

Evaluation of crystallite size distribution by a capillary spinner-scan method in synchrotron powder diffractometry

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Abstract. A method to evaluate the effects of particle statistics in capillary-specimen transmission mode x-ray diffraction measurements has been developed. Average crystallite size of about several μm and dispersion of crystallite size distribution have been evaluated by statistical analysis of spinner-scan diffraction intensity data. The method can be applied to polycrystalline materials and also multi-phase mixtures.

1. Introduction

Physical properties of polycrystalline ceramic materials depend on the size of crystallites. In principle, the crystallite size can be determined by the line profile analysis of observed powder X-ray diffraction (XRD) data [1-5].

However, it is still difficult to evaluate relatively large size of crystallites by the XRD line profile analysis. Line broadening caused by the crystallite size larger than 100 nm is expected to be smaller than 0.1° in diffraction angle, which is comparable with the instrumental line broadening. Application of a model profile defined as the convolution with instrumental function enables the elimination of instrumental effects and extraction of the intrinsic peak profile, but the reduction of accuracy in estimation of crystallite size cannot be avoided because of the finite resolution of the instrument.

On the other hand, we have proposed a spinner-scan method to evaluate the crystallite size of about several to several ten μm with a laboratory Bragg-Brentano powder diffractometer [6]. The method is based on that the variation of observed diffraction intensities on rotation of the specimen shows an almost stochastic behavior, which is mainly caused by the limited number of crystallites that satisfy the diffraction condition. The validity of the method is supported by the theories about particle statistics in powder diffractometry established by the pioneering works of Alexander *et al.* [7] and de Wolff [8], proposed more than 50 years ago.

However, the effective crystallite diameter evaluated by the method, given by

$$D_{\text{eff}} = \left(\langle D^6 \rangle / \langle D^3 \rangle \right)^{1/3},$$

for the average of k -th power of crystallite dimension $\langle D^k \rangle$ is generally different from the area-weighted diameter:

$$D_A = \langle D^3 \rangle / \langle D^2 \rangle,$$

which we can expect straightly to be related to the density of grain boundary. In this study, we have tried to extend and validate the theory for particle statistics to determine the crystallite size distribution by applying well-defined powder samples and the synchrotron radiation as the x-ray source.

2. Theory

The statistical variance of the observed intensity caused by the particle statistics, $\langle(\Delta I)^2\rangle$, is related to the effective number of diffracting crystallites N_{eff} by the following equation,

$$N_{\text{eff}} = \langle I \rangle^2 / \langle (\Delta I)^2 \rangle,$$

where $\langle I \rangle$ is the average intensity. The effective number of diffracting crystallites N_{eff} is also expressed by

$$N_{\text{eff}} = N \rho m_{\text{eff}} f,$$

where N is the number of crystallites irradiated by the source x-ray, ρ is the probability that an irradiated crystallite satisfies the diffraction condition, m_{eff} is the effective multiplicity of reflections, defined by

$$m_{\text{eff}} = \left(\sum_k m_k I_k \right)^2 / \sum_k m_k I_k^2,$$

for the component multiplicity m_k and intensity I_k for overlapped reflections, and f is the factor to modify N_{eff} , defined by

$$f = \left(\int_0^\infty \cdots \int_0^\infty I_j(\alpha_1, \cdots, \alpha_M) d\alpha_1 \cdots d\alpha_M \right)^2 / \int_0^\infty \cdots \int_0^\infty [I_j(\alpha_1, \cdots, \alpha_M)]^2 d\alpha_1 \cdots d\alpha_M,$$

in a generalized formula, when the diffraction intensity from a crystallite is expressed by the function $I_j(\alpha_1, \cdots, \alpha_M)$ of any parameters $\alpha_1, \cdots, \alpha_M$, normalized with respect to the integration. The parameters $\alpha_1, \cdots, \alpha_M$ can include the deviation angles of the orientation of the crystallites from the normal direction, the location of the crystallite in the specimen, volume of each crystallite, *etc.*

Similarly, the skewness of the diffraction intensity distribution S defined by

$$S = \langle (\Delta I)^3 \rangle / \langle (\Delta I)^2 \rangle^{3/2},$$

from the third central moment of the diffraction intensity $\langle (\Delta I)^3 \rangle$, is expressed by

$$S = \left[(m_{\text{eff}} f) / (N_{\text{eff}} m'_{\text{eff}} f') \right]^{1/2},$$

where m'_{eff} is given by

$$m'_{\text{eff}} = \left(\sum_k m_k I_k^2 \right)^3 / \left(\sum_k m_k I_k^3 \right)^2,$$

and f' given by

$$f' = \left(\int_0^\infty \cdots \int_0^\infty [I_j(\alpha_1, \cdots, \alpha_M)]^2 d\alpha_1 \cdots d\alpha_M \right)^3 / \left(\int_0^\infty \cdots \int_0^\infty [I_j(\alpha_1, \cdots, \alpha_M)]^3 d\alpha_1 \cdots d\alpha_M \right)^2.$$

The skewness is proportional to a dispersion parameter defined by $\kappa_{\text{eff}} = \langle D^9 \rangle \langle D^3 \rangle / \langle D^6 \rangle^2$. Further details of the theory will be described elsewhere [9].

3. Experimental

3.1. Sample preparation

For the purpose to examine the validity of the method to evaluate the crystallite size distribution, we have prepared three quartz powder samples #1, #2 and #3, with similar effective diameter of ~ 12

μm , but different degree of dispersion in size distribution, as controlled mixtures of three fraction of pulverized Brazilian quartz powder separated by a sedimentation method, the nominal Stokes's diameter of which are 3-7, 8-12, 18-22 μm , and further characterized by scanning electron microscopy (SEM) image analysis [6]. The powder samples were filled into Lindemann glass capillaries with nominal diameter of 0.5 mm ϕ . The mixing ratio and the values of parameters to characterize the crystallite size distribution are listed in Table 1.

Table 1. The mixing ratios and values of parameters about the crystallite distribution for three quartz powder samples, estimated by SEM image analysis. w_{3-7} , w_{8-12} , w_{18-22} are the weight fractions of the component powder with the nominal Stokes diameter of 3-7 μm , 8-12 μm , 18-22 μm , respectively.

Sample	#1	#2	#3
w_{3-7}	0	0.542	0.926
w_{8-12}	1	0.422	0
w_{18-22}	0	0.036	0.074
D_{eff} (μm)	12.0	11.3	11.3
κ_{eff}	1.68	6.67	11.8
D_A (μm)	10.7	7.5	6.3
D_V (μm)	11.3	9.1	7.7

3.2. Measurements

A high-resolution synchrotron powder diffractometer equipped with a flat Ge (111) crystal analyzer located on the powder diffraction beamline BL-4B2 at the Photon Factory in Tsukuba was used for the transmission and diffraction measurements. The peak wavelength of the source x-ray calibrated with 19 diffraction peak positions of a standard Si powder (NIST SRM640c) was 1.20670(3) \AA .

3.2.1. Evaluation of capillary diameter and absorption coefficient. Diameters and absorption coefficients of the capillary specimens were estimated from the intensity profiles on scanning the vertical position of the specimens. The cross section of the incident beam was restricted to 0.05 mm in the vertical direction. The observed intensity profile $I(z)$ was fitted by a convolution model given by

$$I(z) = I_1(z) * I_2(z),$$

$$I_1(z) = \begin{cases} I_0 \exp\left[-2\mu\sqrt{R^2 - (z - z_0)^2}\right] & \text{for } |z - z_0| < R, \\ I_0 & \text{for } R \leq |z - z_0|, \end{cases}$$

$$I_2(z) = \begin{cases} 1/H & \text{for } |z| < H/2, \\ 0 & \text{for } H/2 \leq |z|, \end{cases}$$

where μ is the linear attenuation coefficient of the specimen, $2R$ the diameter of capillary, z_0 the center position, and H the slit height.

The capillary diameters $2R$ and absorption coefficients μ of the specimens #1, #2, #3 were estimated at $2R = 0.575(1)$, $0.547(1)$, $0.508(1)$ mm and $\mu = 17.12(7)$, $17.33(8)$, $15.49(8)$ cm^{-1} , respectively. The observed profiles and fitting curves are shown in Fig. 1.

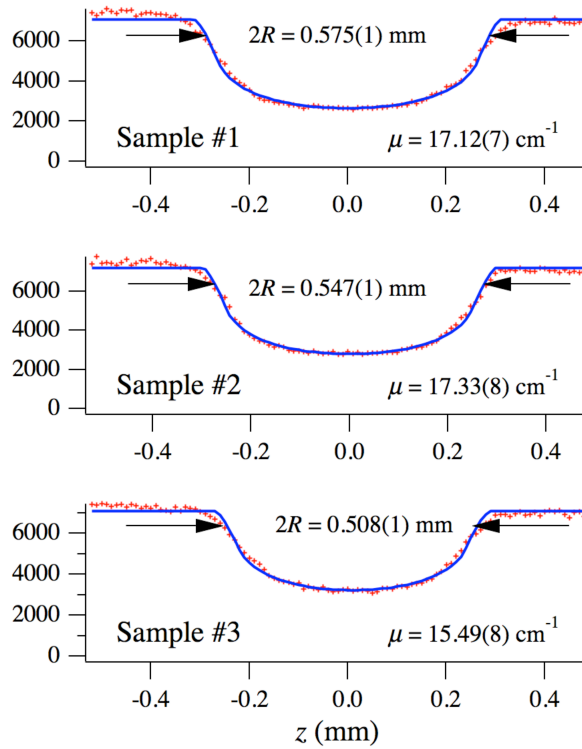


Figure 1. Vertical-position (z) scans for capillary specimens of quartz powder mixtures #1, #2 and #3. The observed intensities are plotted as red crosses and the fitting models are drawn as blue lines.

3.2.2. 2Θ -scan measurement. The diffraction peak profiles of quartz 101/011-reflection were measured for 2Θ range: 20.52° - 20.72° at the step interval of 0.001° with continuous rotation of the spinner at the speed of 2 revolutions/s and the measurement time of 0.5 s per each step.

3.2.3. Spinner-scan measurement. The peak-top intensities of 101/011-reflection were recorded on stepwise rotation of the spinner over the angular range of 360° at the interval of 0.072° with the measurement time of 0.5 s per each step.

4. Results and discussion

4.1. Diffraction peak profile

The 101/011-diffraction peak profiles of samples #1, #2 and #3 are shown in Fig. 2. The observed profiles were fitted by a model function $p_{P7^*A}(x; \gamma_{P7}, \nu, \Psi)$ calculated as the convolution of the Pearson VII function $f_{P7}(x; \gamma_{P7}, \nu)$ and the axial-divergence aberration function $w_A(x; \Psi)$ [10], given by

$$p_{P7^*A}(2\Theta) = b + I f_{P7}(2\Theta - 2\theta; \gamma_{P7}, \nu) * w_A(2\Theta; \Psi)$$

$$f_{P7}(\omega; \gamma_{P7}, \nu) = \frac{\Gamma(\nu)}{\sqrt{\pi}\Gamma(\nu-1/2)} \left(1 + \frac{\omega^2}{\gamma_{P7}^2}\right)^{-\nu}$$

$$w_A(\omega; \Psi) = \begin{cases} |\beta_A|^{-1} \left[(-\omega/\beta_A)^{-1/2} - 1 \right] & \text{for } -1 < \omega/\beta_A < 0, \\ 0 & \text{elsewhere,} \end{cases}$$

$$\beta_A = (\Psi^2/2)(\cot 2\theta + \tan \Theta_A),$$

where b is the constant background, I the integrated intensity, θ and Θ_A are the Bragg angles at the sample and analyzer crystal, respectively, and Ψ is the Soller slit open angle.

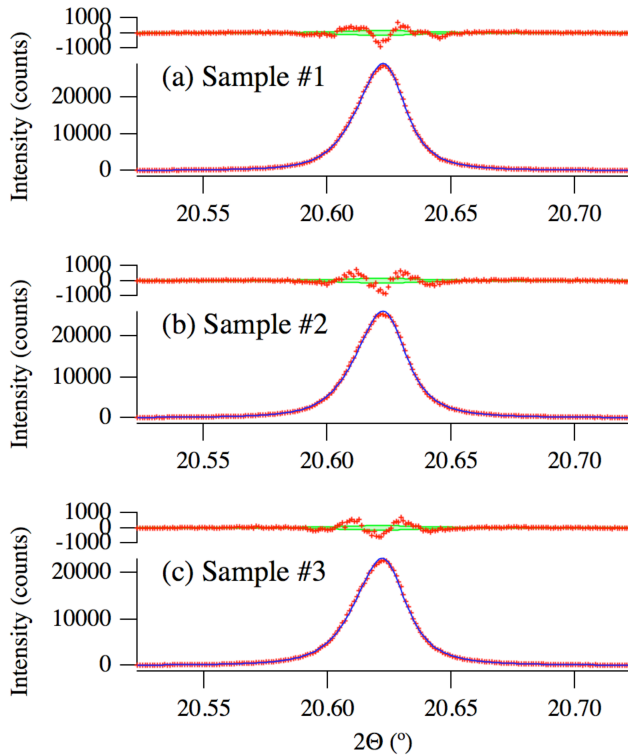


Figure 2. 2Θ -scan peak profiles of samples #1, #2 and #3. The observed intensities (red markers) and fitted curve (blue lines) are plotted in the lower, and the deviation (red markers) and the error range (green lines) are plotted in the upper. The full widths at half maximum of the Pearson VII components are optimized to be 0.0190° , 0.0201° , 0.0205° and the shape parameter ν are 1.480(9), 1.453(9), 1.432(10) for the samples #1, #2, #3, respectively.

The results of curve-fitting analysis are shown in Fig. 2. Slight difference in observed profiles has been detected, but it is considered to be negligible in the later analyses about particle statistics.

4.2. Spinner-scan profile

Spinner-scan diffraction intensity profiles of samples #1, #2 and #3 are shown in Fig. 3. Statistical independence of the data is confirmed by no appearance of systematic variation in the observed intensity profiles. Evolution of asymmetry in the statistical distribution of the observed diffraction intensities for samples with more dispersed crystallite size distribution can directly be viewed in Fig. 3.

The effective multiplicities of the quartz 101/011-reflection are estimated at $m_{\text{eff}} = 10.27$ and $m'_{\text{eff}} = 8.45$ from the component multiplicities $m_{101} = m_{011} = 6$ and the calculated relative intensities of $I_{011} / I_{101} = 2.393$, obtained by a Rietveld analysis using a software *RIETAN-FP* [11].

The effective crystallite diameter of sample #1 estimated at $D_{\text{eff}} = 12.0 \mu\text{m}$ by SEM image analysis is applied as the reference value to calibrate the instrumental constant in this study. That is, the effective equatorial tolerance angle, estimated at $\Delta X = 0.061(2)^\circ$ from the effective number of diffracting crystallites in sample #1, $N_{\text{eff}} = 62(3)$ from the spinner-scan data, is treated as an instrumental constant.

The effective diameters D_{eff} and dispersion parameters κ_{eff} , evaluated from the spinner-scan data are listed in Table 2. The area-weighted and volume-weighted average diameters, D_A and D_V , calculated by assuming the log-normal size distribution are also listed in the table. The values estimated by the XRD spinner-scan method in Table 2 are certainly well coincided with the values listed in Table 1, estimated by SEM image analysis.

It should be noted that this method to evaluate crystallite size can be applied to polycrystalline materials, and even multi-phase mixtures, similarly to the XRD line-broadening analysis, and the values from SEM image analysis is not necessarily more reliable than the values evaluated by the XRD spinner-scan measurements.

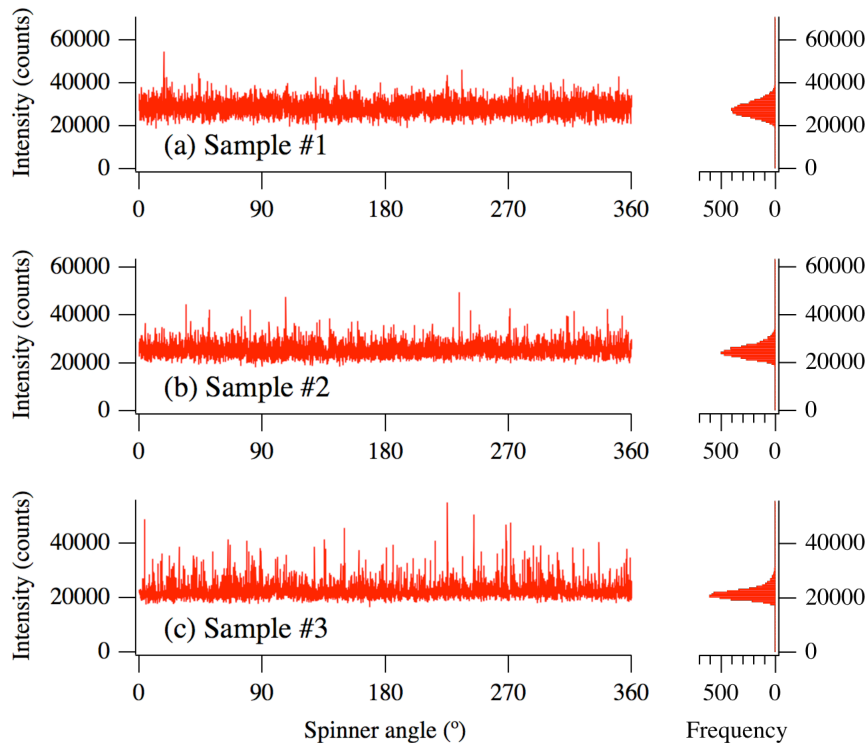


Figure 3. Spinner-scan diffraction intensity profiles of 101/011-reflection of quartz specimens #1, #2, #3 (left). The histograms of observed diffraction intensities are plotted on the right side of the figure.

Table 2. Parameters about the crystallite size distribution of three quartz powder samples, evaluated by the spinner-scan method.

Sample	#1	#2	#3
D_{eff} (μm)	12.0 (fixed)	11.0(7)	11.1(1.2)
\varkappa_{eff}	2.8(5)	6.7(1.0)	14(2)
D_A (μm)	9.5(4)	7.2(1.2)	6.2(1.1)
D_V (μm)	10.7(2)	8.9(1.4)	8.3(1.5)

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