Powder X-ray Diffraction Basic Course Sixth Installment: Evaluation of crystallite size

Masaaki Konishi*

Abstract

Powder X-ray diffraction (PXRD) can obtain a variety of information, not just a single piece of information. In the fifth installment of the powder X-ray diffraction basic course, quantitative analysis was described. This sixth installment describes the evaluation of crystallite sizes.

The Scherrer method is one analysis technique commonly used to evaluate crystallite sizes. This method assumes there is no crystallite size distribution or lattice strain, and simply calculates the crystallite size from the width of a single diffraction peak using the Scherrer equation. This method requires the measurement of a width standard material to correct the width to obtain an accurate crystallite size.

On the other hand, evaluation of crystallite sizes using a FP (Fundamental Parameter) method can be corrected by calculating the width attributed to the equipment. This method can analyze crystallite sizes less than 300 nm with an accuracy of a few nm regardless of the optical system conditions and measurement instruments. Even for large crystallite sizes of 100–300 nm, it is possible to calculate highly accurate crystallite sizes and their distributions and, furthermore, to evaluate them accounting for crystallite anisotropy.

1. Introduction

Crystallite size means the size of the grains regarded as single crystals in a powder sample. This characteristic is known to correlate with chemical and physical properties. Therefore, accurate evaluation of crystallite size is very important in R&D and quality control.

Several methods exist for calculating crystallite size from X-ray diffraction profiles, such as the Scherrer method, the Fundamental Parameter (FP) method[(1)], and the Williamson-Hall method. The Scherrer method is the simplest and calculates a crystallite size for each Miller index, assuming no crystallite size distribution or lattice strain. However, when using this method, accurate crystallite size cannot be obtained without applying a correction determined by measuring a width standard material to estimate the width characteristic to the instrument. In particular, when the crystallite size is 100 nm or larger, the width can be compared to other samples on a relative basis, but it is difficult to accurately calculate an absolute value. On the other hand, in the case of the FP method, the theoretical diffraction peak widths can be calculated based on information about the optical system used for the measurement. Therefore, more accurate crystallite size and crystallite size distribution can be calculated. Recently, methodology and software have advanced, so we can now accurately evaluate large crystallite sizes of 100–300 nm, considering the anisotropy of the crystallite.

In the sixth installment of the PXRD basic course, the basics of crystallite size evaluation and examples of the evaluation using the Scherrer and FP methods will be described.

2. Crystallite Size

The crystallite is the smallest unit contributing to diffraction, defined as a domain that is treated as a single crystal in crystalline grains. In general, a nanoparticle often consists of a single crystallite. On the other hand, a substance with a domain structure is a collection of multiple crystallites. Figure 1 shows how multiple crystallites constitute a single particle. Crystallite size analysis using X-ray diffraction means determining the size of individual crystallites. Note that it is not about determining the particle size. Also, the crystallite size here means the size in the direction of the lattice plane normal that contributes to diffraction.

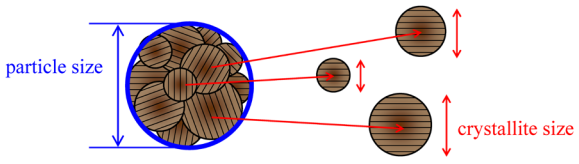

Fig. 1. Crystallite size and particle size.

As the crystallite size decreases, the width of the diffraction peak increases[(2)]. Figure 2 shows the profiles of molybdenum powder samples with different crystallite sizes. The profile of the sample with smaller crystallite size shows broadening of the peak width.

* Application Laboratories, Rigaku Corporation.

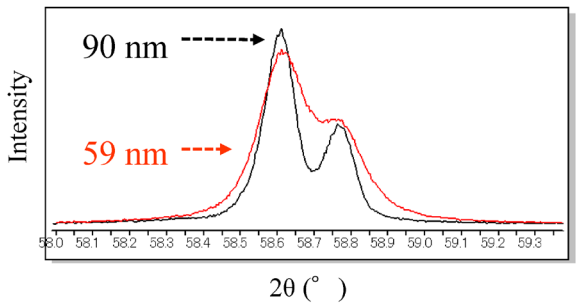

Fig. 2. Profiles of molybdenum powder samples.

3. Lattice Strain

Lattice strain means that the interplanar spacing of the crystal lattice in the sample has changed non-uniformly, as shown in Fig. 3.

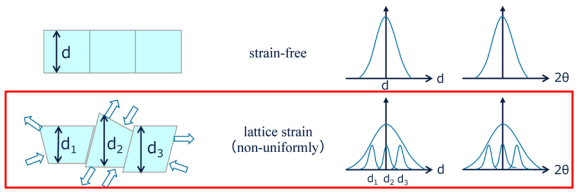

Fig. 3. Peak broadening due to lattice strain.

If there is lattice strain, the lattice is non-uniformly strained and the interplanar spacing of the lattice planes is not uniform. Therefore, peaks with different diffraction angles overlap, resulting in broadened peak widths. Figure 4 shows the simulated profiles of cerium oxide powder samples with and without lattice strain. Lattice strain can be thought of as a state in which the interplanar spacing d has a distribution centered on the d_0 of the strain-free state, expressed in units of percent. If this value is large, it means the lattice strain is large. In the case of the sample with 0.5% lattice strain, it was observed that it is the higher-angle peaks that exhibit increased peak widths.

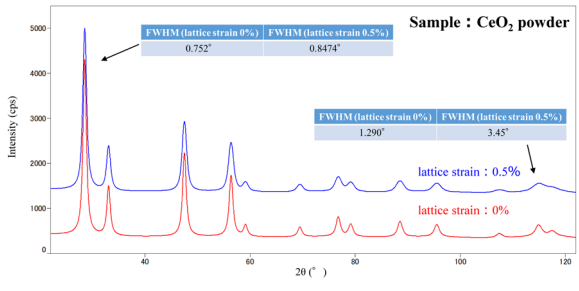

Fig. 4. Simulation profiles for strain-free and non-uniformly strained samples.

In methods for calculating crystallite size that do not consider lattice strain, the existence of lattice strain affects the results of the crystallite size due to the broadening of the peak width derived from lattice strain. Therefore, more accurate values can be obtained if the analysis is performed using peaks on the low-angle side as much as possible, where the broadening of peaks derived from lattice strain is small. When we would like to accurately evaluate lattice strain, it is better to measure to high angles, about 2θ: 120–140°.

4. Crystallite Size and Instrument Width

As previously stated, the width of diffraction peaks broaden not only due to the crystallite size, but also due to lattice strain. The smaller the crystallite size or the larger the lattice strain, the more the diffraction peak broadens. Also, the widths of the diffraction peaks in the observed profiles are different from the diffraction widths attributed to the sample. We need to take into account that the peak width includes broadening attributed to the instrument. Therefore, if we would like to accurately calculate crystallite size, we need to take into account the lattice strain of the sample and measure a standard reference material to correct for broadening due to equipment. The best standard reference material is a sample that has no peak broadening derived from crystallite size or lattice strain. For example, the diffraction width is often corrected using the NIST LaB_6 (Standard Reference Material 660c). The test sample and width standard are measured under the same slit conditions, although the step width and scan speed may be different from each other.

5. Evaluation of crystallite size using the Scherrer method

The Scherrer method is a simple method for determining the crystallite size from the half-width or integral width using the Scherrer equation, which is expressed in Eq. (1).

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where D_{hkl} is the crystallite size, K is the Scherrer constant, λ is the wavelength of incident X-rays, β is the half-width or integral width, and θ is the Bragg angle. Note that β is expressed in radians in Eq. (1). The Scherrer constant depends on how the crystallite size and diffraction peak width are defined[3]. When the crystallite shape is cubic and has no size distribution, if we use half-width for β, the value of K often used is 0.94. This method calculates crystallite size assuming no lattice strain. If lattice strain is present in the sample, the half-width attributed to the crystallite size is overestimated, and a value smaller than the actual crystallite size is calculated. As described in the previous section, if there is lattice strain, the peak width broadening occurs mostly at higher angles. Therefore, when calculating crystallite size using the Scherrer method, it is recommended to analyze low-angle diffraction peaks to prevent the influence of lattice strain as much as possible. The half-width broadening derived from the instrument is measured using a standard material and subtracted by Eq. (2).

$$\beta = \sqrt{B^2 - b^2} \quad (2)$$

where β is the true diffracted width, B is the measured width, and b is the width due to the instrument.

Figure 5(a) shows the profile fitting results for silver powder and (b) shows that for the NIST LaB_6 (SRM 660c). In general, the pseudo-Voigt function is often used as the profile function. The half-widths shown in the peak list of SmartLab Studio II (the integrated X-ray diffraction software) are those of the calculated profile. Therefore, if the fitting of the measured and calculated data does not match, the resulting crystallite size will be in error. The fitting result of the calculated profile to the measured one should be checked.

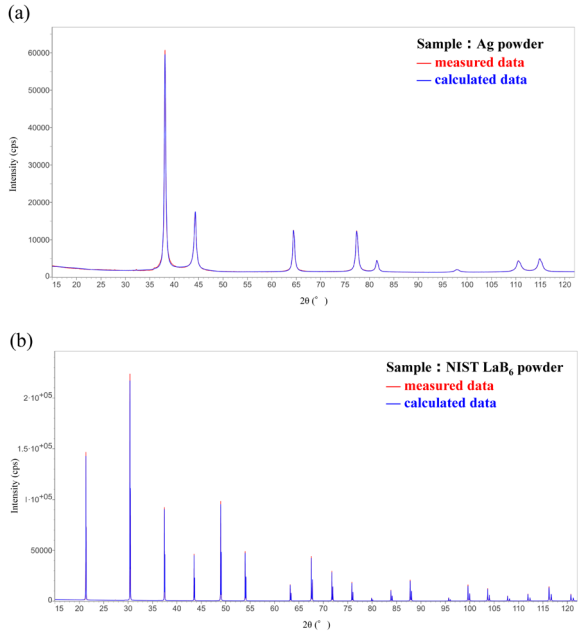

Fig. 5. (a) Silver powder profile fitting. (b) NIST LaB_6 profile fitting.

Several powder samples were measured with Bragg-Brentano optics using a 1D detector. Then crystallite sizes were calculated using the Scherrer method. We used the MiniFlex benchtop X-ray diffractometer and the SmartLab automated multipurpose X-ray diffractometer. First, crystallite sizes calculated using SmartLab are shown in Table 1. Measurements were performed using soller slits of 1.0° and 2.5° to investigate the change in values when the aperture angle of the soller slit was changed.

Table 1. Crystallite size of each powder sample by the Scherrer method using the SmartLab (soller slits: 1.0°, 2.5°).

Sample	*hkl*	Crystallite size D (nm)		$\lvert\Delta D\rvert$ (nm)
		SmartLab	MiniFlex	
Anatase	101	168±3	214±4	46
Rutile	110	255±5	278±7	23
ZnO	101	274±6	278±7	4
Ag	111	36.6±0.4	37.6±0.5	1

Next, Table 2 shows the crystallite sizes measured using the MiniFlex. This time, 2.5° soller slits were used, and the results were compared to the crystallite size calculated using the SmartLab.

Table 2. Crystallite size difference between SmartLab and MiniFlex (Scherrer method).

Sample	*hkl*	Crystallite size D (nm)		$\lvert\Delta D\rvert$ (nm)
		solar slit 1.0°	solar slit 2.5°	
Anatase	101	172±3	168±3	4
Rutile	110	256±5	255±5	1
ZnO	101	283±6	274±6	9
Ag	111	36.2±0.4	36.6±0.4	0.4

These results show that the difference in the crystallite size between soller slits is small, while the difference between instruments is large. The applicable maximum value of crystallite size evaluation using the Scherrer method is 100 nm; therefor, if the crystallite size is 100 nm or less, we can accurately evaluate it. However, if the crystallite size exceeds 100 nm, there are sometimes differences of several tens of nm between instruments, resulting in less accuracy.

6. Evaluation of Crystallite Size Using the FP Method

6.1 Comparison of evaluation between the Scherrer and FP method

A powder diffractometer is equipped with various optical elements, and the observed diffraction profile is the result of the convolution of all these elements. Here, let the profile derived from the instrument be the instrument function g(2θ), and let the profile with a spread derived from the crystallite size or lattice strain be $f(2\theta)$. When the profile in which these functions are convoluted is $h(2\theta)$, the relationship between the three profile functions is expressed by Eq. (3). For details on convolution, please refer to Ref. (2).

$$h(2\theta) = \int f(2\theta - 2\theta_g)\, g(2\theta_g)\, d(2\theta_g) \quad (3)$$

$h(2\theta)$ is calculated based on Eq. (3) by convoluting various profiles (emission profile of incident X-ray, focus size, slit width, etc.) derived from diffractometers. The FP method is a method to refine the parameters of the crystallite size and lattice strain by fitting $h(2\theta)$ to the observed profiles. The FP method can be performed in two ways. One is to perform profile fitting independently for each peak and obtain analysis results for each Miller index. The other is the Whole Powder Pattern Fitting (WPPF) method[4],[5], which applies the FP method as a profile function. This method refines the parameters using the whole pattern and obtains analytical results for each crystalline phase. Conventionally, the FP method has been used to calculate the crystallite size and lattice strain without using a width standard material (e.g., LaB_6

(SRM 660c)). However, if the crystallite size exceeds 100 nm, we can obtain a more accurate crystallite size by measuring the width standard and refining the instrument function as "FP profile standard."

The instrument function parameters used in the FP method for SmartLab Studio II are shown in Fig. 6. If a width standard material is not measured, the instrument function is not refined. On the other hand, if the width standard is measured, the angular aperture of the soller slit, etc., can be refined.

	Item, unit	Value	Value
▸	Goniometer radius, mm	300.0	300.0
	Focus Width, mm	0.04	0.04
	Focus length, mm	8	8
	DS,SS, °	1/3	1/3
	RS, mm	0.075	0.075
	RS length, mm	(a) 20	(b) 20
	Incident Soller slit, °	2.50	2.581(5)
	Receiving Soller slit, °	2.50	2.581(5)
	Sample width (W), mm	20	20
	Sample thickness (H), mm	0.5	0.5
	Sample length (D), mm	20	20
	Linear absorption, 1/cm	384.430	384.430
	Tube tail size, mm	3.000	5.00(5)
	Tube tail ratio	0.0400	0.0113(3)

Fig. 6. FP method parameters displayed in SmartLab Studio II.

Here we describe results of crystallite size calculated using the FP method. The powder samples are the same as those used in the previous section. The analysis was performed by WPPF using the FP method, and the instrument functions used in the FP method were refined. Table 3 shows the crystallite size of each powder sample when using the SmartLab with 1.0° or 2.5° soller slits. Also, Table 4 shows the calculated crystallite size when measured with the SmartLab and MiniFlex.

Table 3. Crystallite size of each powder sample by the FP method using the SmartLab (soller slits: 1.0°, 2.5°).

Sample	Crystallite size D (nm)		$\lvert\Delta D\rvert$ (nm)
	solar slit 1.0°	solar slit 2.5°	
Anatase	159.0±0.6	161.5±0.8	2.5
Rutile	205.9±0.8	207.7±0.7	1.6
ZnO	224.8±0.7	226.8±0.5	2.0
Ag	23.9±0.2	23.6±0.1	0.3

Table 4. Crystallite size difference between the SmartLab and MiniFlex (FP method).

Sample	Crystallite size D (nm)		$\lvert\Delta D\rvert$ (nm)
	SmartLab	MiniFlex	
Anatase	161.5±0.8	164.8±0.6	3.3
Rutile	207.7±0.7	205.9±0.8	1.8
ZnO	226.8±0.5	228.9±1.1	2.1
Ag	23.6±0.1	23.4±0.1	0.2

We would like to compare these results with the crystallite size analysis results using the Scherrer method. If the crystallite size is around 200 nm, the FP method can perform the analysis with an accuracy of a few nm regardless of the soller slit conditions and measurement instruments. In addition, even if measurements are performed using high-intensity mode with a wider soller slit, a highly accurate evaluation can be obtained.

If the crystallite size is less than 100 nm, the Scherrer method can easily and accurately evaluate it. On the other hand, if the crystallite size is 100–300 nm, we can accurately calculate it by refining the parameters used in the FP method based on the measured profile of a width standard material.

6.2 The validity of crystallite sizes determined by the FP method

There are several methods for evaluating crystallite size besides powder X-ray diffraction. In this section, we describe a comparison with other methods to validate the crystallite size values calculated using the FP method[6].

A TiO_2 powder sample of rutile was measured using Bragg-Brentano optics with a 1D detector. Particle size evaluation was performed using other methods: SEM (scanning electron microscope), LD (laser diffraction), and USAXS (ultra-small angle X-ray scattering) for comparison. SEM was performed using a JSM-64060LV (JEOL), LD was performed using a LS 13 320 (BECKMAN COULTER), and a NANOPIX mini (Rigaku) was used for the USAXS measurement. A photograph obtained using SEM is shown in Fig. 7.

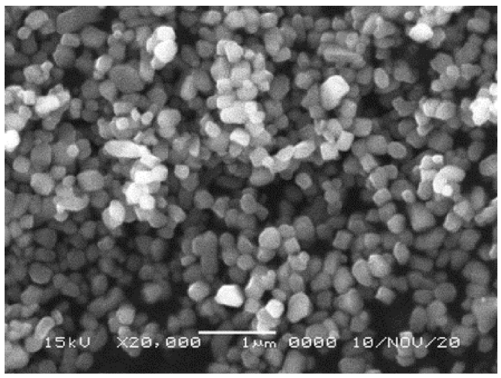

Fig. 7. SEM image of TiO_2 particles.

Crystallite size distribution can also be determined by analyzing the shape of the diffraction peaks using the FP method. The average particle size and median particle size of the TiO_2 powder samples calculated from each method are shown in Table 5. In addition, the cumulative frequency distributions obtained by each method are shown in Fig. 8.

Compared to the average and median particle sizes of TiO_2 particles determined from other methods, the sizes calculated from the powder X-ray diffraction method (the FP method) were similar. From these results, it can be seen that one particle is composed of a single crystallite. Furthermore, because the primary particle

Table 5. Particle and crystallite size of TiO_2 particles obtained by each method.

	Crystallite size D (nm)
a-axis	217.9±1.1
c-axis	235.8±1.5

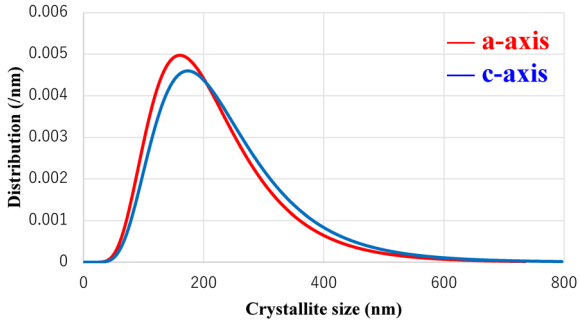

Fig. 8. Cumulative frequency distribution of the TiO_2 particles obtained by each method.

from the SEM image shown in Fig. 7 was calculated to be about 200 nm, it can be assumed that this is similar to a single crystal.

From these results, the crystallite size calculated from the FP method correlates with other measurement methods and this analysis method was found to be highly accurate.

6.3 Evaluation of crystallite size considering anisotropy

In this section, we will consider the analysis of anisotropic crystallites. In general, crystallite size is calculated assuming the crystallite shape is spherical. However, zinc oxide with a hexagonal wurtzite structure has a preferential growth orientation in the c-axis direction. Therefore, it has shape anisotropy in crystal growth and grows into hexagonal columns. In SmartLab Studio II, the crystallite shape can be changed from spherical to ellipsoidal and analyzed. In the case of zinc oxide, the analysis assuming an ellipsoid can be fitted more accurately[7]. The calculation results of zinc oxide crystallite size by WPPF using the FP method are shown in Table 6. Also, Fig. 9 shows the crystallite volume distribution, which is the ratio of volume to the diameter of each crystallite.

If the crystallites are anisotropic, there is a dependence of the peak width on Miller indices. The FP method can evaluate the crystallite size considering anisotropy and confirm the crystallite size for each orientation in the unit cell. The crystallite size distributions for the a-axis and c-axis direction are obtained, which shows that the crystallite size of the c-axis direction is larger than that of the a-axis direction.

Table 6. Crystallite sizes of zinc oxide considering anisotropy.

Method	Average size D (nm)	Median size D_{50} (nm)
LD	189	164
USAXS	190	160
XRD (FP method)	186	168

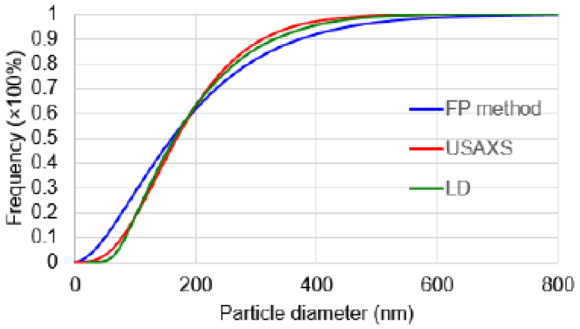

Fig. 9. Crystallite size distribution of zinc oxide.

7. Conclusion

In the sixth article of this series, the powder X-ray diffraction basic course, the basics of "evaluation of crystallite size" were explained with actual examples. In recent years, the performance of analysis software has improved, and the method that refines parameters by the WPPF using the whole profile over a wide 2θ range can be performed easily in a relatively short time. Therefore, if you need accurate crystallite size evaluation for R&D or quality control of industrial products in the future, we would like you to consider adopting the FP method.

In order to perform accurate crystallite size evaluation, it is necessary to obtain high-quality data and to perform correct qualitative analysis. Please refer to Part 2 "Selection of equipment configuration to obtain high-quality data,"[8] Part 3 "Sample preparation and measurement conditions to obtain high-quality data"[9] and Part 4 "Qualitative analysis"[10] as well as this article.

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