The Detection of Monolayer Grain Boundary Segregations in Steels Using STEM-EDS X-Ray Microanalysis

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The detection and measurement of monolayer embrittling segregations to prior austenite grain boundaries of ferritic steels during heat treatment in the temperature range 600 to 850 K can significantly modify their mechanical and chemical properties. These segregations are generally considered to be confined to within a few atom layers of the boundary. Since the segregating species are retained in solid solution, they do not result in directly observable changes in microstructure. Consequently, their identification and measurement using conventional metallographic techniques has not been possible. Indeed, the more usually used electron probe X-ray microanalysis technique has insufficient spatial resolution for detection of such segregation and, to date, surface specific analysis techniques such as Auger electron spectroscopy (AES) have been required. These techniques, however, suffer limitations associated with specimen preparation requirements. More recently the authors have shown that embrittling segregations of elements (atomic number > 11) can be detected in conventional transmission electron microscope thin foil specimens using the scanning transmission electron microscope combined with energy dispersive X-ray spectrometry (STEM-EDS). The purpose of the present paper is to investigate the relative effects of electron probe size, accelerating voltage, and foil thickness on the detection of grain boundary segregations typical of those associated with the impurity element embrittlement of ferritic steels.

I. INTRODUCTION

The equilibrium segregation of Groups IV to VI impurity elements to the prior austenite grain boundaries of ferritic steels during heat treatment in the temperature range 600 to 850 K can significantly modify their mechanical and chemical properties. These segregations are generally considered to be confined to within a few atom layers of the boundary. Since the segregating species are retained in solid solution, they do not result in directly observable changes in microstructure. Consequently, their identification and measurement using conventional metallographic techniques has not been possible. Indeed, the more usually used electron probe X-ray microanalysis technique has insufficient spatial resolution for detection of such segregation and, to date, surface specific analysis techniques such as Auger electron spectroscopy (AES) have been required. These techniques, however, suffer limitations associated with specimen preparation requirements. More recently the authors have shown that embrittling segregations of elements (atomic number > 11) can be detected in conventional transmission electron microscope thin foil specimens using the scanning transmission electron microscope combined with energy dispersive X-ray spectrometry (STEM-EDS). The purpose of the present paper is to investigate the relative effects of electron probe size, accelerating voltage, and foil thickness on the detection of grain boundary segregations typical of those associated with the impurity element embrittlement of ferritic steels.

II. STEM-EDS X-RAY MICROANALYSIS OF GRAIN BOUNDARY SEGREGATIONS

The electron intensity distribution in a STEM electron probe passing through a thin foil may be approximated by:

\[ I(r,t) = I_e \left( \frac{\pi(2\sigma^2 + \beta t^3)}{2} \right) \cdot \exp \left\{ -r^2 \left( 2\sigma^2 + \beta t^3 \right) \right\} \]  \[ \text{[1]} \]

for a total incident electron flux of \( I_e \) where \( I(r,t) \) is the electron flux at a distance \( r \) from the center of the probe and depth \( t \) in the foil, \( \sigma \) is a measure of the incident electron probe size with the probe diameter, \( D \) (FWHM) \( \approx 2.35\sigma \), and \( \beta \) is a parameter defining the electron scattering characteristic of the foil material given by:

\[ \beta = \frac{(4Z/E_0)^2 \cdot (\rho/A) \cdot 500}{C_r \exp(-|x|/w)} \]  \[ \text{[2]} \]

Here, \( Z, A, \) and \( \rho \) 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 \( \text{nm}^{-1} \).

In this work we shall assume a grain boundary segregation profile which is represented schematically in Figure 1 and described by:

\[ C_r = C_0 \exp(-|x|/w) \]  \[ \text{[3]} \]

where \( C_r \) is the concentration of the segregating species at distance \( x \) from the grain boundary, \( C_0 \) is the concentration on the grain boundary, and \( w \) is a length parameter defining the spatial extent of the segregation. For the present work...
we shall assume a monolayer segregation described by a value \( w = 0.1 \) nm.

Combining the electron intensity distribution with this assumed segregation profile gives the X-ray signal from the grain boundary \( I^*(0,t) \):

\[
I^*(0,t) = K \int C_x \cdot I(r,t) \, dV
\]  

where \( K \) is dimensionless constant relating the local electron flux (number of electrons) to the number of detected X-ray counts and \( r^2 = x^2 + y^2 \). Thus, from Eqs. [1], [3], and [4] we obtain:

\[
I^*(0,t) = \frac{K L C_0}{t_f} \int_{-\infty}^{\infty} \int_0^1 \exp(-|x|/w) \cdot \left\{ \left( \frac{\pi(2\sigma^2 + 2\beta^2)}{2\sigma^2 + 2\beta^2} \right)^{1/2} \right\} \exp\left\{ -\frac{x^2}{2(2\sigma^2 + 2\beta^2)} \right\} dxdt
\]  

for a foil thickness of \( t_f \). Here \( K L C_0 \) represents the X-ray intensity recorded from a foil with a uniform composition \( C_0 \).

The integral in Eq. [5] has been evaluated for iron base foils as a function of foil thickness, \( t_f \), at electron accelerating voltages of 100 and 200 kV, and the resulting X-ray intensity ratios \( I^*(0,t)/KLC_0 \) are shown in Figures 2(a) and (b), respectively, for electron probe diameters (FWHM) of 2 and 10 nm. Clearly, the proportion of the total X-ray signal which originates from the grain boundary segregant is improved with decreasing incident electron probe diameter and foil thickness and increasing electron accelerating voltage.

The accuracy of any X-ray measurement is limited by statistical consideration of the finite number of detected X-ray quanta. The significance of any measurement is related to the counting statistics in the characteristic X-ray energy peak, \( N_p \), compared with those in the background of the spectrum \( N_b \) (Figure 3). Confidence in any measured peak intensity (or integrated counts) is dependent on both the peak and background such that for a large number of counts where Gaussian statistics may be assumed (\( N > 20 \)):

\[
\text{Peak Intensity} = N_p \pm (N_p)^{1/2}
\]

\[
\text{Background Intensity} = N_b \pm (N_b)^{1/2}
\]

Thus, the net error (standard deviation) in the measured total intensity to background intensity ratio is given by:

\[
\left[ \frac{(N_p + N_b)}{N_b} \right] \cdot \left[ \frac{(N_p + N_b)^{1/2}}{N_b} \right].
\]  

For any given electron source the total incident electron intensity is related to the electron probe diameter, \( D \), formed on the specimen by:

\[
I_e \propto D^{63}.
\]  

Thus, the total generated X-ray intensity, \( I^*(0,t) \) increases with the incident beam diameter (Eq. [5]). Hence, the statistical confidence in the total X-ray count will improve with both increasing foil thickness and electron probe diameter. However, such changes decrease the proportion of the total X-ray signal derived from the grain boundary segregation (Figure 2). The optimum conditions for detection of the segregation are therefore a compromise between those which minimize electron scattering and those which improve the statistical accuracy of the microanalysis. The latter is controlled by both the background intensity, \( N_b \), and the peak to background ratio \( R_0 (N_p/N_b) \) which is characteristic.