CRYSTALLITE SIZE MEASUREMENT USING X-RAY DIFFRACTION

Introduction

Phase identification using x-ray diffraction relies mainly on the positions of the peaks in a diffraction profile and to some extent on the relative intensities of these peaks. The shapes of the peaks, however, contain additional and often valuable information. The shape, particularly the width, of the peak is a measure of the amplitude of thermal oscillations of the atoms at their regular lattice sites. It can also be a measure of vacancy and impurity element concentrations and even plastic deformation, any factor which results in a distribution of d-spacings.

Crystallite size can also cause peak broadening. The well known Scherrer equation explains peak broadening in terms of incident beam divergence which makes it possible to satisfy the Bragg condition for non-adjacent diffraction planes. Once instrument effects have been excluded, the crystallite size is easily calculated as a function of peak width (specified as the full width at half maximum peak intensity (FWHM)), peak position and wavelength. Warren and Averbach's method takes not only the peak width into account but also the shape of the peak. This method is based on a Fourier deconvolution of the measured peaks and the instrument broadening to obtain the true diffraction profile. This method is capable of yielding both the crystallite size distribution and lattice microstrain.

The Scherrer and the Warren-Averbach methods do not give the same value for the crystallite size.

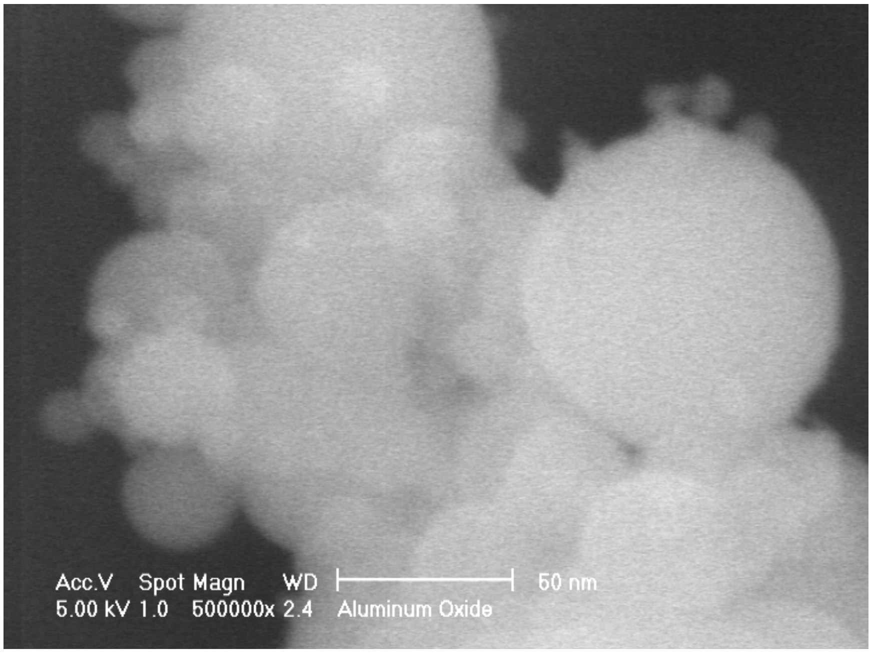

Figure 1. FEG-SEM image of nanosized aluminum oxide powder. Note the magnification and the size of the micron bar. Also note how the smaller particles and the edges of the larger particles appear to be somewhat transparent. This is because much of the 5 kV electron beam can pass through these thinner parts of the particles.

That is because they each yield different characteristic averages from the crystallite size distribution. But by combining the results of the Scherrer and the Warren-Averbach methods and making reasonable assumptions regarding crystallite shape and size distribution it is possible to arrive at a single size distribution.

In this experiment both the Scherrer and the Warren-Averbach methods are used to measure the crystallite size in several fine, even nano-crystalline, powders. Coarser powders, larger than 1 micron, may be analyzed to illustrate the limitations of these techniques.

Background

1. Characteristic Averages

In any distribution there are a number of characteristic averages. The ones we need here are the arithmetic mean

$$\langle D\rangle_{num} = \langle D^{1}\rangle$$

the area-weighted average

$$\langle D\rangle_{area} = \frac{\langle D^{3}\rangle}{\langle D^{2}\rangle}$$

and the volume-weighted average

2. Scherrer Crystallite Size

The crystallite size as measured by the Scherrer method is given by

$$\langle L\rangle_{vol} = \frac{K\lambda}{B_{1/2}\cos\theta_{B}}$$

where $\langle L\rangle_{vol}$ is the volume-weighted size, 2_B is the Bragg angle, 8 is the wavelength of the x-ray and K is a unit cell geometry dependent constant whose value is typically between 0.85 and 0.99. $B_{1/2}$ is the full-width-half-max of the peak after correcting for peak broadening which is caused by the diffractometer. One way to represent $B_{1/2}$ is

$$B_{1/2}^{2} = B_{obs}^{2} - B_{m}^{2}.$$

where B_{obs} is the measured peak width and B_m is the beak broadening due to the machine.

3. The Method of Warren-Averbach

The Warren-Averbach method is based on a Fourier analysis of the diffraction peak. The measured peak profile *h(s)* is actually the convolution of a function for the pure peak profile *f(s)* and a function for the instrumental broadening *g(s)*

$$h(s) = g(s)\otimes f(s)$$

where $s / (2\sin 2)/8$. This can also be represented by the product of the Fourier transforms for instrumental broadening ö *(g)* and the pure peak profile ö *(f)*

$$\mathscr{F}(h) = \mathscr{F}(g)\cdot\mathscr{F}(f).$$

The Warren-Averbach method involves using ö *(g)* obtained from the analysis of a line-width standard such as LaB_6 to solve for ö *(f)* and then performing an inverse Fourier transform on ö *(f)* to obtain *f(s)*. The result can be written as a Fourier series

$$\mathscr{F}(s) = \sum_{L=-\infty}^{\infty} \left(A(L)\cos[2\pi(s-s_0)L] + B(L)\sin[2\pi(s-s_0)L] \right)$$

where *A(L)* and *B(L)* are the cosine and sine coefficients and *L* is the length of a column of unit cells perpendicular to the diffracting planes. A plot of *A(L)* versus *L* is used to determine the area weighted crystallite size $<L>_{area}$ and lattice microstrain. If two peaks in the same family of planes are used in this analysis then the contribution of microstrain to peak broadening can be eliminated.

4. Crystallite Size

The Scherrer and Warren-Averbach methods yield different characteristic averages of the column length *L*. The Scherrer method yields $<L>_{vol}$ while Warren-Averbach yields $<L>_{area}$. In order to obtain a measure of the crystallite size one may assume a shape for the particles. Assuming spherical crystallites the diameter of the sphere can be estimated

$$<D>_{area} = \frac{3}{2} <L>_{area}$$

and

$$<D>_{vol} = \frac{4}{3} <L>_{vol}.$$

5. Crystallite Size Distribution

Size distributions tend to be log-normal, a distribution where there are a relatively large number of smaller particles. The normalized log-normal distribution is given by

$$g_{LN}(D) = \frac{1}{\sqrt{2\pi}\, D \ln\sigma} \exp\left(-\tfrac{1}{2} \left[\frac{\ln(D/D_0)}{\ln\sigma} \right]^2 \right)$$

where D_0 is the median value and F is the width of the distribution. The characteristic averages defined in part 1 are given by

$$<D>_{num} = D_0 \exp\left(\frac{1}{2} \ln^2\sigma \right)$$

$$<D>_{area} = D_0 \exp\left(\frac{5}{2} \ln^2\sigma \right)$$

$$<D>_{vol} = D_0 \exp\left(\frac{7}{2} \ln^2\sigma \right)$$

By doing both the Scherrer and Warren-Averbach analyses and assuming spherical particles we will have both $<D>_{area}$ and $<\mathrm{D}>_{\mathrm{vol}}$. This allows us to solve for D_0 and F, calculate $<D>_{num}$, and plot the complete crystallite size distribution.

6. Example

The following example shows the results of the crystallite size analysis of a powder containing anatase and rutile. The analysis concentrated on the anatase phase.

Figure 2 shows two peaks used in this study.

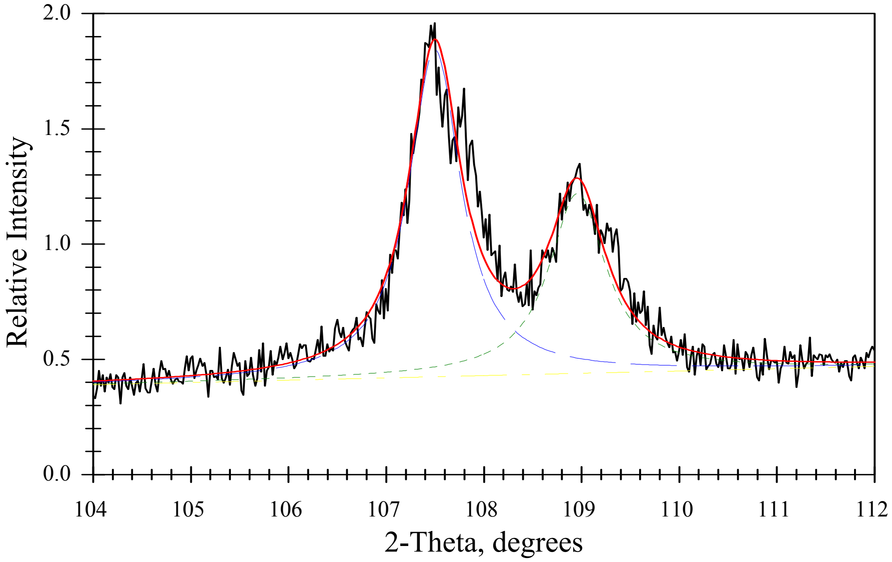

Figure 2. Profile fitting of two of the peaks from the anatase pattern.

The results from this peak and from two others are summarized in table 1. These results show that the Scherrer size is consistently larger than the Warren-Averbach size which was expected given the differences in the volume and area-weighted averages. It also shows a trend in size versus diffraction angle which is especially pronounced for the Scherrer analysis, something that was not expected and initially concerned us.

Table 1. Results of the particle size analyses of a TiO_2 powder.

		Scherrer Analysis	Warren-Averbach Analysis	Equivalent Sizes (Spherical)		Log-Normal Distribution		Average Size
2-Theta degrees	Reflection (hkl)	$\langle L\rangle_{Vol}$ nm	$\langle L\rangle_{Area}$ nm	$\langle D\rangle_{Vol}$ nm	$\langle D\rangle_{Area}$ nm	F nm	D_o nm	$\langle D\rangle_{Num}$ nm
48.0225	(200)	38.50	16.10	51.33	24.15	2.38	3.67	5.35
107.4381	(316)	44.00	18.00	58.67	27.00	2.41	3.88	5.72
108.9347	(400)	50.70	19.20	67.60	28.80	2.52	3.41	5.23
Averages:		44.40	17.77	59.20	26.65	2.44	3.62	5.40

The final size distribution and the characteristic averages are shown in figure 3. Notice how differences in the area and volume weighted averages for each peak turn out to be insignificant once the whole distributions are plotted and compared.

Objective

The single objective of this experiment is to measure the crystallite size distribution in the specimens provided. The results from the Scherrer analysis are useful in obtaining a final result from the

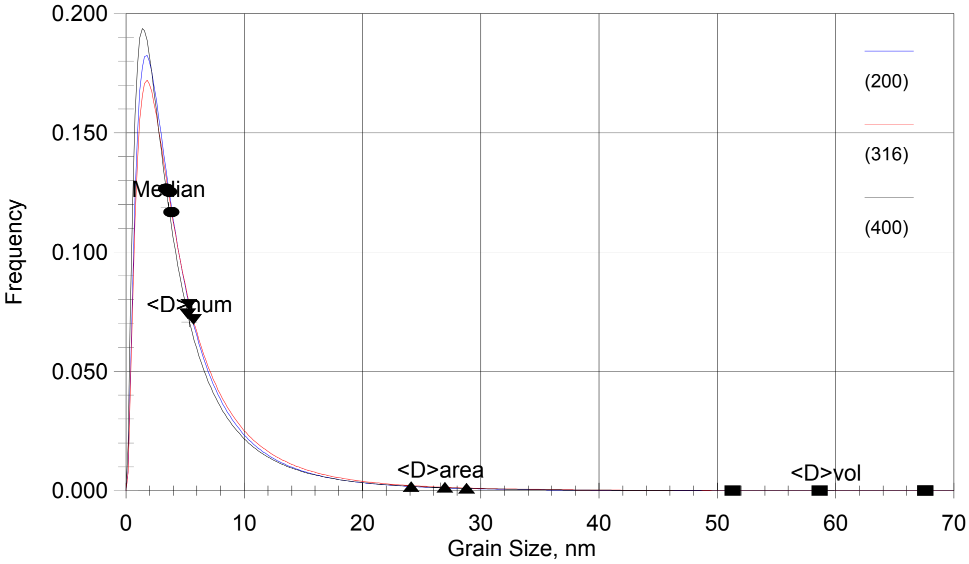

Figure 3. The final log-normal distributions based on the analysis of three leaks in the anatase pattern.

Warren-Averbach method. The results of the Warren-Averbach analysis in combination with the Scherrer crystallite size will be used to produce a plot of the crystallite size distribution.

Materials

Several powders will be available. Some will be conventional 1-25 micron alumina powders such as those used to polish metallography specimens. Nano-crystalline powders of several compositions will be used for the main part of the experiment.

Equipment

The equipment used during this experiment is:

1. Scintag XDS 2000 x-ray diffractometer

2. LaB_6, a NIST-traceable line-width standard (SRM 696)

Procedure

1. Obtain printouts of the powder diffraction files for the specimens that will be analyzed.

2. Perform a preliminary scan of the powder. Locate peaks which might yield good results. If possible, select pairs of peaks that are from the same reflection, for example the (200) and (400) peaks or the (111) and (222) peaks.

3. Scan each peak you selected at a scan rate which will produce good counting statistics. Use the step scan mode and make sure your instrument configuration matches those used to generate the external standards.

4. Run the background stirpping program on the data, but turn off all options so that the data is not changed. This will create the "net intensity" file needed in the next step.

5. Run the profile fitting program on each peak and then run the Scherrer and then the Warren-Averbach programs on these results.

Results

1. You should have Scherrer and Warren-Averbach crystallite sizes for several peaks in each specimen. How do the results for each peak compare?

2. How do the results of the Scherrer and Warren-Averbach analyses compare?

3. Calculate the diameters that correspond to the column lengths reported by the Scherrer and Warren-Averbach analyses.

4. Determine the median crystallite size and the width of the size distribution.

5. Plot the size distributions using the median and widths obtained for each peak.

References

1. C.E.Krill and R.Birringer, *Measuring Grain Sizes in Nanocrystalline Materials*, submitted to Journal of Materials Research