APPLICATION OF AEM TO DIFFUSION-CONTROLLED PHASE TRANSFORMATIONS

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The AEM has been used extensively to measure chemical concentration gradients and compositional data with submicron resolution at grain and phase boundaries. The use of these measurements has contributed to the understanding of diffusion-controlled phase transformations, such as precipitate growth, in metals, ceramics, and other materials. This paper discusses the measurement of chemical composition and the limitations of x-ray microanalysis at the sub-micron level, and gives several examples of the application of x-ray microanalysis data to diffusional transformations in solids.

Numerous types of diffusional transformations take place in solids. Both precipitation and eutectoid transformations involve the formation of phases with a composition different from that of the matrix and therefore long-range diffusion is required. In order to study these transformations it is necessary to measure the chemical gradients that develop as a consequence of the transformation and the interface compositions of the various phases, which are often controlled by the equilibrium phase diagram. This paper discusses the use and limitations of the modern analytical electron microscope (AEM), which allows x-ray microanalysis at the sub-100nm range.

Measurement of Compositional Data

The x-ray intensity from the specimen is usually measured by use of an energy-dispersive x-ray detector (EDS) with a Be window to protect the Si(Li) detector. However, the Be window absorbs low-energy x-rays from the light elements such as B, C, N, and O. New windowless detectors, which require removal of the Be vacuum window and fabrication of a detector with as small a dead layer on the surface of the Si(Li) as possible, have been developed. These detectors can measure the light elements down to boron. Figure 1 shows the presence of C and O in an EDS spectrum obtained from a <10nm carbide by a field-emission AEM.

If we assume that x-ray spectra are obtained from the desired regions of the specimen and that the intensity \( I_A, I_B, \ldots \) of elements A, B, \ldots after continuum background subtraction can be obtained, the composition of the specimen \( C_A, C_B, \ldots \) can be calculated using the ratio technique. The ratio technique can be expressed as

\[
\frac{C_A}{C_B} = \frac{k_{AB}}{I_A/I_B}
\]

where the \( k_{AB} \) factor or the Cliff-Lorimer factor is a constant at a given operating voltage. The values of \( C_A, C_B, \ldots \) can be calculated separately, since the concentration values sum to 1.0. The \( k_{AB} \) factor can be calculated but should be measured from a known standard if at all possible to increase the accuracy of the composition determination. The Cliff-Lorimer factors are all close to 1.0 showing that the correction for matrix effects is relatively small. Equation (1) can be used directly if it is assumed that the specimen is appropriately thin as discussed in the next section.

Limitations of X-ray Microanalysis in the AEM

The spatial resolution or the diameter \( d_1 \) of the x-ray analysis volume is limited by two factors, the size \( d \) of incident electron beam and the amount of beam broadening \( b \) caused by elastic scattering in the specimen. These terms are related by

\[
d_1^2 = d^2 + b^2
\]

and are illustrated in Fig. 2. Since beam broadening is proportional to the thickness of the thin foil and inversely proportional to the operating voltage, one should prepare as thin a foil as possible and operate at as high a voltage as possible. There is a trade off, however, in that x-ray intensity from the specimen is directly related to the thickness of the specimen. To offset a loss in x-ray intensity, a brighter electron gun than W or LaB\(_6\) (such as a field-emission gun, FEG) can be used. The FEG can be used to produce more current in an electron beam of the same size so that a thinner specimen can be analyzed. To obtain quantitative <10nm spatial resolution, an FEG is essential. Figure 1 shows a spectrum obtained from a <10nm carbide with an FEG. Despite the small particle size, this spectrum contains sufficient counts for quantification.

Figure 3 shows a high-spatial-resolution microanalysis of chromium across a carbide plate in a pearlite structure. The analysis was accomplished in a Vacuum Generators FEG microscope operating at 100 kV and the foil was 20 nm thick. Spatial resolution of the order of 2 nm is demonstrated. The spatial resolution is consistent with calculations of beam broadening \( b \); we note for purposes of using Eq. (2) that the incident electron-beam diameter \( d \) is less than 1 nm. An additional advantage in spatial resolution can be derived from the use of accelerating voltages higher than 100 kV, but the resultant spatial resolution is not as good as that predicted by various beam broadening models.

The analytical sensitivity or minimum detectable mass (MMF) of a specimen is limited by the x-ray intensity from the element of interest, the x-ray peak to background intensity, and the analysis time. Figure 4 shows the variation of MMF with spatial resolution, both
FIG. 1.--Windowless x-ray spectrum from <10nm Nb, V carbide on (oxidized) Al replica. Acquisition time 100 s (live) at 100 kV, with use of field-emission gun (courtesy J. R. Michael).

FIG. 2.--Schematic representation of concept of spatial resolution in thin-foil microanalysis. Spatial resolution $d_1$ is determined by beam-incident $d$ and amount of beam spreading in thin-foil specimen.

FIG. 3.--Measurement of Cr concentration as function of position across cementite plate in $1\%Cr-1\%Mn-0.84\%C$ steel transformed at 530 °C for 54 s. Spatial resolution of the order of 2 nm is demonstrated. (From K. D. Sinha and R. S. Sinha, 1983.)

FIG. 4.--Spatial resolution vs elemental sensitivity in x-ray microanalysis. Extrapolations of data to 300 kV are shown as shaded areas. (From C. E. Lyman.)

FIG. 5.--Goat's flight vs minimum mass fraction detectable (wt. %). (From A. J. Garratt-Reed.)

FIG. 6.--Ni-Cr-Mo ternary section at 850 °C as determined by x-ray microanalysis in AEM. (From Raghavan Ayer.)
measured and calculated, for various types of AEMs. Instruments that have smaller MMF and smaller spatial resolution are considered to have better analytical performance. Improvements in both spatial resolution and sensitivity should be derived from the use of intermediate voltages such as 300 kV. More significant improvements are obtained by the use of the field-emission AEM.

Quantification errors that arise from the ratio method of Eq. (1) are typically small as long as the specimens are sufficiently so that absorption effects are less than 3%. Errors in the experimental values of $k_{AB}$ are usually no more than 1-5% and x-ray counting errors are usually no more than 2%. Therefore limits in the measurement of the ratio $C_A/C_B$ from Eq. (1) are usually around 5%. If calculated $k_{AB}$ factors are used, the measurement limit is higher.

The thin-film criterion or the thickness at which absorption effects are significant has been developed for x-ray microanalysis. If absorption must be considered, the thickness of the specimen must be measured and specific corrections must be made to Eq. (1). In the specific case of the light elements, major absorption effects in the specimen and in the Si(Li) detector make it difficult to measure or to calculate $k_{AB}$ factors accurately. In the case of the light elements, analyses at an accuracy level of 10-20% is currently all that can be achieved.

In the use of thin specimens and operating voltages exceeding 100 kV, specimen contamination and specimen damage may occur. Several examples of problems of this type have been described, and as x-ray spatial resolution and sensitivity are improved these factors become more important.

Applications to Phase Transformations

X-ray microanalysis in the AEM has been used to determine appropriate phase diagrams and diffusion coefficients which are the controlling factors in diffusional phase transformations. In the case of phase diagrams, x-ray microanalysis of phases in equilibrium in a two-phase region of the phase diagram yields the line compositions. X-ray microanalysis of phases in equilibrium in a three-phase-region of a ternary phase diagram yields compositions of the three phases and one measurement gives the entire outline of the three-phase field. Figure 5 shows concentration profiles of Cr and Mo across an equilibrated two-phase region in the Ni-Cr-Mo system. The sample was aged at 850 C for 1000 h. Figure 6 displays the complex Ni-Cr-Mo ternary diagram at 850 C determined from the data of Fig. 5 and a series of samples. Even if total equilibrium cannot be achieved between two phases, local equilibrium at two-phase interfaces may exist and tie lines can be measured as has been demonstrated in the measurement of the Fe-Ni-P phase diagram.

In the case of diffusion coefficient measurement, the AEM has been applied only recently. Because the x-ray spatial resolution is at least 50 to 100 times better than that of the electron probe microanalyzer, one can measure diffusivities as much as 10⁶ times smaller when the diffusion experiments are run for the same heat treatment time. Diffusion gradients can be as short as 1 μm and yield adequate data. This improvement in x-ray spatial resolution allows one to measure diffusion data at much lower temperatures than had been possible previously. As an example, Fig. 7 shows a Ni concentration gradient 2 μm in length in a Fe-20 Ni-P vs Fe-25 Ni-P diffusion couple heat treated at 650 C for 121 days measured by AEM techniques.

Recently the AEM was also used to determine intrinsic diffusion coefficients in the Ta-W system.

X-ray microanalysis in the AEM has been applied to a number of different types of diffusional controlled phase transformations. Typical examples of the use of AEM are in precipitation, eutectoid formation, and grain boundary segregation. Figure 8 shows a Ni concentration gradient developed in the austenite phase when ferrite forms during the cooling of a 0.88 Ni, 0.49 P, Fe alloy from 790 to 650 C. Full equilibrium partitioning occurs during the precipitate growth in the Fe-Ni-P system. This type of experimental data has been used to understand the development of the Widmanstatten pattern in iron meteorites. Figure 9 illustrates the partitioning of Si between austenite and ferrite during a step quench treatment at 950 C in an Fe-Si-V-C dual-phase steel. Si and V do not partition during the step quench heat treatment, but local equilibrium is maintained at the ferrite/austenite interface. This figure illustrates the local equilibrium no-partition condition. Several other AEM studies of dual-phase, eutectoid, and microalloyed steels have investigated element redistribution in carbonitride, pearlite, and cementite formation.

As an example, Fig. 3 illustrates the Cr redistribution during pearlite formation in a 1Cr-19Mn-0.84Cr steel. X-ray microanalysis in the AEM has been applied to studies of reactions at or near grain boundaries. Precipitate free zones form at grain boundaries and are generally due to either solute depletion or vacancy depletion. These zones are typically up to 0.5 μm wide, for example in Al-Zn-Mg and Cu-Ni-Nb alloys, and AEM x-ray microanalysis is ideally suited to the study of this type of phase transformation. Other diffusion-controlled phase transformations of this type include sensitization of stainless steels.

More challenging AEM analysis occurs in the case of grain boundary segregation. This type of transformation occurs within 1 mm or less of the grain boundary and the spatial resolution $d_1$ of the x-ray emission volume is much larger, as shown in Fig. 10. Optimization of the spatial resolution and the analytical sensitivity (MMF), as discussed earlier, is essential in this type of analysis. Experimental studies show for example Cr$_2$O$_3$ segregation in NiO, Fe segregation in MgO, and Cr and Sn segregation in low-alloy ferritic steels. Computer calculations based on Monte Carlo or other techniques have been applied with some success in separating the effect of the large spatial resolution of the x-ray source.

In summary, the AEM can be applied successfully to the measurement of compositional data in order to characterize and understand various

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types of diffusion controlled phase transformations. With the advent of intermediate voltage FEG instruments and with better methods of specimen preparation, the spatial resolution of the instrument will be substantially improved. With this improvement, chemical analysis of diffusional phase transformations at the sub-10nm scale will become a reality.

References

2. P. M. Budd and P. J. Goodhew, Microbeam Analysis--1986, 449.

FIG. 7. --Ni composition profile from Fe-20 Ni-P vs Fe-25 Ni-P ternary austenite couple diffused at 650 C. for 121 days. Error bars for individual points and for best-fit profile are given.

FIG. 8. --Ni composition profile measured across ferrite/austenite interface in 6.88 Ni, 0.49 P, Fe alloy cooled from 790 C to 650 C at a rate of 5°C/day. The solid line is composition profile predicted by numerical model.

FIG. 9. --Si composition profile measured across ferrite/austenite interface in 1.7 Si, 0.1 V, 0.1 C, Fe alloy step quenched to 950 C and heat treated for 1 h.

FIG. 10. --Schematic representation of interaction of focused electron beam with thin foil containing segregation in narrow planar region.