X-RAY MICROANALYSIS USING AN HVEM*

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The interfacing of an energy dispersive x-ray spectrometer (EDS) to an HVEM has been suggested during the last few years as a means by which the mass sensitivity of x-ray analysis in a TEM can be increased. The prediction of higher sensitivity is related to the anisotropic distribution of continuum radiation generated by high energy electron excitation of a thin sample. Depending on the geometry, this can result in an increase in the measured peak-to-background (P/B) ratio of a characteristic line relative to excitation using lower energy electrons.[1] In addition, the unique combination of a large pole piece gap and a wide variety of in-situ experimental stages makes an HVEM an ideal candidate for real-time microanalytical measurements during controlled dynamic events such as precipitation and fracture.

The instrument used for the experimental work described below was a Hitachi HU-1000 high-voltage transmission electron microscope operating at an accelerating voltage of 1 MV. In addition to the instrumental modifications discussed in this text, the microscope has been recently converted to support a side-entry goniometer (SEG) stage (GATAN, Inc.) providing a wide variety of specimen holders for in-situ studies. Particularly relevant to this experiment is the accessibility to the sample chamber provided by eight ports symmetrically spaced around the column resulting from the side-entry conversion. With this geometry it was possible to position the x-ray detector perpendicular to the primary tilt axis of the SEG stage, thus minimizing the tilting requirements necessary to obtain characteristic information from the sample.

X-ray measurements were made using a KEVEX Si(Li) solid-state x-ray detector with an active area of 10 mm^2 together with a model 5100 multichannel analyzer. Figure 1 shows the experimental geometry currently in

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use on the HVEM. The detector axis is located 4 mm below the electron exit surface of the specimen, while the distance from the electron-optical axis to the Si(Li) crystal is approximately 5 cm. This arrangement provides a detector observation angle[1] of 85° relative to the forward scattering direction which is the best geometry currently attainable in this instrument. A lead collimator was used to shield the detector from backscattered electrons as well as bremsstrahlung radiation. The minimum thickness used was 4 mm. The entrance window of the collimator was fixed at 2.5 mm in diameter. Unless otherwise specified, all spectra were recorded using a probe diameter of 0.75 μm, at a beam current of $\sim 2.5 \times 10^{-9}$ A for 400 s.

In order to minimize the contributions of systems peaks generated by uncollimated radiation, as well as to optimize the "line-of-sight" x-ray path from the detector to the sample, a special single-tilt stage was designed. The stage block was machined from aluminum, the specimen being supported by a graphite insert. This insert effectively isolates the immediate vicinity of the sample from all material of atomic number greater than six. With this arrangement, characteristic x rays from the sample can be detected with a tilt as small as 10° off the horizontal; furthermore, no aluminum systems peaks have been detected. However, a small copper peak from the objective aperture can be detected.

A single-crystal specimen of β-NiAl of the 50–50 at. % composition was used to evaluate the performance of HVEM based x-ray microanalysis. Fig. 2(a) shows typical x-ray spectra measured under various experimental configurations with the probe static on the specimen, while 2(b) shows the hole-count spectra[2] recorded under identical conditions. The spectra labeled A in both these figures were recorded without any modifications to the electron-optical column other than the insertion of the x-ray detector. Clearly, there is a substantial bremsstrahlung flux as demonstrated by the in-hole spectrum of Fig. 2(b); fluorescence[2] effects are minimal, however. In order to increase shielding of the detector from the huge bremsstrahlung flux the detector assembly in the immediate vicinity of the Si(Li) crystal was subsequently wrapped in lead foil to a thickness of 3 mm. Spectra B in Figs. 2(a),(b) illustrate the corresponding changes in the measured continuum intensity distribution. The

last set of spectra (C) were obtained after the insertion of a special bremsstrahlung aperture and the addition of shielding above the upper pole piece of the objective lens (see Fig. 1). Lead sheet was stacked on top of the pole piece to a thickness of ∿2 cm and an aperture 2 cm thick having a central hole 0.5 mm in diameter was positioned on the optic axis. Furthermore, the detector collimator thickness was increased at this point to 1.5 cm. Even though a 90% reduction in the bremsstrahlung intensity has been achieved at this point, the background intensity measured with the probe on the sample is still indistinguishable from the in-hole count, indicating that additional shielding is necessary. Currently the feasibility of using depleted uranium machined to the proper shape is being investigated to help alleviate this problem.

It is, however, possible to assess the proposed advantage of HVEM based microanalysis at this time by undersaturating the filament emission which results in a substantial decrease in the bremsstrahlung flux irradiating the x-ray detector. Although this creates appreciable electron tails, the validity of the results is not substantially altered at this stage of the experiment. Figures 3(a),(b) show typical spectra obtained under these conditions using a probe current of $\sim 2.5 \times 10^{-11}$ A and a 1000-s acquisition time. As can be seen the in-hole count has been reduced to less than 25% of the specimen spectrum. By subtracting the in-hole from the sample spectrum as a first-order correction P/B ratios of ∿85/1 and 18/1 for Ni K_α and Al K_α , respectively, are obtained. These can be compared to values measured at 120 keV of ∿35/1 (Ni K_α) and ∿11/1 (Al K_α) for the same β-NiAl alloy obtained on a JEOL 100 C TEM/STEM instrument under similar operating conditions. It, therefore, appears that with sufficient instrumental modifications an effective increase in the measured P/B ratio can be realized, and further work is in progress to improve these results.

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References

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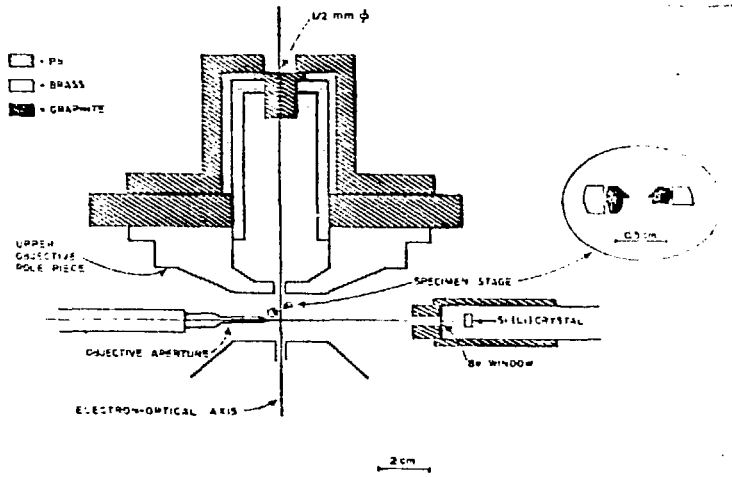

Fig. 1. Experimental geometry for x-ray measurements in Hitachi HU-1000. HVEM.

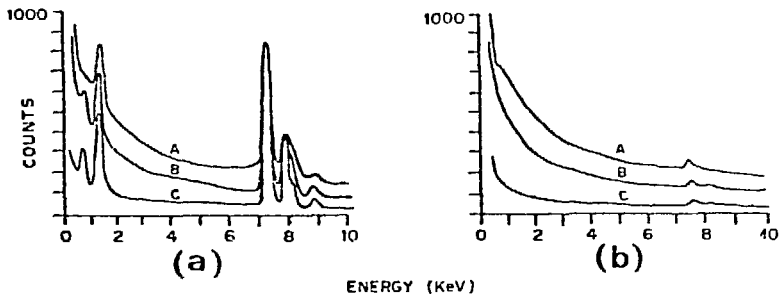

Fig. 2. Variation in sample (a) and hole-count spectra (b) as a function of operating conditions in HVEM (see text for details).

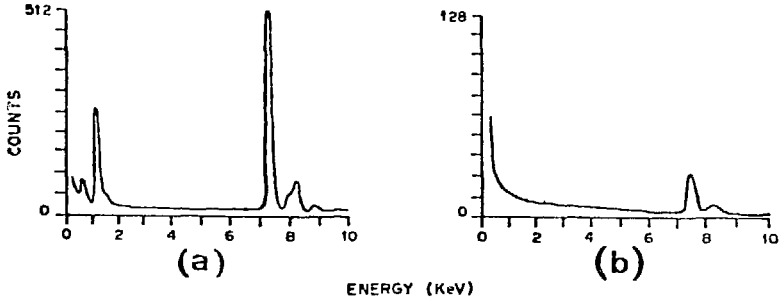

Fig. 3. Effects of reduction of bremsstrahlung flux on the measured x-ray spectrum (see text for details).