

MEASURING CRYSTALLITE SIZE USING X-RAY DIFFRACTION, THE WILLIAMSON-HALL TECHNIQUE (DRAFT)

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. For instance, the width of the peaks increases as the size of the crystalline domains (crystallites) that diffract the x-rays, decreases. In addition, the whole shape of the diffraction peaks can be analyzed, using Fourier techniques, to obtain the distribution of crystallite sizes. Finally, microstrain, short range lattice strains caused by crystalline defects (not macroscopic stresses) also causes peak broadening. X-ray diffraction can be used to measure all three, but the fact that microstrain and crystallite size both lead to peak broadening means that either both size and strain must somehow be measured, or a way to eliminate the effect of one or the other must be found. In this experiment both crystallite size and microstrain are measured where the Scherrer method (which yields the size based on measurements of any one peak when strain is not present) is applied to all diffraction peaks and the variation in size is used to measure the microstrain. This experiment is based on the one described in Suryanarayana and Norton's book [1] and the specific technique, called the Williamson-Hall method [2], has many applications in nano-technology, including characterizing nano-powders (see figure 1) and studying crystallization in glasses.

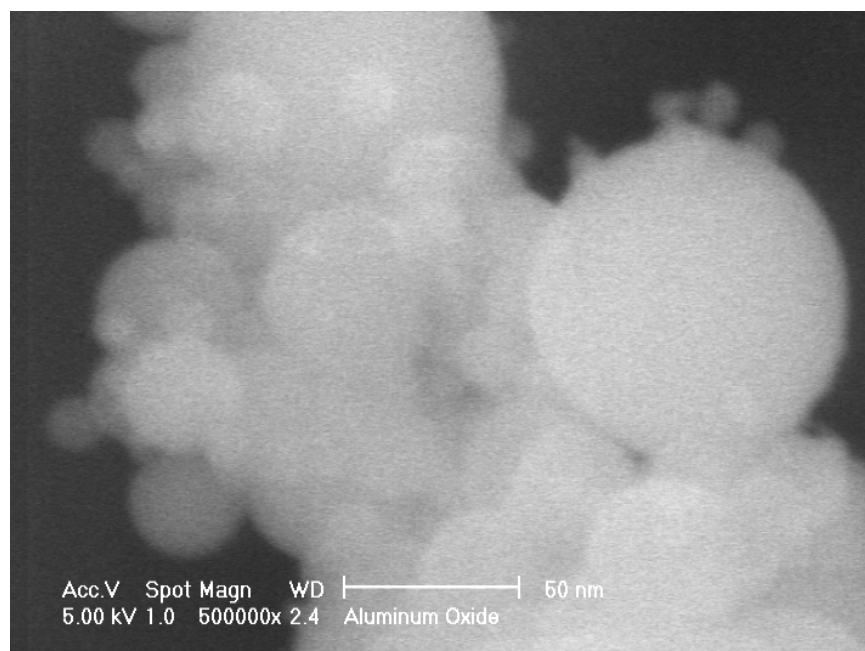


Figure 1. FEG-SEM image of nanosized aluminum oxide powder. Note the magnification and the size of the micron bar. Also note how the smaller particles and the edges of the larger particles appear to be somewhat transparent. This is because much of the 5 kV electron beam can pass through these thinner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

Background

1. Characteristic Averages

The single value of a crystallite size obtained in this experiment is actually a characteristic average value representing a distribution of sizes. In any distribution there are a number of characteristic averages. [3] The arithmetic and geometric means are familiar examples, but there are also many others.

Any characteristic average size of the measured value D can be written as $\langle D^n \rangle$ where ... Using this notation the arithmetic mean is written as

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

while the area-weighted average is

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

and the volume-weighted average is

$$\langle D \rangle_{vol} = \frac{\langle D^4 \rangle}{\langle D^3 \rangle} . \quad (3)$$

In this experiment, the size measured is not a simple diameter or similarly convenient size. Rather, it is an average column length $\langle L \rangle$, which is similar to an average chord length for a circle, but in this case it is the average length of a line, parallel to the diffracting plane, passing through a 3-dimensional object. The Scherrer method yields the volume-weighted column length $\langle L \rangle_{vol}$. Assuming spherical crystallites (see figure 1) the volume-weighted crystallite diameter can be estimated using the equation:

$$\langle D \rangle_{vol} = \frac{4}{3} \langle L \rangle_{vol} \quad (4)$$

Figure 2 shows the results of measurements of crystallite size in which the Scherrer sizes $\langle D \rangle_{vol}$ and

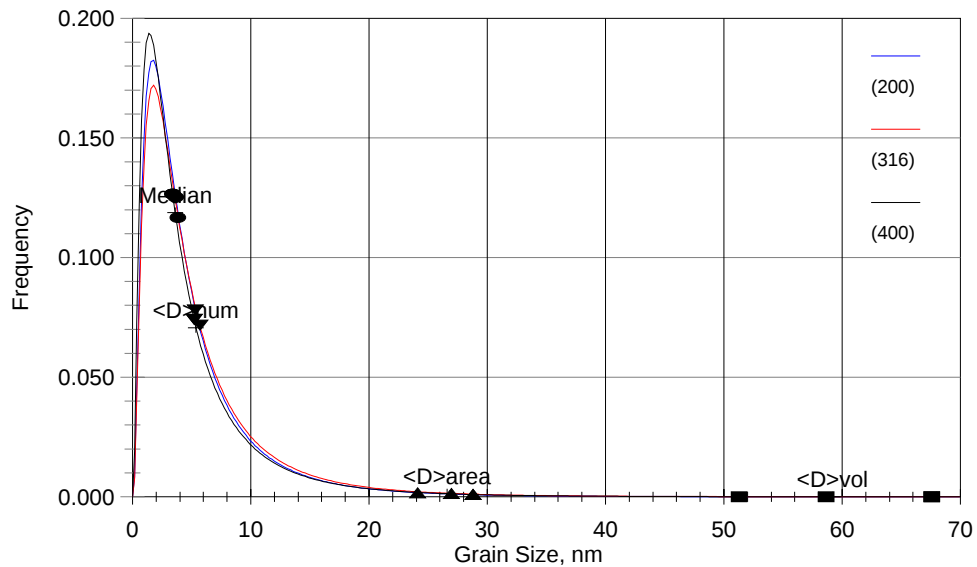


Figure 2. The final log-normal distributions based on the analysis of three leaks in the anatase pattern.

Warren-Averbach (a Fourier-based method) sizes $\langle D \rangle_{area}$ for three different reflections are shown on the same distribution. A log-normal distribution was assumed and these two measured characteristic averages made it possible to determine the median values and the arithmetic averages and to plot the log-normal distribution. Please note that it wasn't the actual values of $\langle D \rangle_{vol}$ and $\langle D \rangle_{area}$ that determined the mean and median values, but rather it was the differences between them.

3. Peak Broadening

Upon close examination of a powder diffraction pattern one should notice that as 2θ increases the peaks become broader. There are a number of reasons for this, including the focusing of the x-rays onto the sample, the angular aperture of the detector, the nature of the sample itself, and of course the nonlinear relationship between d-spacing and 2θ . While one could attempt to account for each of these and many other factors and model the whole system, it is generally sufficient to fit the data to an empirical equation. Second order polynomials can be used to represent this trend, but often the following equation is often used to characterize this broadening for Cauchy profiles

$$FWHM_C = u \tan \theta + \frac{v}{\cos \theta} \quad (5)$$

while for Gaussian profiles the equation is

$$FWHM_G = \sqrt{u \tan^2 \theta + v \tan \theta - w} \quad (6)$$

In both cases u , v , and w are constants determined by fitting the widths of peaks from a line-width standard such as lanthanum hexaboride (LaB_6) to this equation. LaB_6 has the narrowest peaks of any material and for all practical purposes one can consider all measured peak broadening as being due to instrumental factors. Figure 3 shows a plot of peak width as a function of 2θ for three different materials. Note that LaB_6 has the narrowest peaks of the three.

Once the instrumental broadening B_{inst} of a diffractometer has been determined one can extract the pure sample broadening $B_{size+strain}$ from the measured sample broadening B_{obs} . In each case B refers to the full-

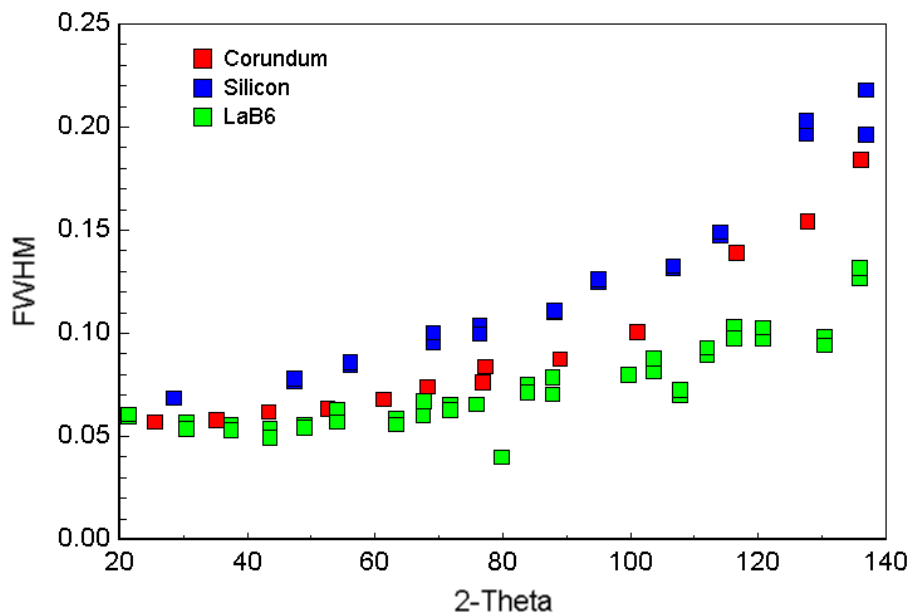


Figure 3 FWHM peak width as a function of diffraction angle for three different samples.

width-half-max of the peak, and for the Cauchy profile

$$B_{size+strain} = B_{obs} - B_{inst} \quad (7)$$

while for the Gaussian profile

$$B_{size+strain}^2 = B_{obs}^2 - B_{inst}^2 \quad (8)$$

3. Scherrer Crystallite Size

The Scherrer equation:

$$B_{size} = \frac{K \lambda}{\langle L \rangle_{vol} \cos \theta_B} \quad (9)$$

offers a simple relationship between crystallite size and peak broadening. Here λ is the wavelength of the x-ray, B_{size} is the width (in radians) of the peak due to size effects, K is a constant whose value is approximately 0.9, and θ_B is the Bragg angle. This equation represents broadening that is due to the finite size of the crystal where for very small crystals the intensity of x-rays at close to, but not exactly, the Bragg condition is not zero [4].

4. Microstrain

Microstrain is due to imperfections within the crystalline lattice, including vacancies, dislocations, stacking faults, and others. The 2θ -dependence of microstrain on peak broadening is

$$B_{strain} = \eta \tan \theta \quad (10)$$

where η is the strain. Note that this 2θ dependence is different than that given in the Scherrer equation and this is what allows us to separate the effects of strain and size on peak broadening.

5. Separating Crystallite Size and Microstrain

The pure sample broadening contains both strain and size broadening and is simply the sum

$$B_{size+strain} = B_{size} + B_{strain} \quad (11)$$

Substitution of equations 9 and 10 gives

$$B_{size+strain} = \frac{K \lambda}{\langle L \rangle_{vol} \cos \theta} + \eta \tan \theta \quad (12)$$

and multiplying through by $\cos \theta$ gives

FWHM is the simplest and easiest to interpret measure of peak width, but a second measure of peak width, integral breadth, is also widely used and is preferred in this type of work. Integral breadth is simply the area under the peak (above background) divided by the peak height. One can visualize this as a rectangle has high has the peak. The use of FWHM, compared to integral breadth, tends to overestimate the crystallite size.

$$B_{size+strain} \cos\theta = \frac{K \lambda}{\langle L \rangle_{vol}} + \eta \sin\theta . \quad (13)$$

which is of the form $y=b+mx$ where η would be the slope of a line on a $\sin \theta - B_{size+strain} \cos \theta$ plot. Once the value of η is known then B_{strain} and can be determined and also $\langle L \rangle_{vol}$.

Objective

The single objective of this experiment is to measure the crystallite size and the amount of microstrain in the samples provided.

Materials

Several powders will be available. Some will be conventional 0.05-25 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. LaB₆, a NIST-traceable line-width standard (SRM 660a)

Procedure

1. Obtain printouts of the powder diffraction files for the specimens that will be analyzed.
2. Obtain a copy of the exported peak file for the line-width standard and analyze the fit the data to a second order polynomial or to an equation such as equation 5.
3. Perform a preliminary scan of the powder. Based on the intensity of the peaks and the counting statistics, you can select a scan rate that will yield a high-quality diffraction pattern in the time allotted for this experiment.
4. Run the background stripping program on the data, but do not perform the $k_{\alpha 2}$ stripping. This will create the “net intensity” file needed in the next step.
5. Run the profile fitting program on each peak. Use the Cauchy profile and include fitting to the $k_{\alpha 2}$ peaks. Store the results and when done export the peak file.
6. Calculate the integral breadth for each peak, then extract the pure sample broadening $B_{size+strain}$ from the measured peak profiles. Plot this data using equations x and y and obtain a value for the Scherrer crystallite size and microstrain.

Results

1. Calculate the diameter that corresponds to the column lengths reported by this Scherrer-based analysis. Does this diameter agree with the size specified in the manufacturer’s literature for the sample?
2. Does the amount of microstrain seem reasonable?

3. Did your sample contain more than one phase? If so, how did you handle the size and strain measurements? Did you get the same results for each phase?
4. How does crystallite size relate to particle size?

References

1. C.Suryanarayana and M.Grant Norton, X-ray Diffraction, A Practical Approach, Plenum Press, New York, pp.207-222, (1998).
2. G.K.Williamson, W. Hall, Acta Metallurgica 1 22 (1953).
3. C.E.Krill and R.Birringer, *Measuring Grain Sizes in Nanocrystalline Materials*, submitted to Journal of Materials Research
4. B.D.Cullity, Elements of X-ray Diffraction, Addison-Wesley, Reading, MA, pp.100-103, (1978).