Challenges in EFTEM Elemental Mapping of Nanostructures

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Although elemental mapping at the nanometer scale by EFTEM is considered well established, new challenges continue to emerge. Examples from three classes of nanostructured materials not only confirm the utility and power of EFTEM, but also illustrate limitations in sensitivity and standard methodologies. The impressive high-temperature mechanical properties of a new class of mechanically alloyed (MA) oxide-dispersion-strengthened (ODS) ferritic steels are due to high concentrations (~10²⁴ m⁻³) of small (~2 nm) clusters enriched in Ti, Y and O. Conventional BF-DF TEM and HAADF STEM proved unreliable for imaging the nanoclusters, but EFTEM methods have provided important information on cluster distributions for structure-property-processing correlations. In particular, Fe-M jump-ratio images, which because of the strong signal can easily be formed with 10-eV wide slits and exposures ~1s, clearly reveal the clusters in dark contrast and are insensitive to unavoidable surface oxide films. However, the contrast (≅ d/t, where d = cluster diameter and t = specimen thickness) requires t ≤50 nm for the smallest clusters to be visible. Ti-L₂₃ maps which have high contrast but low S/N (anti-) correlate well with the Fe-M, but Y mapping has been unsuccessful because of insufficient sensitivity. Surface oxide films generally obscure the clusters in O maps, and even lead to reverse contrast in O jump-ratio images because of the tails of the Ti-L₂₃. In basic studies related to the MA ODS ferritic steels, powders of Ni₂Y and NiO reaction ball-milled at 30 and 100°C were found to transform to a ~10-nm scale complex structure of fcc Ni particles in an almost continuous Y-O amorphous phase, with some residual NiO. Elemental mapping was performed on powder samples thinned by FIB milling. Mapping of O-K and Ni-L₂₃ was straightforward, but reliable mapping with Y-M₄₅ could not be achieved because of the edge shape. Mapping with Y-L₃ was eventually successful. To offset the small signal, a DigitalMicrograph custom script for segmented acquisition allowed extended exposures without concomitant problems from specimen drift. This same segmented acquisition scheme has been employed in attempts at mapping B in Co(Cr, Pt) magnetic recording media, where the issue is not one of small signal but rather one of small signal/background which, together with a complex background shape from the tails of the Co and Cr M edges, limits the reliability of background fitting/subtraction. In these thin films, which typically have 10-nm diameter columnar grains, intergranular segregation decouples the magnetic exchange between grains and is critical for good coercivity and transition noise. Intergranular co-segregation of B and Cr has been confirmed. In all three examples, complementary spectrum imaging in STEM mode has been helpful, especially for EDS measurements of W, Y and Pt [1].

References
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