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To cite this article: P Statham *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **304** 012017

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A convenient method for X-ray analysis in TEM that measures mass thickness and composition

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Abstract. We consider a new approach for quantitative analysis in transmission electron microscopy (TEM) that offers the same convenience as single-standard quantitative analysis in scanning electron microscopy (SEM). Instead of a bulk standard, a thin film with known mass thickness is used as a reference. The procedure involves recording an X-ray spectrum from the reference film for each session of acquisitions on real specimens. There is no need to measure the beam current; the current only needs to be stable for the duration of the session. A new reference standard with a large (1 mm x 1 mm) area of uniform thickness of 100 nm silicon nitride is used to reveal regions of X-ray detector occlusion that would give misleading results for any X-ray method that measures thickness. Unlike previous methods, the new X-ray method does not require an accurate beam current monitor but delivers equivalent accuracy in mass thickness measurement. Quantitative compositional results are also automatically corrected for specimen self-absorption. The new method is tested using a wedge specimen of Inconel 600 that is used to calibrate the high angle angular dark field (HAADF) signal to provide a thickness reference and results are compared with electron energy-loss spectrometry (EELS) measurements. For the new X-ray method, element composition results are consistent with the expected composition for the alloy and the mass thickness measurement is shown to provide an accurate alternative to EELS for thickness determination in TEM without the uncertainty associated with mean free path estimates.

1. Introduction

When an electron beam strikes a bulk specimen, emitted X-ray intensity depends on element composition. A comparison of intensities obtained when the same beam is focussed on a bulk unknown specimen and a bulk standard of known composition gives a direct measure of element concentration. Furthermore, if an energy-dispersive X-ray spectrometer (EDS) is well-characterised, quantitative element composition analysis of bulk specimens in a scanning electron microscope (SEM) can be achieved with only a single measurement on a bulk pure element reference standard using the same electron beam conditions [1]. The benefit of using a reference standard measurement is that results do not have to be normalised so that the analytical total provides a useful diagnostic to detect errors such as missed or misidentified elements or inaccurate matrix corrections.

For a thin specimen in a transmission electron microscope (TEM), X-ray intensity depends on both element composition and specimen thickness so that even if the same electron beam is used on an unknown specimen and a bulk reference standard, a diagnostic analytical total cannot be obtained but if element mass fractions are assumed to sum to unity the measurement on a bulk reference allows the



mass thickness of the specimen to be determined. This approach was used by Dijkstra *et al.* [2] but TEM beam voltages are much higher than in SEM and at a beam current necessary to give adequate X-ray intensity from a thin sample, the X-ray yield from a bulk standard not only caused overload of the EDS but also the high penetration depth for the incident beam introduced inaccuracy because of the very large correction for X-ray absorption in the standard [2]. Boon solved the overload problem by devising a beam current monitor linear over 3 - 4 decades so that a bulk standard could be analysed at much lower current than the thin specimen and intensities corrected for the large difference in beam current but huge X-ray absorption in the bulk standard was still an issue [3].

Watanabe and Williams [4] avoid bulk standards completely in the ζ -factor (zeta-factor) method. However, determination of zeta-factors for a particular instrument requires thin film standards of known thickness, density and composition and such standards are not readily available. Furthermore, a critical requirement is an accurate method of measuring incident current but beam current monitors are not always available, convenient, or of sufficient accuracy.

In what follows, we consider a new method for quantitative analysis in TEM that uses a well-characterised EDS and a single thin film reference standard to achieve measurement of mass thickness and elemental concentration with no requirement to measure beam current.

2. New method

For analysis of thin specimens in TEM, X-ray intensity for the emission line of element A is given by:

$$I_A = (\rho.t)_{sp} \cdot C_A \cdot [N_0/A_A \cdot (Q_A.f_A)] \cdot f(\chi)_A \cdot D_{sp} \cdot (\Omega/(4\pi)) \cdot \epsilon_A \quad (1)$$

for element mass fraction C_A , Avogadro constant N_0 , atomic weight A_A , ionisation cross-section Q_A , fractional emission f_A , self-absorption $f(\chi)_A$, electron dose D_{sp} , detector solid angle Ω , and conversion efficiency ϵ_A . As in previous methods for TEM quantitative analysis, $(Q_A.f_A)$ can be calculated from theory where f_A is usually expressed as the product of fluorescence yield and Coster-Kronig enhancement for the shell and ratio of line emission intensity to total for all emissions from that shell. $f(\chi)_A$ can be evaluated if the composition, mass thickness and geometry are known. Thus, I_A depends not only on beam current (governs D_{sp}) and composition (C_A), but also on density (ρ) and thickness (t). The mass thickness $(\rho.t)_{sp}$ is proportional to the aerial density of atoms in the direction of the electron beam. If we have a reference standard where $(\rho.t)_{ref} \cdot C_{ref}$ is known and an X-ray detector that has been characterised so that conversion efficiency ϵ is known as a function of energy [5] then we can determine $D_{sp} \cdot (\Omega/(4\pi))$ from the measurement on the reference standard in the TEM. Provided we use the same beam current and kV when a spectrum is recorded from the specimen, eq. (1) can be then be used to determine $(\rho.t)_{sp} \cdot C_A$ for each element and $(\rho.t)_{sp}$ is obtained by assuming that the mass fractions sum to unity. Self-absorption can be ignored to obtain first estimates of mass thickness and composition which are then used to calculate $f(\chi)_A$ and further improved estimates obtained by iteration.

Doing a “beam measurement” on the reference standard at the start or end of any session thus replaces explicit measurement of beam current. Besides enabling the analytical results to be corrected for X-ray absorption, the mass thickness value can also be used for lineal thickness measurement if density is known, calculation of electron beam scattering effect on spatial resolution, modelling of image contrast, electron energy-loss spectrometry (EELS) quantification and determination of defect densities for example.

3. Thin film reference standard

For the reference standard we use a self-supporting 100 nm thick silicon nitride TEM support film covering a 1 mm x 1 mm aperture within a standard 3 mm diameter disk of silicon 0.1 mm in thickness. This type of film is usually grown on top of a silicon wafer and the aperture is formed by

etching to remove the silicon support. Although the film is uniform in composition and thickness, the density and stoichiometry depend on the process used to manufacture the film [6]. Therefore, we characterise the thin film standard using an EDS and SEM. To determine the mass thickness for Si, we modelled X-ray emission from bulk Si and thin Si₃N₄ films at 10 kV and 30 kV using Monte Carlo simulation to establish a relationship between mass thickness and k-ratio (intensity from film divided by intensity from bulk). Using a transmission holder for the thin film standard and constant beam current, we measure X-ray intensity from the reference thin film and from a pure bulk Si wafer to obtain k -ratios and thus obtain $(\rho.t)_{\text{ref}} \cdot C_{\text{Si}}$ values at a series of points all over the support film and confirm uniformity over at least the central 0.6 mm x 0.6 mm region.

4. Results

4.1. Instrumentation and materials

For testing the new X-ray analysis method we used a JEOL JEM-2200-MCO-FEGTEM and a low background holder, tilted to 7.2°, with a cut-out section to reduce occlusion of the line of sight to the X-ray detector.

4.2. Determination of occlusion of the detector and beam current stability

Partial occlusion of a detector affects Ω and if occlusion varies with position, any X-ray method for measuring mass thickness will give a variable result even if the thickness is uniform. Therefore, it is imperative to maintain a clear line of sight from the beam spot to the X-ray sensor. Holder cut-outs and slight tilt helps but degree of occlusion may still vary with stage X/Y position and stage tilt, particularly with a large solid angle detector that is positioned very close to the specimen. The characterised reference film covers a large 1 mm x 1 mm area and a beam measurement was taken at many stage positions to determine if the Si-K intensity was constant or affected by occlusion at any position. Repeat measurements at the same position were used to confirm beam current stability before and after specimen exchange.

Figure 1 shows an occlusion map where the bubble diameter shows the reduction of signal relative to the maximum Si-K intensity at several stage positions. It is apparent that although tilting the sample and using a cut-out has reduced any variable occlusion in the direction of the detector, the edge of the cut-out is causing about 20 % occlusion as the stage is moved to $Y = +300 \mu\text{m}$, perpendicular to the detector direction. The occlusion map provides diagnostic information that can be used to improve design of a holder and check detector alignment or can be used as a map of sensitivity for correction of thickness measurements.

4.3. Calibrated test specimen

A wedge-shaped specimen of Inconel 600 was prepared by focussed ion beam etching. The intended wedge angle of $0.5^\circ \pm 0.07^\circ$ was used to calibrate the high angle annular dark field (HAADF) signal as follows. Taking the composition and density to be uniform, HAADF signal $A(x)$ at position x for this type of specimen was assumed to be proportional to thickness and by fitting a straight line to $A(x)$ at a series of stage positions in the direction of the wedge, the gradient m was used to obtain thickness t from HAADF intensity as shown in figure 2.

4.4. Thickness determination by the new X-ray method

The silicon nitride reference film was first used to obtain a beam measurement. Then, without altering microscope conditions, the reference was replaced by the wedge test specimen of Inconel 600 and a series of spectra were obtained along the wedge (white crosses in figure 3). For these measurements the stage was positioned at the point marked with a blue arrow in the occlusion map of figure 1. Using the new X-ray method, measurements of mass thickness were converted to thickness in nm by assuming a constant density of 8.43 g cm^{-3} .

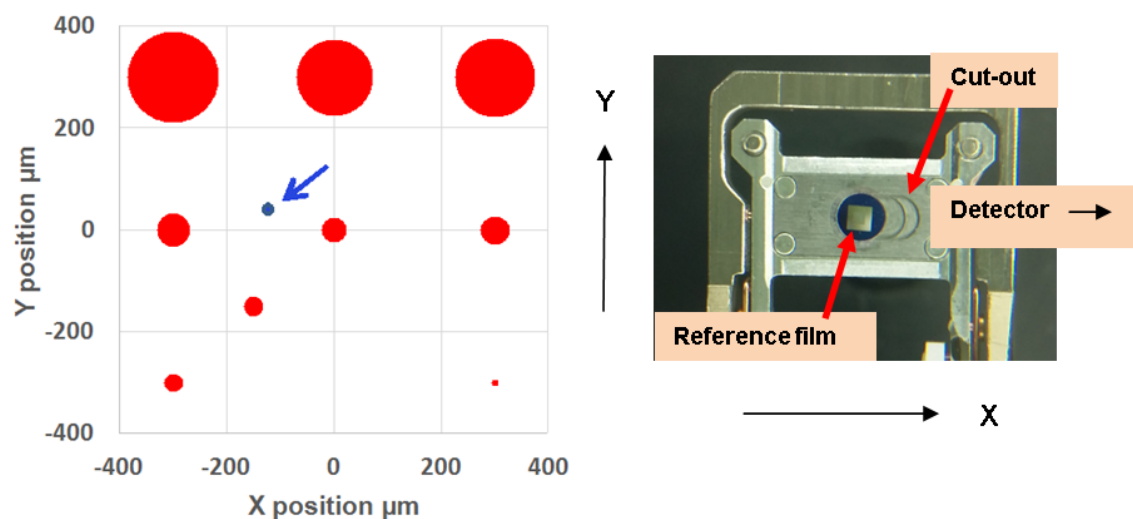


Figure 1. Occlusion bubble map where occlusion (%) = $100 \times (\text{bubble diameter } \mu\text{m})/800$. Right hand image shows relative positions of film, cut-out and X-ray detector and axes for stage movement. Blue arrow indicates stage position that was used for X-ray measurements with the new method.

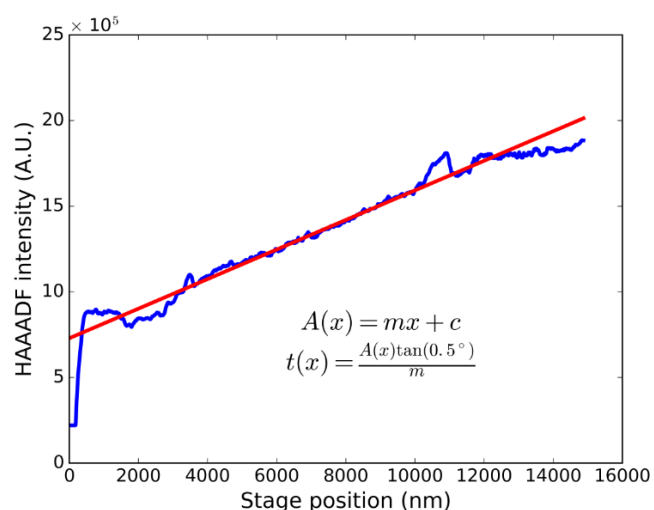


Figure 2. Calibration of HAADF signal with 0.5° wedge specimen to obtain thickness from intensity.

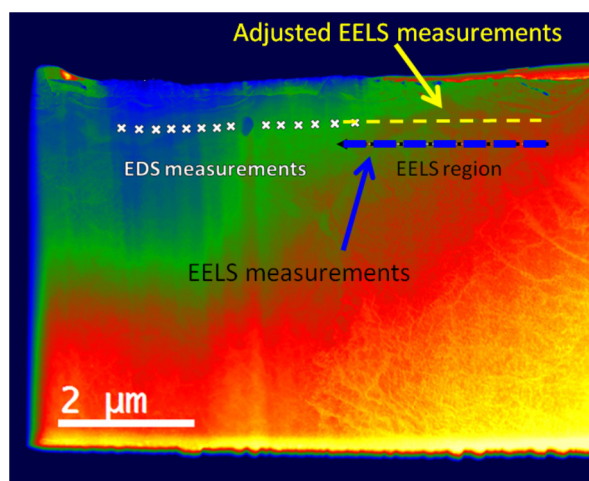


Figure 3. False-colour HAADF image (low intensity blue, high intensity red) of wedge test specimen of Inconel 600 showing regions used for acquisition of X-ray and EELS data.

4.5. Thickness determination by EELS measurements

In a separate session using the same test sample, EELS measurements of areas for total, I , and zero-loss, I_0 , for the spectrum were taken along a line of points and thickness, t , estimated by the formula $t = \lambda \cdot \ln(I/I_0)$. Values for the mean free path λ were calculated by published methods, 81 nm by Malis *et al.* [7], and 109 nm by Iakoubovskii *et al.* [8]. Because the lines used for EELS and X-ray measurements did not overlap, a small correction was made to the EELS results to give equivalent values along the same line as used for the X-ray data by scaling according to the HAADF signal.

4.6. Thickness results

Figure 4 shows the comparison of results from the different techniques. Uncertainty in the FIB angle for the wedge dominates the error bar for HAADF measurement and uncertainty in λ dominates the EELS log ratio method. Nevertheless, it is encouraging that the results for the new X-ray method agree well with the HAADF estimates.

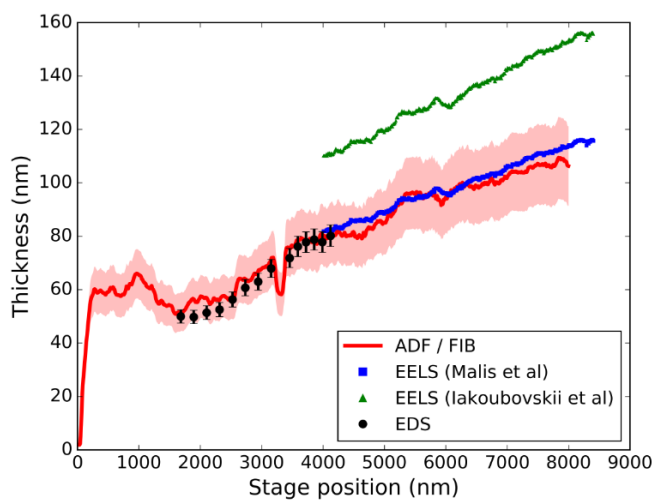


Figure 4. Thickness values at different stage positions. Red line shows the thickness from the HAADF signal calibrated using the known wedge angle with error bar showing the possible variation due to uncertainty in wedge angle. The black dots are the mass thickness results from the new X-ray method, converted to nm using a density of 8.43 g cm^{-3} . The green and blue lines show the results from EELS using estimates of λ obtained by references [7] and [8] respectively.

4.7. Composition results

The X-ray method also produces quantitative results for element weight% and these have been plotted in figure 5 for a series of stage positions. The quantitative results are within the range of compositions expected for Inconel 600 alloy, as shown by the dotted lines.

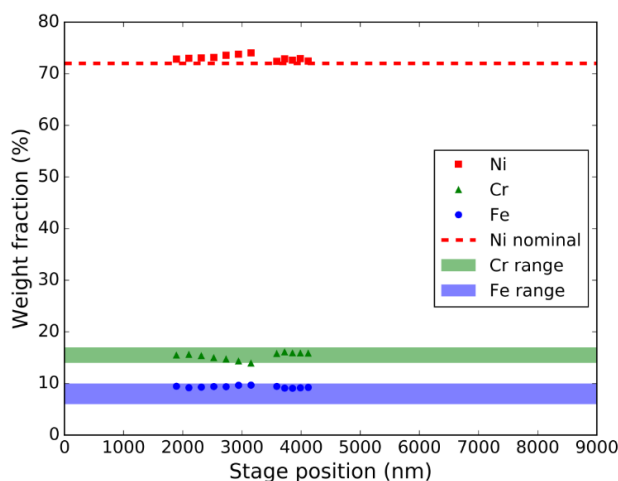


Figure 5. Element composition weight% obtained by the new X-ray method at the analysis positions corresponding to those used in figure 3.

5. Conclusion

The new reference standard with a large (1 mm x 1 mm) area of uniform thickness reveals regions of X-ray detector occlusion that would give misleading results for any X-ray method that measures thickness. With just a single measurement on the silicon nitride reference standard to calibrate the beam, many quantitative measurements can be made on a specimen in an analysis session by simply acquiring an X-ray spectrum at each point. The new X-ray method delivers equivalent accuracy in mass thickness measurement without the need for the accurate beam current monitor that is required for previous methods and quantitative compositional results are automatically corrected for specimen self-absorption. The mass thickness measurement also provides a convenient alternative to EELS for thickness determination in TEM without the uncertainty associated with mean free path estimates.

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