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STEM-EDS X-RAY MICROANALYSIS IN THIN METAL FOILS

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Résumé - Les conditions expérimentales pour optimaliser la détection des ségrégations élémentaires en petits précipités et sur des joints de grains dans des lames minces d'aciers sont décrites.

Abstract - Experimental conditions for optimising the detection of elemental segregations to small precipitates and grain boundaries in iron base thin foils are described.

1. INTRODUCTION

The development of scanning transmission electron microscopes (STEM) combined with energy dispersive X-ray spectrometers (EDS) has provided the possibility of chemical microanalysis to a spatial resolution approaching that which may be obtained in the conventional imaging mode of the transmission electron microscope. Such microanalysis within a microstructure is of importance in establishing the mechanisms involved in its development and in interpreting its mechanical and chemical properties. Microstructural features which are of particular importance include small precipitates and grain boundaries with their chemical composition contributing to the mechanical strength and long term stability as well as the chemical behaviour in corrosive environments.

High resolution microanalysis of small microstructural features using STEM-EDS techniques in thin foil samples suffers practical limitations in that the feature of interest is contained within the foil and is of such a small dimension that the incident electron probe samples the feature together with the surrounding matrix. Thus, the proportion of the recorded X-ray signal derived from the feature depends on its position and distribution within the foil relative to the volume electron flux intensity distribution within the sampling electron probe. Intuitively, use of small incident sampling electron probes with higher incident energies and thinner foils will result in a larger proportion of the recorded X-ray quanta being derived from the feature and therefore optimise the microanalysis. These conditions, however, serve to reduce the total number of emitted X-ray quanta thereby decreasing the statistical confidence in the recorded data. These two competing effects are non-linearly related such that the benefits of increasing the proportion of X-rays emitted from the feature of interest are not directly complemented by an equivalent decrease in the statistical confidence of the data. Thus there exists some compromise between these competing effects that results in a maximum sensitivity for any microanalysis which may be achieved by adjustment of the experimental variables.

The purpose of this paper is to examine the influence of the experimentally adjustable variables of incident electron probe size, total electron flux, electron accelerating voltage and foil thickness on the sensitivity of microanalysis of small precipitates and grain boundaries contained within thin foils.
2. THEORETICAL ANALYSIS OF X-RAY EMISSION FROM SPECIFIC MICROSTRUCTURAL FEATURES.

The spatial resolution of X-ray microanalysis within thin foils using STEM-EDS is controlled primarily by the elastic scattering of the sampling electron probe. The measured characteristic X-ray intensity for a particular element, I', is a convolution of the distributions of electron flux intensity, I(V), and the element concentration, C(V), within the total sampled region of the foil:

\[ I' = K \int I(V) \cdot C(V) \, dV \]  \hspace{2cm} (1)

where K is a constant that describes the efficiency of X-ray generation, emission and detection for the particular element of interest and V is the foil volume. An analytical expression which approximates the electron flux distribution within the foil, I(V), has been given by the authors (1):

\[ I(r,t) = I_e \left\{ \frac{\pi (2\sigma^2 + 8t^3)}{(2\sigma^2 + 8t^3)} \right\} - \frac{r^2}{(2\sigma^2 + 8t^3)} \exp \left\{ -\frac{r^2}{(2\sigma^2 + 8t^3)} \right\} \]  \hspace{2cm} (2)

for a total incident electron flux of I_e where I(r,t) is the electron flux at a distance r from the centre of the probe at a depth t in the foil, σ is a measure of the incident electron probe size such that the probe diameter, B(FWHM) = 2.35σ, and β is a parameter defining the electron scattering characteristic of the foil material given by:

\[ \beta = \left( \frac{4\pi}{E_0} \right)^2 \cdot \left( \frac{\rho}{A} \right) \cdot 500 \]  \hspace{2cm} (3)

Here Z, A and ρ are the atomic number, the atomic weight and density of the foil material and E_0 is the electron accelerating voltage in eV; \( \beta \) is then given in units of \( \text{nm}^{-1} \). Combining this with the volume distribution of the particular element of interest, C(V), provides a means of establishing the proportion of the characteristic X-ray emission, I', derived from the specific microstructural feature.

In this paper we consider the case for small spherical precipitates of diameter, d, contained within the foil volume with a uniform concentration of segregated element with concentration C_o in the precipitate and zero in the surrounding matrix, Figure 1, and that for a positive segregation of an element to a planar grain boundary with a concentration profile given by:

\[ C(x) = C_o \exp \left\{ -\left| x \right|/\nu \right\} \]  \hspace{2cm} (4)

where C(x) is the concentration of the segregated species at distance x from the grain boundary, C_o is the concentration on the grain boundary, and \( \nu \) defines the spatial extent of the segregation, Figure 2.

The detectability of the segregated species in the X-ray spectrum is determined by the number of the characteristic X-ray quanta contained in the peak, \( N_p \), compared with those in the background of the spectrum \( N_b \). Detection of a peak requires its magnitude to be greater than the error in its estimation such that:

\[ N_p > \left( N_p + N_b \right)^{1/2} + \left( N_b \right)^{1/2} \]  \hspace{2cm} (5)

For a given electron source the total incident electron flux, I_e, is related to the incident probe size, B by (2):

\[ I_e \propto B^{8/3}. \]  \hspace{2cm} (6)

Thus the total emitted X-ray intensity increases with beam size. The background X-ray intensity in a recorded spectrum is proportional to the electron probe current, I_e, the foil thickness, t, and the total recording time, T, such that:

\[ N_b = K' B^{8/3} t T \]  \hspace{2cm} (7)

where K' is a constant for a particular X-ray energy and electron illumination.
system which characterises the 'effective' electron intensity for X-ray generation and detection. The number of counts in the X-ray peak, \( N_p \), for the element segregated to the grain boundary is given by the volume integral:

\[
N_p = K' R S^{8/3} T \int_V I(V) C(V) dV
\]

where \( R \) is the characteristic X-ray peak to background ratio obtained from a homogeneous sample of unit composition and \( V \) is the foil volume.

The inequality in Equation 5 defines the condition for detecting a characteristic X-ray energy peak from the segregated species in a recorded X-ray spectrum. \( N_B \) and \( N_p \) may be calculated from Equations 7 and 8 for given values of foil thickness, \( t_1 \) and material, \( \beta \), spectrum recording time, \( T \), electron probe size, \( B \), electron accelerating voltage, \( \beta \), 'effective' electron intensity, \( K' \), and composition distribution (C(V)). Thus we may establish conditions for detecting segregation to any given microstructural feature using STEM-EDS X-ray microanalysis.

3. RESULTS OF THE THEORETICAL ANALYSIS

For any given microstructural feature, the volume integral component of Equation 8 decreases with increasing incident electron probe size i.e. a smaller proportion of the total electron flux interacts with feature. Conversely, the total electron current increases rapidly (Equation 6) such that the resulting total electron flux that interacts with the precipitate will tend to increase. Therefore, the two competing effects define a range of electron probe diameter over which the inequality in Equation 5 is satisfied such that the intensity of characteristic X-rays emitted from the element segregated to the particular microstructural feature may be detected in the recorded spectrum. Clearly for very small features the inequality will never be satisfied in that the volume integral term (Equation 8) tends to zero and the segregation cannot be detected. This overall behaviour is shown schematically in Figure 3 where the electron probe size range for detection is given as a function of the characteristic dimension (\( W \) or \( d \)). For small electron probes the overall X-ray count rate is low such that statistical noise in the recorded spectrum precludes detection whereas for large probes the volume integral term decreases such that the measured \( N_p/N_B \) is reduced to a level below that for which the increasing statistical confidence in the data is able to compensate. The form of the curve defining the bound for detectability therefore displays a minimum which may be considered to represent a measure of the ultimate sensitivity for microanalysis.

The position and shape of the curve, Figure 3, depends on the input parameters for Equations 7 and 8. Results have been evaluated for iron base thin foils and typical conditions which relate to the operation of a commercial 100kV STEM fitted with a thermal tungsten filament and an energy dispersive X-ray spectrometer. Here, the factor \( K' \) is found experimentally for iron base foils to be \( 5 \times 10^{-5} \text{nm}^{-1/3} \text{s}^{-1} \). Typical calculated results for small precipitates and grain boundary segregations are shown in Figure 4(a) and (b) respectively for assumed standard conditions: \( R_C = 1 \), \( T = 100 \text{s} \), \( t_1 = 200 \text{nm} \) and \( E_0 = 100 \text{kV} \). The results in Figure 4(a) show a minimum in the precipitate diameter for the range of electron probe size considered, (1-100nm). This minimum in \( d \) occurs at electron probe sizes \( > 15 \text{nm} \) for combinations of \( R_C = 0.1 - 10 \), \( K' = 10^{-1} - 10^{-5} \text{nm}^{-1/3} \text{s}^{-1} \), \( E_0 = 100 - 300 \text{kV} \), \( t_1 = 100 - 300 \text{nm} \) for precipitates located at the top, centre or bottom of the foil. Thus, for electron probe sizes up to \( = 15 \text{nm} \), the minimum precipitate diameter which may be detected in the X-ray spectrum decreases with increasing probe size. Figure 4(b) shows the minimum detectable width of segregation to a grain boundary as a function of incident electron probe size. Here, as in the case for precipitates over this range of probe size (1-100nm) the minimum detectable width decreases with increasing electron probe size. Since there is no minimum in Figure 4(b), increasing the electron probe size increases the detectability of the segregation for the whole range of parameters given above.
4. DISCUSSION

The above theoretical consideration for undertaking STEM-EDS X-ray microanalysis illustrates the competing effects of reduced spatial resolution and improved counting statistics associated with increasing the electron probe size. In general, the experimental detection of elemental segregations to these small features in iron base foils is optimised by increasing the sampling electron probe size.

The 'effective' electron intensity parameter, $K'$, characterises the electron source brightness. For a JEOL JEM 100CX STEM combined with a Link Model 860 EDS microanalysis system, $K'$ has a value of $5 \times 10^{-5} \text{ mm}^{-1/3} \text{s}^{-1}$ for iron Kα radiation using a conventional thermal hairpin tungsten filament at 100kV. The maximum count rate which can be recorded with this EDS system is $\sim 2000 \text{ s}^{-1}$ for a processing time of 40μs. This count rate limits the maximum beam diameter which may be used in iron base foils of thickness $= 200 \text{ nm}$ to about 13nm. In general, for this EDS system $K't, B^{8/3} < 10$ such that for higher values of $K'$, associated with brighter electron sources, the X-ray count rate limitation further reduces the maximum probe size which may be used for X-ray excitation. When considered in conjunction with the results in Figure 4, we obtain a lower limit to the precipitate diameter and segregation profile width, which may be detected as a function of the parameter $K't$. These results are shown in Figure 5 for (a) spherical precipitates at the centre of the foil, and (b) segregations to grain boundaries for the standard conditions above. The results show that a tenfold increase in electron source brightness or efficiency in X-ray detection only improves the detectability by a factor of less than two.

Thus the finite X-ray count rate which may be processed by the EDS system is a controlling factor in defining the minimum precipitate diameter or grain boundary segregation width which may be detected in the X-ray spectrum. Increases in electron source brightness and accelerating voltage have relatively little effect for foil thicknesses in the range 100-300nm typically used for microanalysis. Thus, any attempt to improve the sensitivity of X-ray microanalysis by increasing $K'$ through improvements in electron flux intensity within the probe would have to be accompanied by a corresponding improvement in the maximum X-ray count rate which may be accommodated by the EDS system.

6. CONCLUSION

For STEM-EDS X-ray microanalysis of small microstructural features contained within iron base thin foils, the optimum electron probe size for detecting elemental segregations is limited by the maximum X-ray count rate that may be accepted by the energy dispersive spectrometer. Thus, experimental conditions are optimised by using the largest electron probe size which produces sufficient X-rays to saturate the EDS system.

7. ACKNOWLEDGEMENT

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8. REFERENCES


FIGURE 1.
(a) Transmission electron micrograph showing small VC precipitates in a $\frac{4}{3}\%$CrMoV steel.
(b) Schematic representation of precipitate particle contained within the foil.
(c) Assumed composition profile of element segregated within the precipitate.

FIGURE 2.
(a) Transmission electron micrograph showing a prior austenite grain boundary in a temper embrittled $1\%$CrMo steel.
(b) Schematic representation of the grain boundary orientation within the thin foil.
(c) Assumed composition profile of the segregated embrittling species.

FIGURE 3. Schematic diagram showing the influence of sampling electron probe size on the detectability in the recorded X-ray spectrum of segregations to small microstructures contained within a thin foil.
FIGURE 4. The calculated limits of detectability for:
(a) spherical precipitates of diameter \(d\) at the centre of a thin foil
(b) grain boundary segregations of width \(2w\) in an iron base foil
as a function of incident electron probe size, \(B\), with \(t_1 = 200\)nm,
incident electron energy = 100kV, effective electron intensity
\(K' = 5 \times 10^{-5}\)nm\(^{-1}\)\(\mu\)m\(^{-3}\)s\(^{-1}\), recording time \(T = 100s\), and parameter \(K_C = 1\).
Units of \(B\) and \(d\) in nm.

FIGURE 5. Calculated limits of detectability for:
(a) spherical precipitates of diameter \(d\) at the centre of a thin foil
(b) grain boundary segregations of width \(2w\)
as a function of the 'effective' electron flux, \(K'T\) (nm\(^{-1}\)\(\mu\)m\(^{-3}\)) in an
iron base foil with maximum incident electron probe size limited by
an X-ray count rate accepted into the ED spectrometer of 2000s\(^{-1}\).