OVERVIEW OF QUANTITATIVE COMPOSITIONAL X-RAY ANALYSIS BY AEM

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During the last four years an expanding amount of work has been based on the technique of x-ray microanalysis of thin films in the analytical electron microscope (AEM). However, several problems remain that make x-ray microanalysis in the AEM a challenge: corrections for x-ray absorption, determination of beam spreading-spatial resolution, and measurement of the composition at phase interfaces and grain boundaries. The purpose of this overview is twofold: (1) to review advances in instrumentation and in compositional analysis, and (2) to discuss areas of active research in techniques for thin film x-ray microanalysis.

Recent Developments in Techniques for Thin-film X-ray Microanalysis

Ratio Method. Cliff and Lorimer\(^1\) have outlined a simple technique for quantitative analysis of thin foils in which x-ray absorption and fluorescence can be neglected. The following expression may be used:

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

where \(I_A\) and \(I_B\) are the measured characteristic x-ray intensities, and \(C_A\) and \(C_B\) are the weight fractions of any two elements A and B in the thin film.

To obtain the scaling factor \(k_{AB}\) one can either use measured or calculated values. Cliff and Lorimer\(^1\) and Lorimer et al.\(^2\) have obtained calibration curves of \(k_{ASi}\) using various silicate standards with known compositions. Figure 1 shows such a measured calibration curve for \(k_{ASi}\) obtained at 100 kV in an EMMA-4 instrument. Calibration curves should differ from one instrument to another primarily due to variations in the characteristics of the EDS. Until recently,\(^3\) very few \(k_{AB}\) factors have been measured.

Various authors have attempted to calculate \(k_{AB}\) directly.\(^4,5,6\) Figure 1 also shows an example of a \(k_{ASi}\) calibration curve calculated by Goldstein et al.\(^5\) The agreement is reasonably good except for the elements Na, Mg, and Al. Calculated \(k_{AB}\) values vary from one investigator to another owing to differing choices of the ionization cross section and the fluorescence yield for a given inner shell.\(^5,6\) The largest uncertainties occur from the choice of the ionization cross section\(^5\) when L/K or M/K combinations are considered. Further progress in the calculation of \(k_{AB}\) factors awaits the measurement of ionization cross sections for the 80-200 kV range.

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Extraneous X Rays. Investigators have been aware for some time that the measured EDS spectrum may contain x rays generated from other than the sample region excited by the focused electron beam. These additional x rays are called spurious or extraneous radiation; this problem has received much attention. It appears that the spurious x-ray signal is caused by two major effects: (1) stray radiation in the illumination system, and (2) specimen interaction with the primary electron beam.

The elimination of extraneous x rays due to stray radiation in the AEM illumination system is largely an instrument-dependent problem. With the latest AEM instruments, various modifications are now being incorporated which reduce extraneous x rays from electron and x-ray sources to acceptable levels. Various authors have suggested subtracting the spurious spectrum from the measured spectrum. In many cases the spurious spectrum may not be localized and may not be representative of the region of analysis. Such a situation argues against a simple subtraction of the spurious spectrum.

Extraneous x rays produced by scattered electrons are still somewhat instrument-dependent, but may be suitable light-element inserts that either reduce the backscatter coefficient or produce x rays not detectable in the EDS. The effect of self fluorescence can be minimized by use of thin-film specimens rather than disks and by use of high take-off angle detectors (standard on some STEMs or AEMs and being developed on others), with the specimen as close to the horizontal as possible. With such ideal microanalytical configurations, it is possible to reduce spurious contributions to the x-ray spectrum to levels at which they do not limit the accuracy of quantification.

Measurement of EDS Peak and Background Intensity. Once the sources of spurious or extraneous x rays are minimized, the measured EDS spectrum contains the information generated from the desired region of interest. Problems of EDS spectrometer resolution and artifacts such as peak broadening, Si escape peaks, absorption edges, etc. are similar to those described for the scanning electron microscope (SEM) and electron microprobe (EMP), and are well documented.

Of particular interest in the high-voltage AEM is the increased possibility of high-energy backscattered electrons that may penetrate the Be window, and of high-energy x rays generated in the specimen that may limit the acceptable count rate allowed for the EDS detector from the >10keV x rays. This latter effect is rarely a problem: in most AEM instruments the analyst faces the problem of obtaining a sufficient count rate from the thin specimen.

Methods for background modeling, background filtering, and handling peak overlaps, etc., are well documented in the SEM-EMP literature and can be applied directly to x-ray microanalysis of thin specimens. These methods produce the necessary characteristic peak intensities with the continuum background intensity removed.

Improvements in Instrumentation. In order to obtain statistically reliable values of I_A and I_B, one must accumulate sufficient x-ray counts for each x-ray peak. Until recently the effects of contamination of the analysis point limited not only the analysis time but also the amount of electron current in the focused beam. To minimize contamination, two distinct approaches are taken. The first is to minimize the contributions from the instrument. The manufacturers have recognized this problem and have developed and used oil-free vacuum systems, specific cryo-pumping around the specimen area, metallic o-rings, etc. The second approach is to minimize specimen-borne material. With contamination effects minimized, the analyst can accumulate an x-ray spectrum for analysis times of several minutes to obtain good x-ray statistics. However, specimen drift must also be limited to below 1-5 nm in the typical counting time of about 100 s or the spatial resolution of the instrument will be sacrificed.

Areas of Active Research in Techniques for Thin Film X-ray Microanalysis

Data Handling—Statistics. Only a few papers have discussed methods for determining analytical sensitivity, detectability limits, and the total error for a given analysis. In x-ray microanalysis of thin specimens, calculations of these parameters are critically important. The count rates and the peak to background levels in EDS analysis are typically low, and yield much poorer sensitivities and larger errors than in EMP analysis.

The Cliff-Lorimer relation (Eq. 1) uses the x-ray ratio I_A/I_B. The relative error for this ratio is the sum of the relative errors for I_A and I_B. For example, at the 2σ confidence level, even total accumulated counts of 10 000 for I_A and I_B still introduce a minimum
error of about 2%. Relative errors for \( k_{AS1} \) given by Cliff and Lorimer\(^1\) are of the order of 5% or more. Therefore any analysis based on these \( k \) factors has a minimum error of 5% plus the error due to the measurement of \( I_A \) and \( I_B \). New \( k_{AB} \) factors with a minimum relative error of less than 3% have been measured\(^3\) and are clearly necessary if more exact quantitative analyses are to be obtained.

The \( k_{AB} \) Factors. Figure 1 shows the large disagreement between measured\(^1\) and calculated\(^5\) \( k_{AS1} \) factors for Na, Mg, and Al. The discrepancies between measured and calculated \( k \) factors are much smaller for Mg and Al although the Na values are quite different.

Zaluzec and Fraser\(^8\) have shown that absorption of generated x-rays due to carbon contamination on the specimen can have a significant effect on the measured characteristic x-ray intensity ratio. Recent measurements of \( k_{AS1} \) factors for Na, Mg, and Al by Wood et al.\(^9\) in an environment free from carbon contamination have shown that such discrepancies continue to exist (Fig. 2). However, the \( k_{AS1} \) value of 1.12 ± 0.03 is in excellent agreement with the calculated \( k \) factor of 1.15. In addition, \( k \)-factor data such as that produced by Wood et al.\(^3\) can help provide more accurate compositional data as well as a better understanding of theoretically calculated \( k \) factors.

Absorption Correction. Criteria are available that indicate when an absorption correction must be made.\(^5,26\) If the calculation is necessary, Eq. (1) can be modified to the following form:

\[
\frac{C_A}{C_B} = k_{AB} \left( \frac{I_A}{I_B} \right) \frac{\mu/\rho}{\Sigma_{SPEC} \mu/\rho} \frac{B/\Sigma_{SPEC}}{A/\Sigma_{SPEC}} \frac{1 - \exp(-\mu/\rho)}{1 - \exp(-\mu/\rho)} \frac{B}{A} \frac{\text{spec} \sec \alpha(\psi t)}{\text{spec} \sec \alpha(\psi t)}
\]

where \( \mu/\rho \) is the mass absorption coefficient of A or B in the specimen, \( \rho \) is the density of the thin film of thickness \( t \), and \( \alpha \) is the take-off angle, the included angle between the plane of the specimen and the EDS. The effect of absorption can be calculated if \( \mu/\rho \), \( \rho \), \( \alpha \), and \( t \) are known. Unfortunately \( \mu/\rho \) and \( \rho \) are a function of \( C_A \) and \( C_B \) and an iterative technique must be employed. If non-normal electron beam incidence is used a modification of Eq. (2) may be necessary.\(^6\)

Equation (2) assumes that the x-ray generation is constant with depth. As discussed by Williams and Goldstein in another article in these proceedings\(^27\) this assumption is not always valid. Furthermore, most of the terms in Eq. (2) contain significant errors. These factors combine to make the accuracy of the absorption correction one of the major barriers to acceptable quantification of x-ray data from many materials of scientific and commercial interest.

Beam Spreading--Spatial Resolution. The spatial resolution for chemical analysis in a thin foil is a function of atomic number \( Z \), specimen thickness \( t \), and the accelerating voltage \( E_0 \). Goldstein et al.\(^5\) have based an estimate of the amount of beam spreading on a single-scattering model where electron scattering takes place at the center of the thin film. The equation which relates beam broadening of a point probe as a function of \( Z \), \( t \), and \( E_0 \) is

\[
b = 625 Z \left( \frac{\rho}{A} \right)^{0.5} 1.5 t
\]

where \( b \) is the broadening (cm), \( A \) is the atomic weight, \( E_0 \) is the voltage in kV, \( \rho \) is the density of the film in g/cm\(^3\), and \( t \) is the thickness in cm. One derives the beam-
broadening equation by assuming that the source size can be defined as that within which 90% of the electron trajectories lie.

Monte Carlo calculations of beam broadening in thin-film x-ray microanalysis have been performed by numerous investigators. The advantage of this calculation procedure is that the effect of initial beam size and interface geometries within the specimen can be taken into account. These investigators calculated the beam spreading for the 90% condition and the point probe used by Goldstein et al. and showed that the deviations in b are no greater than 40% for any of the Z and t values considered.

Doig et al. have proposed that the intensity distribution of electrons within a thin foil is analogous to the solution of the equation for the radial diffusion of heat from a point source. They argued that the incident beam intensity given by a normal distribution decays to a broader normal distribution within the foil depth. It is not clear whether this analogy is a valid one. However, if an analytical description of the electron scattering can be developed, it will be most useful for solving problems of x-ray generation at phase interfaces and grain boundaries.

Hutchings et al. have measured the spatial resolution for x-ray microanalysis in Si thin films. For the 500nm foil thicknesses normally used in defect analysis in silicon, the spatial resolution compares well with that calculated by the single scattering model or the Monte Carlo model. In addition, the experimental results for reasonable thicknesses of Si are consistent with the t and l/E dependence predicted by the single-scattering formula. Most other experimental studies of beam spreading have used a vertical interphase boundary with a step function in composition to measure the 90% probe size. Figure 3 shows such a composition profile of Ni taken every 25 nm across an α/γ interface in a 150nm thin foil of an Fe-30.7 wt.% Ni alloy.

FIG. 3.--Concentration profile across two phase region of Fe-30.7% Ni aged 120 days at 450°C; operating conditions are 100 kV with a 20nm-diameter electron probe.

FIG. 4.--Predicted Fe profile for 2.5nm beam scanned across 10nm-thick slab of iron at grain boundary of Mg thin foil; measured data are from Hall and Vander Sande.

The spatial resolution of the AEM due to beam broadening is invariably not adequate for direct measurement of the concentration of the segregant within a few nanometers of a grain boundary. The amount of x rays generated by the segregant is only a small fraction of the x rays generated from the interaction volume. Doig and Flewitt have developed a model to take this spatial-resolution problem into account. The model assumes a slab of a thickness
δ along the boundary and a cylindrical x-ray source with a spatial resolution b. In this or any other model, δ is much smaller than b. The measured concentration using the Cliff-Lorimer\(^1\) approach can be used to calculate the concentration of the grain boundary segregant.

The Doig and Flewitt model\(^3^4\) has been improved by incorporation of the single scattering model\(^3^5\) and by the use of the Monte Carlo approach.\(^3^6\) Figure 4 shows a predicted profile for a 2.5 nm beam scanned across a 10 nm-thick slab of iron at the grain boundary of an Mg thin foil.\(^3^6\) Measured data by Hall and Vander Sande\(^3^7\) are also displayed. The apparent beam spreading is about 10 nm; the calculated value of beam spreading from Eq. (3) is about 30-50 nm depending on t. This apparent disagreement in the amount of beam spreading is not real. The slab has a width much smaller than the diameter of the x-ray source and the electron trajectory density is not a constant in the interaction volume in thin foils.\(^2^9,3^0\) Therefore, the concentration profile developed in this case is very different from that obtained across a planar interface between two phases of differing composition and does not yield a measurement of beam broadening.

Vander Sande et al.\(^3^8\) have also calculated the effect of beam spreading assuming an incident probe with an electron density described by a Gaussian distribution function and a broadened distribution with depth described by Eq. (3). Differing from Newbury and Myklebust,\(^3^6\) they assume that the solute is distributed with distance from the boundary described by a Gaussian function rather than in the form of a slab. Their calculations also predict that the concentration profile is insensitive to foil thickness and that the peak concentration falls with increasing foil thickness/beam broadening. Several models explain the very few experimental results on grain-boundary segregation that are available. Improvement in the Monte Carlo and analytical models will occur as soon as more experimental data become available.

References


