14YWT, Ti-Y-based NCs impart creep strengths several orders of magnitude superior to conventional steels, and NCs are hypothesized to provide tremendous tolerance to neutron irradiation in reactors. Because Fe-Cr alloys are ferromagnetic, FIB-preparation is helpful to reduce aberrations of the electron beam in a STEM column. Neutron-irradiated specimens should be FIBed to reduce the specimens' radioactivity hazard and gamma-induced EDS dark counts. Due to non-uniform dose profiles, ion-irradiated specimens should be FIBed to find the desired dose depth in a large irradiated coupon. Because even the best FIB specimens of stainless steels are typically 20~60 nm thick and passivated with Fe-Cr-oxide on the top and bottom faces, STEM experiments are less ideal than in, for instance, ion-milled cross-sections of epitaxial films. Identifying a single 2-nm O- and vacancy-enriched NC in a 20~60 nm foil requires high signal levels. High spatial resolution requires a small probe size. The 200+ keV electron probes cause sputtering damage of the foil [2,3]. Maximizing the acquired signal at a given probe size requires high-efficiency detectors, bright sources, and aberration-corrected optics, which are available on FEI Titan platforms with ChemiSTEM technology [4]. Even with this advanced tool, signal levels will still be low in absolute terms, and MVSA methods [5] are needed to clearly identify features, such as NCs and grain boundary segregation.

We examined ion-irradiated 14YWT NFA [1] in the North Carolina State University FEI Titan with ChemiSTEM technology, using the four-detector EDS system to acquire spectrum images, which were then interrogated with the Sandia Laboratory AXSIA [5] code. In an unirradiated region, NCs ~1 nm or smaller are visible in both on-zone and off-zone oriented grains (Figure 1). Grain-boundary (GB) solute enrichment is observed (and likely influences the creep properties), and a distribution of small (<1 nm) to large (>5 nm) NCs are observed. In a cryo-irradiated region of the same specimen (5~10 dpa [displacements per atom] radiation damage), few NCs survive the cryo-irradiation, having been ballistically mixed into the matrix (Figure 2). The W-enriched GB component (MVSA#2) in Figure 2 is broader than in Figure 1, and indicates small levels of W enrichment. Combined high-efficiency EDS and MVSA identified the GB component even after dispersal by the irradiation. These microstructural insights are only possible due to the combination of high-efficiency aberration-corrected EDS and MVSA data reduction [6].

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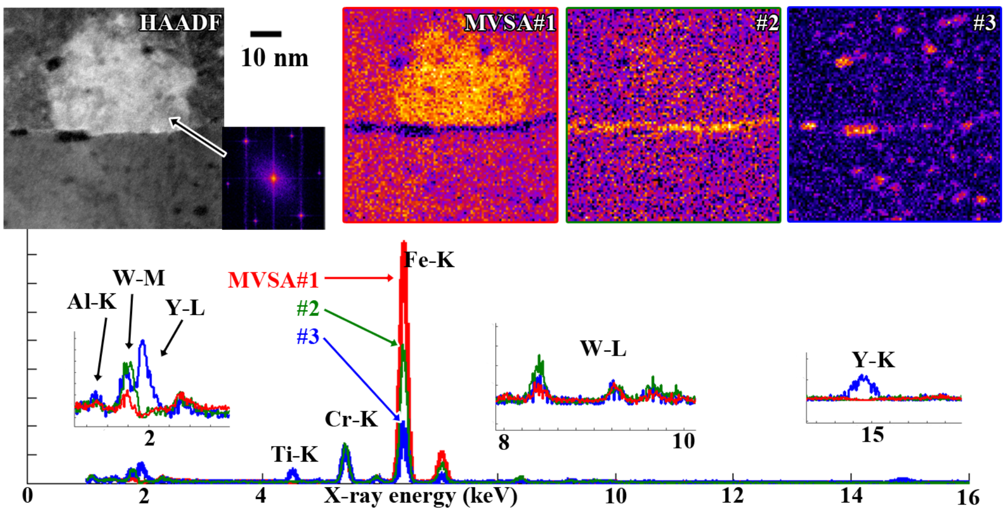

Figure 1: Left, STEM-HAADF image of several grains in NFA. Inset indicates the bright grain is at <111> orientation. Right, MVSA of EDS spectrum image, showing three components. Third component (blue outline and blue EDS loading spectrum) is Ti-Y-rich NCs with sizes ~1 nm detected in the 20~50 nm-thick foil.

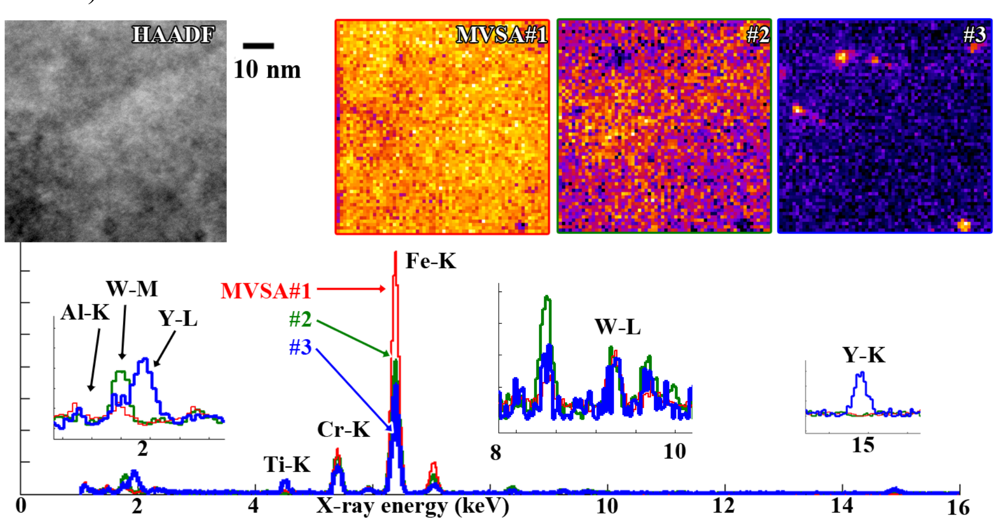

Figure 2: Left, STEM-HAADF image of several grains in cryo-irradiated NFA. Right, MVSA of EDS spectrum image, showing three components. Second component (green outline and EDS loading spectrum) is a diffuse grain boundary indicting blurring of the sharp segregant profile. Third component (blue outline and EDS loading spectrum) shows a low density of NCs, indicating ballistic dissolution of many NCs leaving only remnants of the larger particles.

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