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Numerical modeling of specimen geometry for quantitative energy dispersive X-ray spectroscopy

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ABSTRACT

Transmission electron microscopy specimens typically exhibit local distortion at thin foil edges, which can influence the absorption of X-rays for quantitative energy dispersive X-ray spectroscopy (EDS). Here, we report a numerical, three-dimensional approach to model the geometry of general specimens and its influence on quantification when using single and multiple detector configurations. As a function of specimen tilt, we show that the model correctly predicts the asymmetric nature of X-ray counts and ratios. When using a single detector, we show that complex specimen geometries can introduce significant uncertainty in EDS quantification. Further, we show that this uncertainty can be largely negated by collection with multiple detectors placed symmetrically about the sample such as the FEI Super-X configuration. Based on guidance provided by the model, we propose methods to reduce quantification error introduced by the sample shape. The source code is available at https://github.com/subangstrom/superAngle.

1. Introduction

Energy dispersive X-ray spectroscopy (EDS) is widely used to determine the composition of materials in transmission electron microscopy [1]. Recent X-ray detector advances have dramatically enhanced collection efficiency through an enlargement of total detector area [2] using either single or multiple detectors. In particular, these advances have been pioneered by four-quadrant [3,4] and dual, large-area detector configurations [5,6]. Advanced EDS systems also incorporate windowless silicon drift detectors (SDDs) [7,8], which further increases the collection efficiency of low-energy X-rays. These above developments have greatly improved the signal-to-noise ratio for two-dimensional mapping, offering many advantages, particularly elemental determination on an atom-column by atom-column basis [9–13].

Although the development of multi-detector collection systems has enabled new possibilities, the increased complexity has brought new challenges as well. One of which is X-ray shadowing by the specimen holder when using multiple detectors [14–17]. If only using a single detector, the holder shadowing can be avoided by tilting the sample towards that detector. Because this strategy is no longer an option when using multiple detectors, holder shadowing reduces the total detector solid angle for X-ray collection. Beyond holder shadowing effects, X-ray absorption calculations also become more complicated. As X-rays are collected from different orientations, local inhomogeneities of specimen shape become a critical factor for absorption correction. For example, local distortion is often seen in thin regions of TEM foils, impacting both the total X-rays collected as well as their ratios. This is particularly problematic for material systems with strong absorption effects, such as Al-K absorption in Ni-Al alloys or materials containing light elements. A typical wedge-shaped Ni_3Al specimen, for example, is presented in Fig. 1a. The bright-field TEM image shows bend contours across the thin edge, indicating local distortion. On average, these bend contours repeat every 5–7 μm along the thin edge, and extend to about 4–5 μm into the foil. These bend contours are representative of those found in general TEM thin foils, particularly after polishing and ion-milling.

Distortion at the edge of thin foils can also be directly characterized via cross-sectional SEM imaging. Fig. 1b shows the wave-like morphology at the thin edge with an oscillation amplitude of 70–80 nm. By tilting the sample 4° along the vertical axis, the locally distorted peaks and valleys can be viewed from a different vantage point. In addition to bending along the direction, further sample distortion is observed in the Y direction, perpendicular to horizontal, as shown in the SEM image with a 4° off-tilt. While surface indentions and foil folding are found at regions near the edge, the overall wedge thickness is linear as shown in Fig. 1a. Beyond local distortion, the specimen surface is also inclined 5° relative to the support grid, resulting from slight misalignment of the sample when it was glued to the grid.

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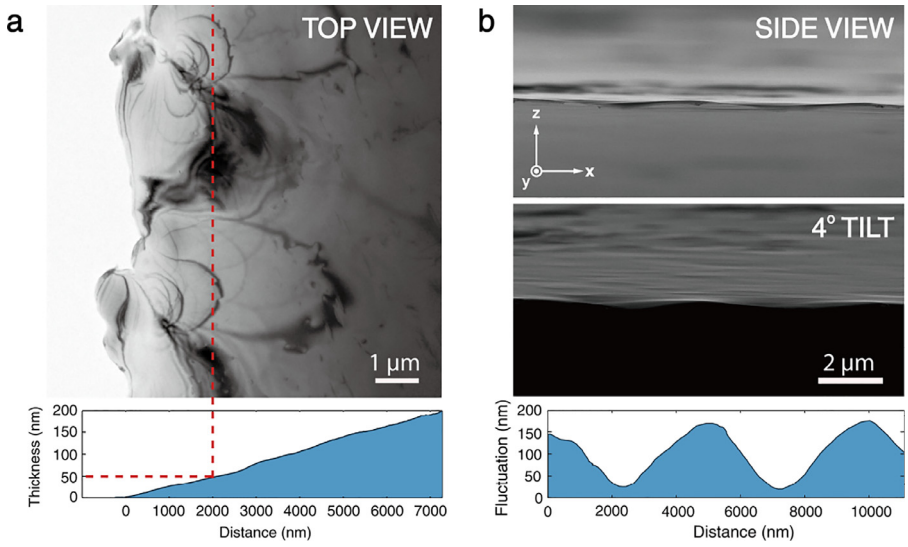

Fig. 1. (a) Bright-field TEM image of a typical Ni_3Al thin foil edge with corresponding thickness, calibrated from EELS. As highlighted by the (red) dashed lines, large local distortion is present in a typical thin region. (b, top) Secondary electron SEM images of the specimen and (b, bottom) sample distortion measured along the z direction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For a typical sample, the regions of interest are often within the thin and distorted areas. Understanding how distorted specimen geometry affects X-ray absorption is thus critical for quantitative EDS analysis. As such, analytical solutions to correct for X-ray absorption have been proposed for flat plate and wedge-shaped samples when using single [18–20] or multiple detectors [16,21]. In addition to absorption, holder shadowing and detector geometry have also been analytically included for electron tomography [15,22].

Towards realistic simulations of X-ray absorption, the authors have previously introduced a comprehensive numerical model to incorporate detector geometry, holder shadowing, and Be holder filtering. The combination of this model with dynamical electron scattering simulations enabled standard-less atomic resolution elemental quantification [23,24]. To correct X-ray absorption, however, the model assumes that the specimen is a homogeneous, plate-shaped object. A universal model for complex specimen geometry is thus needed, particularly for arbitrarily shaped thin TEM foils. In particular, the impact of specimen geometry on quantification with multiple EDS detectors is still unclear. Such understanding is fundamentally important for new approaches or strategies to reduce the quantification uncertainty due to the specimen shape.

In this paper, a three-dimensional, numerical approach is developed to model X-ray absorption correction for complex specimen geometries. The model predicts absorption correction factors using a mesh-based 3D object combined with the angular discretization of X-rays following the authors' prior work characterizing multi-detector EDS [16]. With this approach, absolute X-ray counts and their ratios are predicted for realistic specimen shapes. Through a systematic study of distorted specimens, fundamental insights into the influence of complex sample geometry on quantitative EDS are provided.

2. Materials & methods

Ni_3Al served as an ideal model material to study the influence of distorted specimen geometry on quantitative EDS due to the large attenuation coefficient of Al-K X-rays in the material [18]. A Ni_3Al super-alloy was thinned to electron transparency by wedge-polishing and low energy ion-milling. In addition, MgO particles were obtained by collecting the smoke of Mg burning in air. Formvar stabilized carbon grids, 75 mesh, were used to support the collected MgO particles. The X-ray parameters used to model these materials are provided in Table 1.

Table 1
X-ray modeling parameters.

	Cross-section (barn)	Fluorescence Yield	Detector Efficiency [4]
Ni	255 [25]	0.414 [25]	0.980
Al	2264 [19]	0.0357 [26]	0.982
Mg	2955 [27]	0.032 [26]	0.981
O	7980 [25]	0.0085 [25]	0.923

An FEI Quanta 3D FEG instrument was operated at 30 kV to determine the specimen geometry. Bright-field TEM imaging was conducted using a JEM-2000FX at 200 kV. For STEM-EDS, a probe-corrected FEI Titan G2 TEM/STEM operated at 200 kV and equipped with a four-quadrant FEI Super-X detector was used throughout the study. The nominal EDS collection solid angle was 0.7 sr as reported elsewhere [3]. Sample thickness was determined using the electron energy loss spectroscopy (EELS) log-ratio method implemented by the Digital Micrograph EELSTools suite [28,29].

For EDS experiments using Ni_3Al, spectra were acquired over an area of approximately 100 nm × 100 nm as a function of tilt about the X-axis (α tilt on FEI microscopes). For each sample tilt, an EDS spectrum was collected for a live time of 207 s using each individual detector. The probe current was measured to be 7.83×10^8 e/s via a CCD camera calibrated using the EELS drift tube method [30,31]. The specimen position was -0.22 mm, 0.10 mm and 0.28 mm in x, y and z-coordinates relative to the holder, calibrated from a FIB sample grid.

The specimen edge was parallel to the X-tilt axis of the holder with the thick region located closer to detectors 1 & 2. The specimen thickness was kept at a constant value of 40 nm. The constant thickness approach reduced possible position variations, which potentially introduces uncertainties in thickness determination. Strong electron channeling was avoided by selecting appropriate tilts about the X axis. To further reduce channeling, the sample was tilted −1° tilt about the Y axis.

To explore the influence of complex specimen geometry on materials containing light elements, X-rays from an MgO particle were collected with a live time of about 450 s (900 s total acquisition