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TITLE ➡ MATERIALS SCIENCE APPLICATIONS OF A 120kV FEG TEM/STEM: TRISKAIDEKAPHILIA

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The introduction by several manufacturers of 200kV transmission electron microscopes (TEM) equipped with field emission guns affords the opportunity to assess their potential impact on materials science by examining applications of similar 100-120kV instruments that have been in use for more than a decade.[1] This summary is based on results from a Philips EM400T/FEG configured as an analytical electron microscope (AEM) with a 6585 scanning transmission (STEM) unit, EDAX 9100/70 or 9900 energy dispersive X-ray spectroscopy (EDS) systems, and Gatan 607 serial- or 666 parallel-detection electron energy-loss spectrometers (EELS). Examples in four areas that illustrate applications that are impossible or so difficult as to be impracticable with conventional thermionic electron guns are described below.

Imaging. The high brightness and coherence of illumination provides outstanding TEM phase contrast imaging performance. Not only is this useful in high resolution electron microscopy (HREM) lattice imaging studies, for example dumbbell splitting in Si <110> images was observed with 0.3s exposures,[1] but also in lower resolution work such as imaging the Fe-rich α and Cr-enriched α' nm-scale isotropic modulated structures caused by spinodal decomposition of the ferrite phase of aged duplex CF8 stainless steel.[2] Improved phase contrast in glancing-incidence reflection electron microscopy (REM) increases the fine structure in images of surface steps and dislocations and has allowed the detection of sub-0.1-nm surface steps on α-Al_2O_3.[3] Bright- and dark-field STEM image resolution for a FEG instrument is superior to that of a non-FEG instrument but is still normally inferior to that of equivalent TEM images. However, in STEM, "dynamical" contrast effects (e.g. bend contours) can be suppressed and image contrast can be adjusted electronically. High-angle annular dark-field (so called Z-contrast) STEM images are even more useful. A nearly equivalent Z-contrast TEM mode has been demonstrated but a FEG provides no advantage.[4]

Diffraction. The highly coherent (parallel) illumination with a FEG allows extremely fine detail in selected area diffraction (SAD) patterns to be easily viewed and recorded. For example, in SAD patterns of SiC made by chemical vapor deposition, the "streaks" along the $<111>_\beta$ (or $<0001>_\alpha$) growth direction are revealed to consist of finely spaced maxima. This material has one-dimensional disorder with neighboring regions corresponding to various α polytypes (predominantly 2H, 4H, and 6H) as well as β, each only one or a few unit cells thick. Similar, but more periodic, maxima are observed in diffraction patterns from long period polytypes. Although a FEG provides no fundamental advantage for producing convergent beam electron diffraction (CBED) patterns containing high-order Laue zone (HOLZ) lines, the fine structure is easily visible on the viewing screen. This was of benefit in determining the long-range-order parameter of $(Fe,Ni,Co)_3V$ alloys from changes in lattice parameter measured from changes in the accelerating voltage at which 3 HOLZ lines intersected at a point in <111> CBED patterns.[5] Similarly, crystal symmetry determination from CBED, an important part of phase identification, can be much easier with a FEG, even though equivalent data could be obtained with a thermionic source. In the identification of $Al_{12}Mo$ pseudo-lamellar second phase in annealed molybdenum-implanted aluminum, the ease-of-use and good shadow image resolution were not inconsequential factors in determining the space group by CBED from the highly buckled precipitates.[6]

X-ray microanalysis. Most of the advantages of a FEG-AEM for X-ray microanalysis result from the high source brightness. The compositions of precipitates in stainless steels can be complex, requiring good statistical accuracy for confident modeling of the behavior of minor alloying additions. For the analysis (on extraction replicas) of particles with a size of only a few nm the high current density probes from a FEG are almost essential. Radiation induced segregation (RIS) in stainless steels can lead to dramatic changes in materials behavior and has been studied extensively, not least because of the practical importance for operating nuclear reactors. The

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depletion of chromium at grain boundaries is of particular concern, and whereas AEMs with thermionic sources can detect a composition change, a FEG-AEM can provide a more accurate measure of the minimum Cr levels reached and other important subtle details of the segregation profiles for even the minor alloying elements.[7] An even more challenging problem is posed by the measurement of equilibrium segregation of minor or trace solutes at grain boundaries, since the segregant is confined to one or two atomic planes at the boundary. Statistically significant (3σ) levels as low as 0.?6 at.% P in the excited volume, corresponding to 6% of a monolayer coverage of the grain boundary, were measured in studies of type 304L stainless steel.[8] The <2-nm-diameter probe was maintained on the (edge-on) boundary through monitoring the diffraction pattern. In earlier work, antimony segregation was detected at individual grain boundary dislocations in an antimony-doped stainless steel.[9] The atom location by channeling enhanced microanalysis (ALCHEMI) technique has been applied to determine the sublattice occupancies of ternary additions to CuAu alloys which have the $L1_0$ structure and typically are micro-twinned as a result of their tetragonality.[10] ALCHEMI analyses thus required the use of small probes. The good shadow image resolution was also helpful in setting up the appropriate diffracting conditions.

Electron energy-loss spectroscopy. The high source brightness of a FEG is likewise an advantage for small area analyses by EELS. Although, in principle, small areas can be selected from high magnification images with the EELS entrance aperture, the chromatic aberrations of the image-forming system limit the area selection for most core-loss studies, and operation in the diffraction mode with area selection by the probe is necessary. These effects were clearly important in the analysis of sub-10-nm intragranular particles of B_4C in crept, sintered α-SiC.[11] The measurement of RIS profiles in stainless steels by PEELS has been performed to complement EDS measurements.[12] For some conditions, the potential higher spatial resolution from the reduced importance of beam spreading, can give more accurate compositions. Another advantage over EDS is the ability to analyze for small manganese levels in radioactive neutron-irradiated steels, or even to be able to analyze very radioactive specimens at all.[12] A final aspect of EELS with a FEG is the improved energy resolution. With cold field emission, less than 1 eV resolution is routinely achievable, opening up many possibilities for detailed low-loss and near-edge fine structure analyses, such as in diamond films or oxide ceramics.

Two kinds of improvement are expected for a 200kV FEG AEM – resolution and penetration. With electron holography, the present HREM performance of 300 or 400kV instruments may be exceeded. The increased penetration may be most helpful in EELS (e.g. less sensitivity to unwanted surface films). With some new FEG designs, the availability of larger spot sizes and beam currents for conventional TEM operating modes could be an important practical improvement.

As for our 120kV FEG AEM, there are, of course, features of the performance (probe size, vacuum, etc.) that are exceeded in newer or more specialized instruments, and limitations that are shared by other instruments (such as beam damage and hole drilling), but the 13 examples described above and 13 years of productive use seem to us to be grounds for triskaidekaphilia.[13]

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