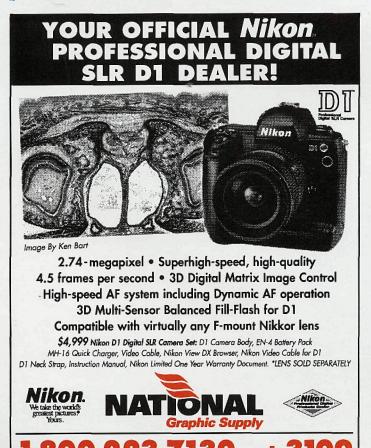# ENERGY-FILTERED IMAGING

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Over the several years that imaging energy filters have been available commercially, numerous and wide-ranging applications have demonstrated elemental mapping with a resolution approaching 1 nm. A few reports have even shown resolutions <0.4 nm. Elemental mapping by energy-filtered transmission electron microscopy (EFTEM) is clearly an attractive and powerful tool, but some aspects of the techniques can be complex, with many pitfalls awaiting the unwary. This tutorial aims to cover some practical aspects of elemental mapping by EFTEM. It is based largely on the author's work at the ORNL SHaRE User Facility, where EFTEM research has been performed since 1994 with a Gatan imaging filter (GIF) interfaced to a Philips CM30T operated at 300 kV with a LaB_6 cathode.[1-20] Most of the applications have been to metals and ceramics, emphasizing interfacial segregation and precipitation.

For quantitative composition mapping by EFTEM a number of interrelated parameters [field of view, resolution (δ), collection angle (β), energy window or slit width (Δ), incident beam divergence (α), illumination uniformity, probe current (i), drift rate, exposure time (T), and local specimen thickness (t)] should be properly selected and controlled. For example, the collection angle should be large enough for a strong signal, but not so large that the signal/background (S/B) and chromatic-aberration-limited spatial resolution are both degraded.[15] For optimum signal/noise with minimum exposure and just-sufficient over-sampling, m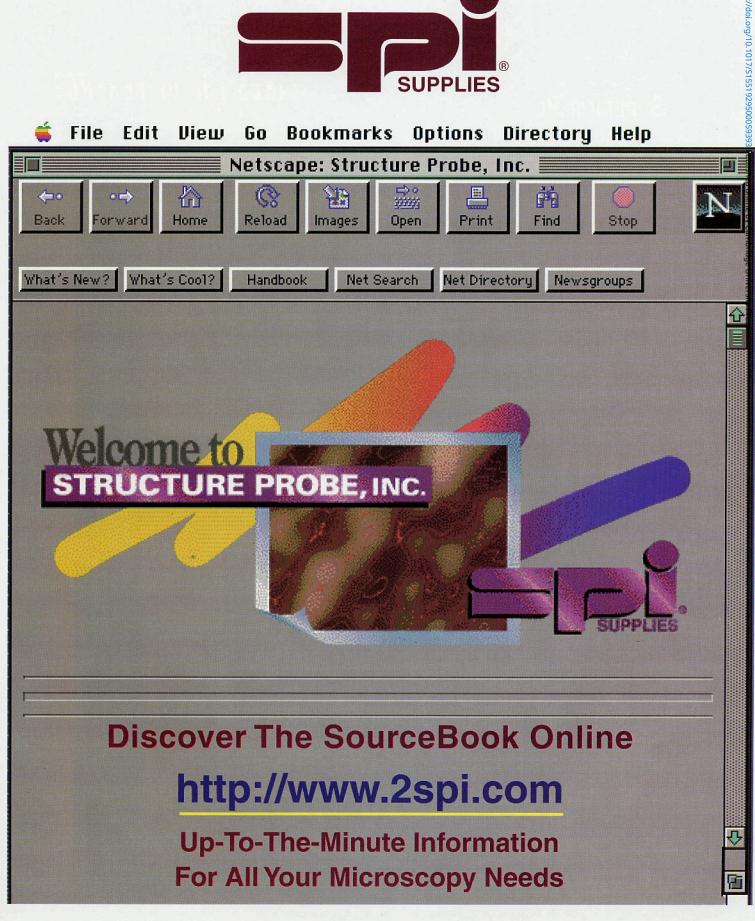icroscope magnification and on-chip binning should be adjusted so the desired (or achievable) resolution is 2 or 3 pixels. A typical configuration for mapping with 3d transition-metal L edges used by the author is: α=2.9 mrad, β=4.8 mrad, i=200 nA, Δ=30 eV, T=15 s, 2x on-chip binning (512 x 512 pixels), ~4000x TEM magnification, ~0.6 nm/pixel, δd~1 nm, >10^4 CCD counts/pixel, and t/λ=0.5 ± 0.2 (where λ is the inelastic scattering mean free path). Jump-ratio (2-window) and net core-loss intensity (3-window) maps are routinely produced and compared, in part to help detect artifacts. Zero-loss I_0 (Δ<10 eV), low-loss I_k (same Δ as used for core-loss images), and unfiltered images I_T are also routinely recorded, as are electron energy-loss spectra (EELS). Local thickness is monitored from maps of t/λ = ln(I_T / I_0). Based on established EELS procedures, first-order correction of weak diffraction contrast can be made by dividing net core-loss intensity images ("elemental maps") by I_k, yielding areal concentrations. Further division by t/λ (as an approximation for t) yields image intensities proportional to concentration in atoms/vol.[2,5] This method assumes λ is constant, often a good approximation for segregation in single-phase materials. However, defocusing the illumination to record I_0, I_k and I_T causes subtle changes in diffraction contrast and in the angular distribution of scattering, so the corrections are not exact. Alternatively, a ratio of net core-loss intensity maps for two elements minimizes diffraction contrast effects. For analytical situations where elemental concentration ratios are useful, this latter method is often more effective than the low-loss normalization scheme.[16] Quantitative compositions are obtained with calculated ionization cross-sections or k-factors. Given the small window widths (typically 30 eV), which are contrary to good EELS practice, and the effects of near-edge structure (such as white lines) on the accuracy of calculated cross-sections, compositions are often surprisingly accurate.

An important performance parameter in elemental mapping is sensitivity. However, as in EELS, sensitivity depends critically on the particular combination of elements and edges; it is difficult to provide even general rules-of-thumb. The critical parameter determining sensitivity is the S/B ratio. The expected signal for a particular composition and set of measurement conditions is relatively well understood and can be calculated. The background is not as amenable to calculation since it arises from the tails of all the lower-energy edges, plasmons, and valence excitations. (Researchers are still waiting for the development of an "EELS simulator" that would be equivalent to DTSA for X-ray microanalysis.) The L_{23} edges of the 3d transition metals are well suited to EFTEM elemental mapping; they have large cross-sections, sharp onsets (some with strong white lines) and the background is generally well described by an inverse power law (AE^{-r}). These desirable characteristics have been exploited to achieve high sensitivity measurements in steels,[1,4,5] superalloys,[2,3,5-8] and magnetic recording media.[12,13,16] With their sharp onsets, K edges are also well suited to EFTEM core-loss mapping, but their smaller cross sections can lead to poor sensitivity. For example, carbon and boron maps of precipitates in structural alloys are often of limited quality as a result of low S/B.[5,7] Some M edges, especially those with white lines, provide high sensitivity.[4,6] For edges with delayed maxima, however, background extrapolation becomes the limiting factor, especially in non-power-law regions such as <200 eV, and reliability is degraded. Satisfactory jump-ratio maps can usually be produced but provide only qualitative information.[4] For many elements the low-energy edges are unsuitable for 3-window mapping

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and higher-energy edges produce too low a signal. Such elements are thus not amenable to high-resolution quantitative composition mapping with good sensitivity.

The long exposures and intense illumination commonly used for composition mapping mean specimen drift is almost unavoidable. Accurate alignment of the component images in a series is critical to avoid artifacts. Misalignments of just one pixel can lead to strong black-white (B-W) contrast. Even sub-pixel misalignment can result in B-W artifacts at strong contrast gradients. As an alternative to cross-correlation, which often does not cope well with the contrast reversals in core-loss imaging, minimizing B-W contrast effects (or quantitatively the variance) of the ratio of two images has been found to work reliably and sensitively, even for low-contrast fine image detail. Drift within the duration of each component exposure of a series has been reduced by the use of multiple shorter exposures at each energy-loss. Since the images in each sub-series should have identical contrast, alignment by (automated) cross-correlation is appropriate. A log-polynomial background-fitting scheme has been developed for use where power-law dependence is not sufficiently accurate, such as for energy losses <200 eV.[14] Closely spaced edges present a challenge for EFTEM elemental mapping. For the case of Cr-L_{23} and O-K edges, a 4-window method has been developed and applied with considerable success. Reliable Cr-L_{23} intensities have been mapped for Co-Cr based magnetic recording media[16] and for ferrite in a dual-phase steel,[17] both instances where surface oxide films on TEM specimens seem almost unavoidable. To

achieve the optimum performance, deconvolution of the point spread function of the detector should be performed. This is especially true for sharp local minima in concentration where the "tails" from the adjacent high-concentration area(s) can lead to substantial increases in the apparent minimum concentration.

Near-edge fine structure can be a rich source of chemical bonding information. With narrow energy-selecting slits, it has been demonstrated that in favorable cases bonding information can be mapped with high spatial resolution by EFTEM. The valence of 3d transition metal cations in oxides has been mapped through the L_3/L_2 white line intensity ratio, which depends sensitively on valence.[18,19] Differences in the ratio of sp^2 to sp^3 bonding in carbon films have been mapped through the ratio of π^* to σ^* intensities.[20] Such EFTEM methods have some advantages over methods based on scanning transmission electron microscopy (STEM). In fact, spectrum imaging by EFTEM rather than STEM should be seriously considered as the method of choice in situations where electron dose is not an issue and where data for many (e.g., 10^6) image pixels are required.

Often in materials science, one-dimensional variations in composition or bonding normal to interfaces control material properties. Spectrum lines produced in the TEM mode with a GIF provide one-dimensional information on variations in fine structure (low-loss region or core-loss edges).[9-11,20] This TEM spectrum-line method is based on the fact that in spectroscopy mode the GIF optics produce a line focus with one-dimensional spatial information retained normal to the energy dispersion direction. A 2 x 0.5 mm Au slotted washer mounted in the GIF entrance aperture normal to the energy dispersion direction has been used to select image areas. Interfaces are aligned edge-on and normal to the slot

with a tilt-rotation specimen holder. The chief limitation of the TEM spectrum line method is that, just as in compositional mapping, spatial resolution is determined by chromatic aberration [$\delta = C_c.(\Delta/E).\beta$, where E is the incident energy]. Thus, widely separated edges are incompatible with high spatial resolution, and <1nm is achievable only for a limited energy range (typically 20 eV).

Finally, in some applications, plasmon imaging can be used to monitor composition indirectly. The large signal means high sensitivity can be achieved and video-rate recording is possible. Again ~1nm resolution has been achieved, e.g., in studies of metallic Al particles in ion-implanted $MgAl_2O_4$ spinel.[5] Background subtraction was even attempted with some success. For situations that produce only small plasmon shifts, effective EFTEM mapping may be precluded, but spectrum-lines at interfaces may offer advantages over the alternative, spectrum imaging in a STEM.[21] ■

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