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A simple approach for thickness measurements using electron probe microanalysis

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Abstract: A simple and fast method for thickness measurements using electron probe microanalysis (EPMA) is described. The method is applicable on samples with a thickness smaller than the electron depth range and does not require any knowledge of instrumental parameters. The thickness is determined by means of the distance that electrons travel inside the sample before crossing it. Samples are first deposited on a substrate that, when reached by transmitted electrons, produces an X-ray signal. The measured characteristic X-ray line intensity of the substrate is later used to determine the energy of transmitted electrons, which is proportional to the distance that electrons travel inside the sample. The study was performed on spherical K411 glass particles and cylindrical particles of U-Ce oxide with a size ranging from 0.2 to 4 μm . The measured thicknesses of all the studied particles showed good agreements with the real ones. Although the method is only validated on particles with usual shapes, it can be applied to determine a local thickness of thin samples with irregular morphologies. This can help solving multiple issues in analysis with EPMA of non-bulk samples exhibiting complex geometries. 3D microscopy imaging could also find a good utility in the described method.

Keywords Electron probe microanalysis. Electron microscopy. Thin samples.

Microparticles. X-ray emission. Thickness measurement.

INTRODUCTION

Morphological and elementary analysis of thin samples using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) presents a considerable challenge. The difficulties with regards to analysis with SEM are mainly associated with the lack of knowledge of the sample size in the direction of the incident electron beam (z direction) as imaging is only performed in the x-y plane. The determination of the thickness of samples is important during image analysis and can provide useful information about their 3D geometry. In EPMA, having the possibility to measure the thickness of thin samples could give insight into the amount of corrections needed to account for absorption and fluorescence effects inside the sample (Armstrong, 1991). Several approaches for thickness measurement using EPMA were developed for thin films and stratified samples deposited on a substrate (Sweeney et al., 1960); (August & Wernisch, 1987); (Hombourger et al., 2002); (Hombourger et al., 2003); (Pereyra et al., 2020). Although these approaches provide satisfactory results, they were tested on thin films with a thickness ranging from few to hundreds of nanometers and their adaptability to micro sized samples is not certain. In addition, most of the available thin film programs (Guillaume et al., 1992); (Llovet & Merlet, 2010); (Oxford Instruments, n.d.); (Pouchou & Pichoir, 1990) are not free.

Among other methods that were reported as efficient for thickness measurements are those based on the use of transmission electron microscopy (TEM) such as energy loss spectroscopy (EELS) (Zhang et al., 2012); (Shi et al., 1996) and convergent-beam electron diffraction (CBED) (Delillea, 2001). EELS was shown to provide thickness calculation for samples in a much wider thickness range (~15-500 nm) than the one provided by CBED (~150-300 nm) (Iakoubovskii et al., 2018); (Mitchell, 2006); (Egerton & Cheng, 1987). In EELS, the thickness can be determined from the low-loss spectrum by means of the Kramers-Kronig (KK) sum-rule (Egerton & Cheng, 1987) or the log-ratio method (Malis et al., 1988). Despite

the fact that thickness calculation with EELS is fast to perform, the accuracy of KK and log-ratio models depends on the knowledge of the optical refractive index for the former and the inelastic mean free path for the latter. These parameters are however difficult to evaluate for many materials (Iakoubovskii et al., 2018). Moreover, the application of TEM based techniques is limited by both complexity with regards to sample preparation and the sensitivity of image analysis to the thickness of the studied specimen.

An approach for thickness measurement that is adapted to samples thicker than those analyzed with TEM can be advantageous for morphological analysis using electron microscopy. Typical example of analyses requiring the use of such approaches are those performed on industrial powder composed of a large number of particles exhibiting different sizes. Contrary to TEM, samples can be easily imaged in SEM. This makes the combined use of SEM and EPMA more optimal for morphological and elementary analysis of powder. However, industrial powders, such as those studied in environmental science or in the nuclear industry, contain particles with complex geometry. The thickness of these particles in the direction of the incident electron beam cannot be determined accurately through 2D observations with SEM. The inability to measure the thickness can also be problematic for chemical analysis with EPMA where the correction of size effects is required (Essani et al., 2020a, 2020b).

Many attempts were made to perform 3D imaging with SEM (Tafti et al., 2015). The fastest approaches are those based on the recombination of 2D images obtained from different tilt angles and a further 3D reconstruction (Monteiro et al., 2020). Although good 3D surface reconstruction can be obtained with these approaches, the determination of the sample's thickness through a 3D reconstruction of its volume is not guaranteed. Most advanced procedures for 3D volume representation include serial sectioning using a focused ion beam combined with SEM for imaging (Groeber et al., 2006); (Titze & Genoud, 2016). These methods can be highly efficient with regards to the determination of the material 3D complex

microstructure but they are destructive, time consuming and not optimal for tasks as simple as thickness measurements. An optimal morphological analysis of samples with SEM therefore raises the need for a fast and accurate approach for thickness measurements.

We present in this work a fast and simple method that can be used for thickness measurements using an energy dispersive spectrometer (EDS) attached to a scanning electron microscope. Thickness measurements were carried out on NIST (National Institute of Standards and Technology) K411 glass spherical particles and cylindrical particles of U-Ce Oxide. The thickness of each particle was determined from the measured X-ray intensities corresponding to the $K\alpha$ line of the substrate on which the particle is deposited. Analyses were performed on particles exhibiting different thicknesses, which enabled to assess the validity of the approach on a sufficiently wide thickness range (~ 0.2 to $4 \mu\text{m}$).

MATERIALS AND METHODS

Measurements. X-ray measurements were performed using an Oxford EDS attached to a Merlin field-emission SEM. The spectrometer is composed of a silicon drift detector and an AP3 Moxtek window supported by a rigid silicon grid. The take-off angle of the detector is equal to 35° . The working distance and the distance between the spectrometer and the sample were set at 11.5 mm and 19.5 mm, respectively. This enabled to collect a maximum number of emitted photons. In order to obtain a good resolution (~ 125 eV FWHM at Mn $K\alpha$) and a counting rate that do not exceed 30% in dead time, all measurements were performed using the longest shaping time and an electron probe current of 0.2 nA. The acquisition time for all the spectra was set equal to 100 s. Uncertainties associated with counting statistics were evaluated by acquiring 8-10 spectra of pure samples (e.g. carbon and silicon) and were estimated within 1-3% for characteristic lines and around 4 to 8% for the background intensities.

Thickness measurements. The thicknesses were determined from the X-ray intensity associated to the $K\alpha$ line of the substrate on which particles were deposited. This was achieved by probing each particle using a focused electron beam with an energy high enough for the transmission of electrons to occur. After being transmitted through the particle, electrons strike the substrate at a sufficient energy and induce the emission of characteristic X-rays (Figure 1). Being proportional to the number and energy of transmitted electrons, the X-ray intensity emitted from the substrate was used to determine the energy loss of electrons, which enabled measuring the thickness of the analyzed particle. The approach presented in this study is based on the following assumptions: (i) the particle is dense enough and the distance travelled by electrons inside the particle is representative of its thickness, (ii) the composition of the particle is homogeneous and different from the one of the substrate, (iii) the X-ray emission of the substrate is induced by a monoenergetic electron beam at the exit of the particle, (iiii) the electron beam is focused enough so that the influence of its size on the trajectories of electrons inside the particle can be neglected.

Based on the Kanaya-Okayama model (Kanaya & Okayama, 1972), the energy E'_0 (keV) of transmitted electrons can be expressed as:

$$E'_0 = E_0 \left(1 - \frac{t}{R}\right)^{3/5} \quad (1)$$

where E_0 (keV) is the energy of the primary electrons, t (μm) is the mean distance travelled by electrons before being transmitted and R (μm) is the Kanaya-Okayama electron depth range (Kanaya & Okayama, 1972). Equation (1) can be re-written as:

$$E'_0 = E_0 \left(1 - \frac{J}{E_0^{1.67}}\right)^{3/5} \quad (2)$$

with

$$J = \frac{t Z^{0.89} \rho}{0.0276 A} \quad (3)$$

where Z is the mean atomic number of the sample, ρ (g cm⁻³) its density and A its mean atomic mass (g).

The approach adopted in this work is based on the determination of the parameter J and a further calculation of the thickness. The X-ray spectra of each particle are first measured at different acceleration voltages. This enables to collect characteristic X-ray intensities $I^s_k, k=1,2..n$ emitted from the substrate at different electron energies E_{0k} . On the other hand, the dependence of the characteristic intensity I on the overvoltage $U = E_0/E$ (E being the ionization energy of the electron shell involved in the production of the characteristic X-rays) can be expressed by (Green & Cosslett, 1961):

$$I \propto U \ln U - U + 1 \quad (4)$$

Now if we consider the absorption of X-rays emitted from the substrate inside both the particle and the substrate, we can write for k measured intensities I^s_k :

$$I^s_k \propto f_k(\chi^s, E'_{0k}) f_k(\chi^p, E_{0k}) \frac{E'_{0k} \ln \frac{E'_{0k}}{E^s} - E'_{0k} + E^s}{E^s} \quad (5)$$

where $f(\chi)$ is the absorption factor, $\chi = \left(\frac{\mu}{\rho}\right) \text{cosec}(\theta)$ with $\left(\frac{\mu}{\rho}\right)$ the mass absorption coefficient and θ the take-off angle of the X-ray detector. The indices s and p stand for absorption inside the substrate and the particle, respectively. E^s (keV) is the photon energy corresponding to the K line of the substrate element.

It is worth noting that the X-rays generated inside the substrate undergo different path lengths before reaching the detector. Absorption factors $f(\chi^{s,p})$ inside both the substrate and the particle are therefore hard to evaluate. Moreover, determining the energy loss of electrons from equation (5) requires accounting for the intensity loss caused by absorption in the X-ray detector. Determining the detector efficiency adds more complications, especially in cases where the thickness of layers in the spectrometer window are not known with sufficient accuracy.

In order to cope with these difficulties, the dependence of the substrate emission on instrumental parameters and absorption factors was canceled by normalizing on the intensity value corresponding to one of the energies E_{0k} , $k=1,2..n$. Obviously, this suggests that the dependence of the absorption factors $f(\chi^{s,p})$ on E_0 is no longer considered. However, such a consideration can lead to inaccurate results if the difference between the energies E_{0k} and the one used for normalization is large. I^s_k were therefore measured using close energy values ($|E_{0k\pm 1} - E_{0k}| = 1$ keV) so that the energy difference between the lowest (or highest) accelerating voltage and the normalizing accelerating voltage remains small. The intensity used for normalization was chosen as the one corresponding to the median energy $E_{0\frac{n}{2}}$. The normalized intensities $I^n_k = I^s_k / I^s_{\frac{n}{2}}$ can now be expressed as:

$$I^n_k = \frac{\sigma_k \left(E_{0k} \ln \left(\frac{E_{0k} \sigma_k}{E^s} \right) - E_{0k} + \frac{E^s}{\sigma_k} \right)}{\sigma_{\frac{n}{2}} \left(E_{0\frac{n}{2}} \ln \left(\frac{E_{0\frac{n}{2}} \sigma_{\frac{n}{2}}}{E^s} \right) - E_{0\frac{n}{2}} + \frac{E^s}{\sigma_{\frac{n}{2}}} \right)} \quad (6)$$

with

$$\sigma_i = \left(1 - \frac{J}{E_{0i}^{1.67}} \right)^{\frac{3}{5}} \quad (7)$$

According to Green and Cosslett, equation (4) can also be expressed as $I \propto 0.365 (U - 1)^{1.67}$ with an error less than 10% in the overvoltage range $1.5 < U < 16$.

After introducing this formula in equation (5), we can express I^n_k as:

$$I^n_k = \left(\frac{\sigma_k E_{0k} - E^s}{\sigma_{\frac{n}{2}} E_{0\frac{n}{2}} - E^s} \right)^{1.67} \quad (8)$$

The parameter J can afterward be obtained by fitting I^n_k values with equations (6) or (8). For comparison, the fit was performed in this work with both equations using the Levenberg-Marquardt non-linear least square method (the free GNUPLOT software can be used to that

end or the C library `lmfit` (Wuttke, n.d.) for programming purposes). To a first approximation, the thickness can be considered equal to the mean distance t that electrons travel inside the particle. This approximation can be refined by increasing the beam electron energy so as to reduce the amount of side scattered electrons and obtain electron trajectory segments that are more parallel to the direction of the incident electron beam. The thickness was further calculated from the parameter J using equation (3).

RESULTS AND DISCUSSION

Spherical K411 glass microparticles. Analyses were performed on five spherical particles of K411 glass, two deposited on a nickel (Ni) substrate (particles S1 and S2) and three on aluminum (Al) (S3, S4 and S5) (Figure 2). The X-ray spectra of all the particles showed an intense characteristic X-ray line of the substrate indicating the significant transmission of electrons through the particles. Because the energy of transmitted electrons E'_0 increases as the thickness decreases, the substrate emission was observed to be more important for particles with low diameters (e.g. X-ray spectrum of particles S1 and S2 shown in Figure 3).

Particles were probed at a normal incidence of the electron beam using five to seven electron energies E_{0k} . This enabled collecting different X-ray intensities of the substrate. The normalized intensities I^n were further determined for each energy and fitted using equation (6) and (8). The parameter J was obtained through the fitting, which enabled calculating the thickness of each particle using equation (3). An example is shown in Figure 4 where the normalized intensities obtained by analyzing particles S1 and S2 are presented along with their fitting.

The thicknesses were calculated for all the particles from J values using both equations (6) and (8) (table 1). The results presented in table 1 indicate clearly the good accuracy of the approach with regards to thickness measurements. The deviations between the diameters of particles and the mean values of their calculated thicknesses are less than 10%. Results

obtained with equations (6) and (8) also show good agreements with deviations between calculated mean thicknesses not exceeding 11%. Although this shows the validity of both equations, with the exception of particle S5, equation (6) generally provides more accurate thickness calculations. This suggests that equation (4), adopted in equation (6), probably gives a better description of the dependence of the characteristic X-ray intensity on the overvoltage. It is important to note that thickness measurements were performed using raw characteristic intensities of the substrate, i.e. the background was not extracted from the measured spectra. Although it is more practical to work with net intensities ($I^s - B^s$, B^s being the *Bremsstrahlung* intensity of the substrate) the background associated to the substrate is hard to evaluate. This is due to the contribution of the particle's *Bremsstrahlung* to the measured background. The measured characteristic X-ray intensities of the substrate should therefore be intense enough so that deviations between net intensities and raw ones can be neglected. In this work, good measurements were obtained when the condition $\frac{B}{I^s} \leq 5\%$ was satisfied, with B the measured *Bremsstrahlung* intensity under the X-ray line of the substrate.

Cylindrical microparticles of U-Ce oxide. Thickness measurements were carried out on three particles of U-Ce oxide (C1, C2 and C3) deposited on an Al substrate. Image analysis with SEM showed particles exhibiting a cylindrical form with a diameter in the interval [0.20 : 0.24 μm] for C1, [0.53 : 0.60 μm] for C2 and [0.80 : 0.88 μm] for C3 (Figure 5). The red circles in Figure 5 indicate the zones of analysis performed on each particle. The thicknesses are therefore determined locally at the region where the electron beam enters the particle.

The characteristic X-ray intensities of the Al substrate were further measured using different electron energies E_{0k} ranging from 12 to 19 keV. After fitting the normalized intensities I^n , the parameter J was obtained for each particle which enabled calculating their thicknesses. Table 2 shows the calculated thicknesses corresponding to the regions presented by red circles in Figure 5. It can be seen that both equations provide results that are in satisfactory

agreements with the expected values. Less accuracy is however obtained in the case of particle C2-zone 1 where the calculated thicknesses are slightly overestimated. This being said, some U-Ce oxide particles do not have a perfectly cylindrical shape and their thicknesses might differ, to a lesser extent, from their widths. Another parameter that could also contribute to the observed deviation is the influence of electron energies on thickness measurements.

As shown in table 3, thicknesses determined for C2-zone 1 depend on the values of energies E_{0k} . It can be observed that calculated thicknesses are lower at high energies. A probable cause of such an observation can be related to the decrease of elastic scattering of electrons inside the particle as E_0 increases. In fact, as the electron energy decreases, the amount of scattered electrons becomes important. Electrons might therefore undergo path lengths larger than the diameter of the cylindrical particle leading to an increase of their energy loss. The calculated thicknesses are therefore expected to be somewhat higher when working with low energies. On the other hand, the deviation between results obtained with equations (6) and (8) is significant at high energies (~30%). It is likely that this results from errors associated to the approximation of equation (4) as a power of $(U - 1)$.

CONCLUSION

Simple thickness measurements using EPMA is achieved. The proposed approach was validated on particles with a size smaller than the electron depth range. Thicknesses were determined by means of the substrate X-ray emission on which the particles were deposited. The X-ray intensity emitted from the substrate can provide a good estimation of the energy loss of electrons inside the particle. Being proportional to the mean distance travelled by electrons inside the particle, the energy loss of electrons enables the determination of the thickness.

The use of normalized X-ray intensities emitted from the substrate enables, to a reasonable degree, taking account of the intensity loss caused by absorption effects and instrumental parameters. This allows obtaining a direct dependence between measured intensities of the substrate and the energy loss of electrons inside the particle. The thickness can be further determined by fitting the normalized intensities using equations (6) and (8). Although equation (8) might lead to inaccurate thickness calculation at high electron energies, it is recommended to use both equations in order to verify the consistency of the determinations.

The fast thickness measurements provided by this approach can be advantageous for powder characterization as it offers the possibility of performing optimal morphological analysis of a large number of particles. Thickness mapping of particles or thin samples is an interesting application that could also benefit from the improved timeliness of thickness measurements offered by the approach.

It is worth noting that the necessity to work with K lines of the substrate may prevent the application of the approach to substrates composed of heavy elements (e.g. electron probes operating at a maximum acceleration voltage of 40 kV). The adaptability of the method to L and M lines is therefore an interesting topic and will probably be discussed in future studies. Other limitations of the method that should also be mentioned are related to i) thickness measurements of nanoparticles where the size of the electron beam becomes an influencing parameter and ii) analysis of hollow or highly porous particles in which the thickness does not correspond to the distance travelled by electrons in matter.

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Figure captions

Figure 1. X-ray emission of the substrate induced by electron transmission through the particle.

Figure 2. SEM Images of K411 glass spherical microparticles showing a diameter of 0.75 μm for S1, 1.35 μm for S2, 1.48 μm for S3, 4.01 μm for S4 and 0.64 μm for S5.

Figure 3. X-ray spectra acquired at an electron energy $E_0 = 20$ keV for particles S1 and S2 deposited on a Ni substrate.

Figure 4. Normalized intensities I^n_k obtained by analyzing particles S1 and S2 and their fit using equations (6) and (8). The values of I^n_k were obtained using five electron energies $E_{01} = 18$ keV, $E_{02} = 19$ keV, $E_{03} = 20$ keV, $E_{04} = 21$ keV and $E_{05} = 22$ keV with E_{03} the median value used for normalization.

Figure 5. SEM images of cylindrical microparticles of U-Ce oxide.