DETECTABILITY LIMIT AND SPATIAL RESOLUTION IN STEM X-RAY ANALYSIS: APPLICATION TO Fe-Ni ALLOYS

A. D. Romig Jr. and J. I. Goldstein

When performing x-ray analysis of thin films in the scanning transmission electron microscope (STEM) one must be aware of the limiting factors of spatial resolution and analytical sensitivities or detectability limits. A series of experiments were undertaken to determine detectability limits and spatial resolution in a "typical" metallurgical thin film of an FeNi alloy. This study was performed on a first-generation Philips 300 TEM/STEM (transmission electron microscope/scanning transmission electron microscope) equipped with a rear entry NSI-EDS detector. The sensitivity limits are a function of several variables. One group of variables is instrument dependent and includes the efficiency and collection configuration of the x-ray detector, the spurious x-ray counts, the current in the primary electron beam, and the contamination characteristics of the microscope. The last variable directly limits the total time one can collect x-rays from a given point. These variables have been optimized in our instrument. The second group of variables includes the electron probe size, foil thickness, and number of repetitions of the analysis, all of which can be controlled by the experimenter.

Spatial Resolution

The spatial resolution for x-ray analysis in a thin foil is a function of atomic number, specimen thickness, and accelerating voltage. Goldstein et al.\(^1\) have estimated the effective beam broadening \(b\) by assuming that scattering takes place at the center of the thin film, that the dominant process causing beam spreading is elastic scattering by atomic nuclei, and that the electron beam is a point source. This development yields an equation for broadening:

\[
b = 625 \frac{Z}{E_0} \sqrt{\frac{\rho}{A}} t^{3/2}
\]

where \(b\) is in cm, \(Z\) is the atomic number, \(A\) is the atomic weight, \(E_0\) is in keV, \(\rho\) is in g/cm\(^3\), and \(t\) is the film thickness in cm. The broadening varies inversely as \(E_0\) and increases with film thickness. For example, in a pure Fe foil \(b\) equals approximately 190, 350, and 540 Å for foils 1000, 1500, and 2000 Å thick, respectively. The broadening equation assumes the electron beam impinges the sample at a point. The beam is not a point probe; it has a finite diameter. Hence, the total x-ray spatial resolution is approximately equal to the sum of the broadening \(b\) and the size of the electron beam \(d\) impinging on the sample.

Monte Carlo calculations of beam broadening have been performed by Kysar and Geiss.\(^2\) These calculations should be expected to provide the best estimates because they include such effects as the electron beam size, electron back scattering, multiple scattering, etc. In general, the relatively good agreement between the results of the simple scattering model and the Monte Carlo model tend to validate Eq. (1).

Few experimental measurements of x-ray resolution are available in the literature. One of the most successful methods used in electron probe microanalysis (EPMA) is to move the electron beam point by point across an interface between two phases, which shows a concentration discontinuity.\(^3\) The finite volume from which x-rays are excited in a sample causes the true concentration profile to appear "smeared." One can determine the width of the x-ray excitation region by drawing a tangent to the measured concentration profile at the midpoint of the discontinuity and measuring the intercept on the distance axis at

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the composition of each phase.

In the STEM the foil must be tilted so that the α/γ interface is parallel to the incident electron beam. If one phase overlays another, it would be impossible to determine the interface compositions accurately. Figure 1 shows a typical α + γ assemblage in a Fe-34.7 Ni alloy. This is the ideal structure for measuring concentration profiles with STEM techniques.

![TEM micrograph of α/γ structure in Fe-34.7 wt% Ni alloy](image)

**FIG. 1.** TEM micrograph of α/γ structure in Fe-34.7 wt% Ni alloy: A--α (bcc), G--γ (fcc), scale bar = 1 μm (10,000 Å).

A concentration profile measured in 500Å steps across a two phase interface of α and γ in a 14.7 wt% Ni-Fe alloy heat treated at 500°C for 127 days is shown in Fig. 2. Contamination prevented smaller steps from being used. The operating conditions are 100 kV with a 200Å-dia. electron beam. The foil is about 1500 Å thick. The total width of the x-ray excitation measured from Fig. 2 is about 500 Å. Several other investigators have reported similar spatial resolutions in other ferrous alloy systems. Table 1 summarizes the experimental data currently available. The validity of Eq. (1) is demonstrated by these experimental data.

**Detectability Limits**

One determines the detectability limit (CDL) for a given element in a sample of interest by collecting the appropriate data from the sample thin foil. The analysis requirement is to detect significant differences between the intensity of the element of interest and the continuum background generated in the sample. For the detection of Ni in an FeNi alloy the peak intensity $I_{Ni}$ is significantly larger than the background $I_{B,Ni}$ when

$$I_{Ni} - I_{B,Ni} > 3 (2I_{B,Ni})^{1/2}$$

This x-ray count criterion for detectability limit (CDL) can be converted to wt% using the Cliff-Lorimer thin foil equation

$$\frac{C_{Fe}}{C_{Ni}} = k_{FeNi} \frac{I_{Fe}}{I_{Ni}}$$

![Ni profile across an α/γ interface in Fe-14.7 wt% Ni alloy](image)

**FIG. 2.** Ni profile across an α/γ interface in Fe-14.7 wt% Ni alloy.
TABLE 1.--Selected summary of calculated and measured x-ray resolution for ferrous materials.

<table>
<thead>
<tr>
<th>Reference</th>
<th>System</th>
<th>Foil Thickness (Å)</th>
<th>E₀ (kV)</th>
<th>Beam Size (d, Å)</th>
<th>Spatial Resolution b(Å)</th>
<th>Total Broadening (Å) calculated (d + b) measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyman, et al.⁴</td>
<td>Stainless Steel</td>
<td>1500</td>
<td>100</td>
<td>10-50</td>
<td>350</td>
<td>360-400 ~ 300</td>
</tr>
<tr>
<td>Rao and Lifshin⁵</td>
<td>Stainless Steel</td>
<td>1000-1200</td>
<td>200</td>
<td>50</td>
<td>100-270</td>
<td>150-320 ~ 500</td>
</tr>
<tr>
<td>Williams and Goldstein⁶</td>
<td>Fe-Ni</td>
<td>1500</td>
<td>100</td>
<td>200</td>
<td>350</td>
<td>550 ~ 500</td>
</tr>
<tr>
<td>Romig⁷</td>
<td>Fe-Ni</td>
<td>~1500</td>
<td>100</td>
<td>200</td>
<td>350</td>
<td>550 ~ 500</td>
</tr>
<tr>
<td>Pande et al.⁸</td>
<td>Stainless Steel</td>
<td>1000-1500</td>
<td>100</td>
<td>100</td>
<td>190-350</td>
<td>290-450 ~ 500</td>
</tr>
</tbody>
</table>

where \( k_{FeNi} \) is the Cliff-Lorimer constant, which varies with operating voltage but is independent of foil thickness and composition.

Substitution yields

\[
\frac{I_{Ni} - I_{Ni}^b}{I_{Fe} - I_{Fe}^b} = \frac{3(2I_{Ni}^b)^{1/2}}{I_{Fe} - I_{Fe}^b} = \left( k_{FeNi}^{-1} \right) \frac{C_{DL}}{C_{Fe}}
\]

or

\[
C_{DL} = \frac{3(2I_{Ni}^b)^{1/2}}{I_{Fe} - I_{Fe}^b} C_{Fe} k_{FeNi}
\]

where \( C_{Fe} \) and \( k_{FeNi} \) are known quantities and \( C_{DL} \) is the detectability limit of Ni in the FeNi alloy. The x-ray intensities \( I_{Ni} \), \( I_{Fe} \), \( I_{Ni}^b \), and \( I_{Fe}^b \) are measured experimentally. Unfortunately, the peak and background intensities are functions of foil thickness. Thicker foils produce greater intensities and therefore smaller detectability limits. Furthermore, x-ray intensity is linearly proportional to thickness, so long as the thin-film criterion is not violated. Once absorption effects become significant, the linear relationship is no longer valid. Figure 3 demonstrates the relationship between x-ray intensity and foil thickness for a pure Ni foil analyzed by a STEM operated at 100 kV with a 200Å probe size and a counting time of 60 sec. Foil thickness was determined by tilting of the foil following the STEM analysis and measurement of the separation of the contamination spots on the top and bottom of the foil. Given the spot separation, amount of tilt, and magnification one can calculate the foil thickness from simple geometry. Figure 4 shows the calculated detectability limits from Eq. (5) for a Fe-5.13 wt%Ni alloy as a function of foil thickness. Typical ion thinned metallurgical thin foils of Fe about 1500 Å thick yield a detectability limit of approximately 0.5 wt%Ni. Similar data were obtained from a homogeneous Fe-14.5 wt% alloy and yielded the same detectability limit. In all cases, peak intensities were obtained by integrating the region of the peak defined by 1.2 full width at half maximum to optimize the peak intensity and peak-to-background ratio. Backgrounds were determined by averaging the integrated continuum intensities taken on both the high- and low-energy sides of the characteristic FeKα and NiKα peaks.

High-brightness guns (LaB₆ or field emission) improve the detectability limits since they increase the x-ray intensity. A larger counting time increases the x-ray intensity but the counting time is limited in practice by contamination and/or specimen drift. Oppolzer and Knauer¹⁰ analyzed a metallic glass (B, P, Cr, Fe, Ni) foil which was about
FIG. 3.--Intensity versus thickness relationship measured on a pure Ni foil. Operating conditions: 100 kV, 200Å probe diameter, 60 sec counting time, 36° specimen tilt. Thickness determined by the measurement of the distance between contamination spots on the top and bottom of the foil after further tilting.

500 Å thick with a STEM equipped with a field-emission gun. The data were taken at 100 kV with a 50Å-dia. electron probe. Use of their data in Eq. (5) gives detectability limits for all elements (except B) of approximately 0.15 wt%.

Attempts have been made to predict detectability limits from first-principle equations. Joy and Maher have calculated the detectability limit of Fe in silicon to be approximately 4 wt% using a STEM with a LaB$_6$ gun operated at 100 kV, with a 100Å-dia. electron probe. This detectability limit can be reduced to approximately 2 wt% by use of a field-emission gun. For a STEM operated at 100 kV and equipped with a thermal emission gun, with a 200Å diameter probe, this theoretical approach gives a detectability limit of 4.8 wt%Ni in an Fe-Ni alloy. It is not clear why experimentally measured detectability limits are so much smaller than calculated limits.

**Independent Determination of $k_{\text{FeNi}}$**

To perform a STEM x-ray analysis using Eqn. (3), one needs to know precisely the value of $k$. The value of $k_{\text{FeNi}}$ can be calculated from first principles as shown by Goldstein et al. or obtained from the $k_{\text{FeSi}}/k_{\text{NiSi}}$ experimental values. At 100 kV, the calculation technique of Goldstein et al. yields $k_{\text{FeNi}} = 0.92$. The Cliff-Lorimer values yield $k_{\text{FeNi}} = 1.27/1.47 = 0.86$. The best method is to measure $k_{\text{FeNi}}$ on a homogeneous one-phase-alloy thin foil. Several alloys were used in this series of experiments. Nine separate $k_{\text{FeNi}}$ measurements were made on a Fe-14.5 wt%Ni alloy thin foil, 500-200 Å thick, with a 200Å diameter probe and a counting time of 60 sec. The measured $k_{\text{FeNi}}$ was 0.88 ± 0.04 at the 95% confidence level. Seventeen measurements were made similarly in an Fe-5.13 wt%Ni alloy. At the 95% confidence level $k_{\text{FeNi}} = 0.85 ± 0.08$. The calculated $k_{\text{FeNi}}$ and original Cliff-Lorimer $k_{\text{FeNi}}$ agree, within experimental error, with the value determined directly in this study. When this value of $k_{\text{FeNi}}$ is used in later data reduction, any error in the measurement of the Ni content of the homogeneous alloy must be added to the measured uncertainty.

**Summary**

For a Philips 300 TEM/STEM operating at 100 kV (with a 200Å probe diameter and a thermal emission gun):

1. the spatial resolution, as determined by measuring concentration profiles across
α/γ interfaces in Fe-Ni alloys, is 500 Å in thin foils which are approximately 1500 Å thick;
2. the detectability limit of Ni in an Fe-Ni matrix is about 0.5 wt%Ni in a thin foil sample 1500-2000Å thick; and
3. $k_{\text{FeNi}} = 0.88 \pm 0.04$ at 95% confidence level.

References