QUANTITATIVE X-RAY MICROANALYSIS FOR THE STUDY OF NANOMETER-SCALE PHASES IN THE AEM

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ABSTRACT

Secondary excitation can be a large source of inaccuracy in quantitative X-ray microanalysis of inhomogeneous specimens in the AEM. The size of the secondary excitation component in the measured X-ray spectrum is sensitive to the geometry of the thin foil specimen. Secondary excitation has been examined in a self-supporting disc specimen of composition NiO-20 wt.% TiO₂ which has been partially masked by a gold slot washer. The ratio of the intensities of the characteristic K_α peaks of Ti and Ni in X-ray spectra from a periclase-structured phase, of nominal composition NiO, has been measured to be $N_{Ti} / N_{Ni} \approx 0.005$. There is no apparent Ti L_{2,3} signal in the corresponding electron energy-loss spectrum. The secondary excitation contribution to the characteristic Ti K_α-peak from all sources can therefore be no larger than 0.5%. It should be possible to reduce this modest level of secondary excitation still further with a better masking arrangement.

INTRODUCTION

For compositional analysis, the principal strength of X-ray microanalysis or energy-dispersive X-ray spectroscopy (EDXS) in the analytical electron microscope (AEM) relative to electron probe microanalysis is its high spatial resolution. However, when the composition of the volume being analyzed is markedly different than the average composition of the specimen, the relative contribution of the extraneous signal from the remainder of the specimen to a characteristic X-ray peak can be significant.¹ This extraneous signal arises from the excitation of characteristic X rays by fast electrons that have been scattered through large angles or by X rays that have been excited in the probed volume.² Especially when a major constituent of the specimen is a minor or dilute constituent of a phase being analyzed, the characteristic X-ray intensity of this element that emanates from locations in the specimen that are remote from the analysis volume can be comparable to that excited in the analysis volume itself.³

The size of the secondary excitation component in the measured X-ray spectrum is sensitive to the geometry of the thin foil specimen. The most effective strategy for minimizing secondary excitation is to restrict the amount of material that can be so excited. To this end, Williams et al.^{4,5} have advocated a specimen-geometry consisting of thin flakes of the material to be analyzed that have been dispersed in low concentrations on a beryllium grid. The thin flake specimen-geometry is suitable for EDXS when all portions of the specimen are equally suitable for examination. However, this specimen geometry is impractical for many microanalysis problems. When only a limited portion of the specimen is of interest, such as when a thin film is analyzed in cross-section, the analyst may have difficulty finding a flake of the specimen containing the area of interest. The thin flake specimen-geometry may also be inappropriate when the position of the region being analyzed must be known relative to a microstructural feature of the specimen; this information may be lost. In such situations, the analyst must rely on a geometry that leaves the specimen intact.

Recently, it has been shown that one type of secondary excitation, secondary fluorescence, is expected to be small for self-supporting disc specimens and for the dimpled and ion-milled specimen in particular.⁶⁻⁸ Basic geometrical considerations indicate that the secondary fluoresced intensity from self-supporting disc specimens should be modest relative to that from specimens with other geometries since the fractional solid angle subtended by the self-supporting disc specimen relative to the thin edge being analyzed is small.

The drawback of the self-supporting disc specimen relative to, for example, a cleaved wedge specimen is that it subtends a large area from the perspective of both the electron-optical column and the EDX spectrometer. A just-perforated specimen presents to the column a 3 mm disc (area $\sim 7 \text{ mm}^2$), whereas a cleaved wedge of thickness 100 μm protruding 0.5 mm from a supporting washer presents a target of area 0.05 mm^2 , more than two orders of magnitude smaller. The large target provided by the disc specimen increases the contribution to the measured spectrum of X rays excited by uncollimated radiation (in the hole count) and potentially by high-angle-scattered electrons when the specimen is tilted with respect to the beam.²

The area of the specimen presented to the electron-optical column and to the EDXS detector can be substantially reduced by partially covering the self-supporting disc specimen with a masking washer. For a specimen with a small perforation, the exposed area of the disc specimen can be easily reduced by a factor of 50. As long as the characteristic X-ray lines of the washer material do not overlap with the X-ray lines characteristic of the analysis volume, the reduction in the area of the specimen exposed to the detector leads to a corresponding reduction in the extraneous contributions to the X-ray lines of interest. Furthermore, it has been shown that the secondary fluorescence contribution to the measured EDX spectrum can be kept to a fraction of a percent if the dimpled and ion-milled specimen is suitably masked with an "X ray opaque" washer having an aperture of a few hundred micrometers diameter.⁸

The purpose of the present paper is to study the level of secondary excitation in the measured EDX spectrum characteristic of the masked dimpled and ion-milled specimen-geometry. A model specimen for this study would have a phase that contains little (or none) of an element that is one of the major constituents of the overall specimen. A specimen of average composition NiO-20 wt.% TiO_2 has been chosen for this purpose. When a specimen of this composition is equilibrated at $\sim 1500^\circ\text{C}$, quenched, and subsequently annealed, periclase-structured regions of $\sim 100 \text{ nm}$ dimension and nominal composition NiO are found throughout the specimen.⁶ These regions provide nanometer-scale volumes of the specimen containing little titanium in a specimen with a large relative titanium concentration.

EXPERIMENTAL PROCEDURE

Powders with the composition NiO-20 wt.% TiO_2 were equilibrated in air at 1488°C for 142 h and quenched in water, as has been detailed elsewhere.⁹ The quenched specimens were subsequently annealed in air at 1200°C for 30 minutes and air quenched. The loosely sintered specimens were embedded in epoxy¹⁰ and then cut into 200 μm -thick slices with a low-speed diamond saw. Thin-foil specimens suitable for AEM investigation were prepared with standard mechanical techniques: embedded slices were cut into 3 mm disks with an ultrasonic drill; these disks were lapped to $\sim 100 \mu\text{m}$, dimpled to $\sim 20 \mu\text{m}$, and ion-milled to perforation. The final stage of ion-milling was performed at a relatively low energy (3 keV) and incident angle (12°). A thin coat of carbon was applied in order to mitigate charging effects.

The specimens were examined at ORNL with a Philips EM400T AEM equipped with a field-emission electron gun (FEG) and operated at 100 kV. X-ray microanalysis and electron energy-loss spectrometry (EELS) were performed with an EDAX 9100 energy-dispersive X-ray spectrometer and a Gatan 666 parallel-collection electron energy-loss spectrometer, respectively. The specimens were cooled to -130°C during spectrum acquisition using a Gatan double-tilt cooling holder. For X-ray microanalysis, the majority of the specimen was masked by a gold washer with a 0.5 mm $\times$ 2.0 mm slot, as shown schematically in Figure 1a. Care was taken to avoid shadowing effects. An alternative masking geometry is shown in Fig. 1b.

RESULTS

The nickel-titanate specimens were found to contain phases of the periclase, spinel, and corundum structures with a microstructure of dimension $\sim 100 \text{ nm}$.¹¹

Figure 2 shows the EDX spectrum measured from the periclase-structured phase and the corresponding hole count, in the energy range 2 - 12 keV. This energy range contains the Ti K and Ni K lines characteristic of the specimen and the Au L and Au M lines of the masking washer.

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Figure 1. Schematic representations of masking geometries for self-supporting disc specimens: (a) the geometry used for this study, with the specimen masked by a washer with a 0.5 mm $\times$ 2.0 mm slot; (b) the specimen masked by a circular aperture. Plan view and cross-sectional views of these geometries are shown.

Figure 2. EDX spectra in the energy range 2 - 12 keV show the intensities characteristic of the hole count (shaded) relative to those acquired from the periclase-structured phase. The two spectra are of the same scale.

Figure 3 shows an EDX spectrum characteristic of the periclase-structured phase, after hole-count subtraction, in the energy range 4 - 9 keV and at two vertical scales. When the spectrum is scaled such that the entire Ni K_{α} peak is depicted (line), no Ti K_{α} peak is apparent; the spectrum is therefore also depicted with the vertical scaling increased by a factor of twenty (dots). The ratio of the Ti K_{α} to Ni K_{α} intensities, N_{Ti} / N_{Ni} , is 0.0050.

Electron energy loss spectra of the periclase- and corundum-structured phases, acquired in the second-difference collection mode, are shown in Figure 4. The portion of the spectra shown is the energy range between 425 eV and 575 eV and depicts both the Ti $L_{2,3}$ edge at ~456 eV and the O K edge at ~532 eV. The scales of the two spectra are such that the sums of the absolute values of the number of counts recorded across the O K edges of the two spectra are equal. There is no apparent Ti $L_{2,3}$ edge in the spectrum of the periclase-structured phase.

DISCUSSION

Analysis of the periclase-structured phase by EELS, Fig. 4, indicates the apparent absence of any titanium, whereas the EDX spectrum shown in Fig. 3 has a distinct Ti K_{α} peak which is 0.5% of the Ni K_{α} intensity. Linear superposition of the two spectra in Fig. 4 suggests that a titanium concentration of even 0.2% would have yielded a detectable Ti $L_{2,3}$ signal given the level of the noise in the spectra; therefore, most if not all of the Ti K_{α} intensity in the EDX spectrum in Fig. 3 is the result of secondary excitation. Other normalization schemes for the EEL spectra, such as equating the peak to valley ratios of the O K edges, do not substantially change these conclusions.

The secondary excitation component to the measured Ni K_{α} intensity may be greater or smaller than that of the Ti K_{α} peak depending upon the predominant type of secondary excitation. Secondary fluorescence would yield only a Ti K_{α} peak since Ni K X rays can fluoresce Ti K X rays but not *vice versa*. Conversely, excitation by high-angle-scattered electrons would be expected to yield secondary excitation peaks for both nickel and titanium with intensities comparable to their relative concentrations (~4:1). Therefore, if the measured Ti K_{α} peak in Fig. 3 is due primarily to secondary fluorescence, the extraneous Ni K_{α} intensity may be smaller than 0.5 %, whereas if high-angle-scattered electrons are primarily responsible for the measured Ti K_{α} intensity, then the extraneous Ni K_{α} intensity may be as much as 2 %. These levels of inaccuracy are nevertheless modest and suggest that secondary excitation would not limit the accuracy of the compositional analysis of the spinel- or corundum-structured phases in the specimen.¹¹

The masking geometry shown in Fig. 1a is only partially successful at reducing the intensities of the characteristic lines of interest in the hole count spectrum, as shown in Fig. 2. Optimally, the Au L lines in this spectrum should be larger than the Ti K and Ni K lines. Whereas the Ni K_{α} intensity in the hole count is just a few percent of the corresponding intensity in the spectrum of the periclase-structured phase, the Ti K_{α} intensity in the hole count spectrum is about half that in the measured EDX spectrum of the periclase-structured phase. A better masking geometry, such as shown in Fig. 1b, would reduce the characteristic intensities both in the hole count and due to secondary excitation. In addition, formulae are available for the calculation of the secondary fluorescence intensity of dimpled and ion-milled specimens that have been masked with a washer having a circular aperture.⁸

There is potential concern that the use of a high-Z masking material like gold may unduly increase the continuum background level, thus degrading the quality of the EDX spectrum and, in particular, leading to reduced detectability limits. In Fig. 2, the Au L signal in the raw spectrum (line) is comparable to that in the hole count (shaded) so that the characteristic lines of the gold are mostly due to the hole count with only a small secondary excitation component; the residual continuum background due to secondary excitation of the gold washer may be expected to be similarly small. The level of the continuum background in the hole count relative to that in the measured spectrum increases with increasing X-ray energy from ~5% at 2 keV to ~20% at 12 keV. However, particularly if the residual increase in the background level after background subtraction is only a small fraction of these percentages, the background levels are not sufficiently increased by the use of the high-Z masking washer to affect practical detectability limits.

The choice of masking material is dependent upon the elements composing the specimen. Gold was chosen as a washer material for this study because it is a strong absorber of X rays and because its characteristic peaks are not in the energy range of interest for the specimen, namely that

Figure 3. X-ray spectrum of the periclase-structured phase, of nominal composition NiO, in the specimen of overall composition NiO-20 wt.% TiO₂; the spectrum is also magnified 20 × to show the relative size of the titanium K_α peak. Also visible are a small Ni K_α "escape peak" (at 5.74 keV) and a small Fe K_α peak (at 6.40 keV), the latter presumably due to secondary excitation of the objective pole-piece.

Figure 4. Electron energy-loss spectra, acquired in second-difference mode, showing the Ti L_{2,3} and O K edges of the periclase-structured and corundum-structured phases. There is no Ti L_{2,3} edge apparent in the spectrum of the periclase-structured phase.

containing the K_{α} lines of the 3d-transition-metals. For the analysis of GaAs-based heterostructures, copper or nickel masks would be appropriate. Copper, nickel, and gold masking washers are commercially available with a variety of aperture sizes. Optimally, a masking washer might be designed specifically for EDXS. Such a washer could have a beryllium layer facing the electron gun and layers of increasing atomic number thereafter, culminating with a gold layer adjacent to the specimen. In principle, such a masking washer would have a high absorbing power but would nevertheless contribute a low continuum background and no characteristic peaks to the measured spectrum. Moreover, such a masking washer could be used to mask any specimen, regardless of composition.

CONCLUSIONS

The masked self-supporting disc specimen yields a relatively modest secondary excitation contribution to the measured X-ray spectrum. In this study, the contributions of all secondary excitation effects to the measured Ti K_{α} intensity was only ~0.5% of the intensity of the measured Ni K_{α} intensity. A still lower secondary excitation intensity is expected if the specimen is masked with a washer having a small circular aperture.

Given a suitable choice of masking washer, the masked self-supporting disc is a versatile specimen-geometry for quantitative X-ray microanalysis. The commercial availability of copper, nickel, and gold masking apertures with a variety of aperture sizes makes the routine use of this specimen geometry a convenient one. This geometry could become even more versatile given a masking aperture designed specifically for EDXS.

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