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Nanocrystallite Characterization of Milled Simulated Dry Process Fuel Powders by Neutron Diffraction

Ho Jin Ryu, Kwon Ho Kang, Je Sun Moon, Kee Chan Song, and Yong Nam Choi

Korea Atomic Energy Research Institute
150, Deokjin-dong, Yuseong-gu, Daejeon 305-353, KOREA

Abstract

The nano-scale crystallite sizes of simulated spent fuel powders were measured by the neutron diffraction line broadening method in order to analyze the sintering behavior of the dry process fuel. The mixed UO_2 and fission product oxide powders were dry-milled in an attritor for 30, 60, and 120 min. The diffraction patterns of the powders were obtained by using the high resolution powder diffractometer in the HANARO research reactor. Diffraction line broadening due to crystallite size was measured using various techniques such as the Stokes' deconvolution, profile fitting methods using Cauchy function, Gaussian function, and Voigt function, and the Warren-Averbach method. The r.m.s. strain, stacking fault, twin and dislocation density were measured using the information from the diffraction pattern. The realistic crystallite size can be obtained after separation of the contribution from the non-uniform strain, stacking fault and twin.

Introduction

The dry process fuel is a kind of an advanced nuclear fuel cycle to recycle fissile material in pressurized water reactor(PWR) spent fuels for use in the heavy water reactor(CANDU)[1]. The benefit of the dry process fuel includes the saving of uranium resources and the reduction of spent fuel at the same time. The fabrication process of the dry process fuel does not include the separation of plutonium, which is another advantage of the dry process fuel cycle in light of the non-proliferation policy. The simulated dry process fuel is used to investigate the fabrication process and properties of the dry process fuel using natural uranium oxide and stable isotopes of fission product elements due to the high radioactivity of the dry process fuel. The simulated dry process fuel contains about 3 wt% fission product elements such as Zr, Mo, Nd, Ru and Ce. The homogeneous distribution of the fission product elements is required for similarity between the dry process fuel and the simulated dry process fuel. Mechanical milling is used to fabricate fine and homogeneous distribution of the fission product elements in the simulated dry process fuel. The powders of uranium oxide and fission product were milled in an attritor and the size of the powders was decreased to nanometer

scale with increased milling time. The crystallite size of the powder is important because it affects the fabrication properties such as sintering behavior. In this study, the size of milled powders of the simulated dry process fuel was measured from the line broadening of neutron diffraction profiles.

Experimental Procedures

The amount of fission products in spent fuels was calculated by the ORIGEN-2 (Oak Ridge Isotope Generation and Depletion) code[2] and the oxides of stable isotopes were added into the natural uranium oxide. The mixed UO_2 and fission product oxide powders were dry-milled in an attritor with a rotation speed of 200rpm, ball-to-powder ratio of 4:1 for 30, 60, and 120 minutes. The simulated dry process fuel powders were compacted into pellets under a pressure of 3 ton/cm^2 and 4 pellets were stacked in a vanadium can for neutron diffractometry by the high resolution powder diffractometer in HANARO at the Korea Atomic Energy Research Institute. The wavelength of neutron beam was 0.18348 nm, and the monochrometer was a Ge(331) single crystal. The diffraction patterns were obtained from 20 to 155° by 2θ interval of 0.05°, and the maximum intensity was about 20000 counts. Diffraction line broadening due to crystallite size was measured using various techniques such as the Stokes' deconvolution, profile fitting methods using the Cauchy function, Gaussian function, Voigt function, and the Warren-Averbach method.

Results and Discussion

Fig. 1 shows transmission electron micrographs showing the powders of UO_2. While the particle size is easily characterized by laser scattering or scanning electron microscopy, the crystallite size is difficult to measure even if transmission electron microscopy is employed due to severe aggregation of the particles of UO_2.

The diffraction line broadening method was suggested by Scherrer in order to measure the crystallite size of the powders. The crystalline size(D) is expressed as a function of wavelength(λ), breadth of diffracting line(β) and diffraction angle(θ) as shown in the following equation[3],

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where K is 0.9 when full width at half maximum(FWHM) is used as breadth, K is 1.0 when integral breadth is used.

Fig. 2 shows neutron diffraction patterns of the simulated dry process fuel of the sintered pellet and milled powders with varying milling time from 30 min to 120 min. FWHMs of milled powders and the reference materials were fitted by using the Caglioti relation as shown in Fig. 3[4],

$$FWHM^2 = U\tan^2\theta + V\tan\theta + W \quad (2)$$

Stokes reported that the observed broadening profile, h(x), is expressed as a convolution of microstructural broadening, f(x), from crystalline size or non-uniform strain and instrumental

broadening, g(x), as follows.

$$h(x) = g(x) * f(x) = \int_{-\infty}^{\infty} g(y) f(x-y) dy \quad (3)$$

It is required to use the Fourier deconvolution method for the extraction of microstructural broadening from the observed broadening, h(x) as shown in the so called Stokes' deconvolution method[5]. Whereas the Stokes deconvolution method is more mathematically rigorous, the error increases in the cases of severe overlap between each line profile or weak microstructural broadening.

Fig. 4 shows microstructural broadening of the (220) peak of 30 min milled dry process powder deconvoluted by Stokes' method using the FOURYA program[6]. The ripple at a profile tail was induced by the truncation effect. Because the integral breadth of the deconvoluted profile was unstable by varying the truncation point, the Stokes' deconvolution method was not used in this study to exclude the bias.

Each peak of the diffraction pattern was fitted with various profile functions such as Cauchy(Lorentzian), Gaussian and Voigt functions. Fig. 5 shows the (220) peak of 30 min milled dry process powders fitted by Gaussian, Cauchy, and Voigt function using nonlinear least square fittings in the ORIGIN 6.1 program. The largest correlation coefficient was obtained when the Voigt function, which is a convolution of the Cauchy function and the Gaussian function, is used to fit the (220) peak of 30 min milled dry process powders. In this study, the instrumental broadening and microstructural broadening were separated using the relations of the Cauchy factor and the Gaussian factor in the Voigt function[7].

Williamson and Hall used a simplified integral breadth method assuming the Cauchy function for size broadening and strain broadening as follows[8]:

$$\beta_{microstructure} = \beta_{size} + \beta_{strain} \quad (4)$$

When Gaussian function is used for profile fitting, the relation is expressed by,

$$\beta^2_{microstructure} = \beta^2_{size} + \beta^2_{strain} \quad (5)$$

Fig. 6 shows the Williamson-Hall type plot of the dry process powders milled for 120 min using a Cauchy-Cauchy relation and a Gaussian-Gaussian relation. The y-intercept and slope of each plot represent the value of crystallite size and non-uniform strain, respectively.

It has been known that microstructural broadening is a convolution of a broadening due to the crystalline size and a broadening due to the non-uniform strain which both have Cauchy characters and Gaussian characters at the same time. Therefore the simplified integral breadth methods cannot be used to measure the crystallite size and non-uniform strain. Balzar have suggested the Warren-Averbach method for the Voigt function which is a convolution of Voigt type size broadening and the Voigt type strain broadening[9]. The Warren-Averbach analysis using Fourier transformation was carried out by the BREADTH program after obtaining the integral breadth of Voigt profile for each diffraction peak of the dry process powders[10].

The crystallite size measured from the Warren-Averbach method is actually an effective crystallite size. The contribution of stacking fault and twin should be corrected according to the diffraction theory as expressed in Eq. (6).

$$\frac{1}{D_{eff}} = \frac{1}{D_{true}} + \frac{1}{4} \cdot \frac{3\alpha + 2\beta}{2d_{111}} \quad (6)$$

Stacking fault probability (α) can be obtained from the diffraction peak shift between a

standard and the sample as shown in Eq.(7)[11]. In this study, the stacking fault probabilities of each sample were measured around 0.01.

$$\alpha^{(111)} = \left[\frac{2\pi^2}{45\sqrt{3}}\right]\frac{\Delta(2\theta^o)}{\tan\theta^{(111)}} \tag{7}$$

Twin probability(β) can be measured from the asymmetry of the diffraction peak which is the expressed difference between the peak maximun position and the centroid of the peak as shown in Eq.(8)[12]. The twin probabilities of the samples were also around 0.01.

$$\Delta C.G.(2\theta^o)_{111} = 11\cdot\beta\tan\theta_{111} \tag{8}$$

Dislocation density of the samples were calculated using the equation of Wlliamson and Smallman as shown in Eq. (9)[13].

$$\rho = \frac{(3nK)^{1/2}\langle\varepsilon^2\rangle^{1/2}}{bD} \approx \frac{\sqrt{12}\langle\varepsilon^2\rangle^{1/2}}{aD} \tag{9}$$

Column length distribution can be obtained using the Warren-Averbach method because the column length distribution is proportional to the second derivative of the Fourier coefficient and the second derivative of the Voigt function is expressed as shown in Eq. (10)[14].

$$\frac{d^2A_S(L)}{dL^2} = [(2\pi L\beta_{GS}^2 + 2\beta_{CS})^2 - 2\pi\beta_{GS}^2]A_S(L) \tag{10}$$

Volume-weighted column length distributions of mechanically milled UO_2 powder obtained by the Warren-Averbach method became narrower as the milling time increased as shown in Fig. 7.

Table 1 shows crystallite size of mechanically milled dry process powders obtained from various line broadening methods. Considering the bias of Stokes' deconvolution and the Voigt character of size broadening and strain broadening, the Warren-Averbach analysis using Voigt fitting is found to be the most reliable technique to measure the crystallite size and size distribution. The contribution of stacking fault and twin should be corrected to obtain more realistic crystallite size in mechanically milled powders according to the diffraction theory.

Conclusions

The nano-scale crystallite size of mechanically milled UO_2 powders in a dry process nuclear fuel were measured by line broadening analysis using neutron diffraction. Neutron diffraction line broadening of mechanically milled oxide nuclear fuel powders is fitted best when the Voigt function is used. Warren-Averbach analysis for Voigt-fitted microstructural broadening measures the most reliable crystallite sizes ranging from 62 nm to 40 nm with milling time from 30 min to 120 min. The crystallite size distributions of mechanically milled UO_2 became narrower as milling time increased. Line broadening analysis of mechanically milled UO_2 is effective in estimating the crystallite size distributions statistically.

Acknowledgements

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Table 1. The crystallite size of dry process powders according to various methods.

Methods		Milling time		
		30 min	60 min	120 min
Simplified Line Breadth Cauchy-Cauchy		368.2 nm	313.6 nm	123.7 nm
Simplified Line Breadth Cauchy-Gaussian		144.9 nm	126.9 nm	59.2 nm
Simplified Line Breadth Gaussian-Gaussian		56.5 nm	53.1 nm	36.4 nm
Voigt Single Line (111)		46.0 nm	42.7 nm	35.2 nm
Warren-Averbach using Voigt fitting	D_{eff}	28.5 nm	25.9 nm	21.3 nm
	D_{SF}	41.5 nm	37.3 nm	31.6 nm
	D_{twin}	61.7 nm	52.6 nm	39.6 nm

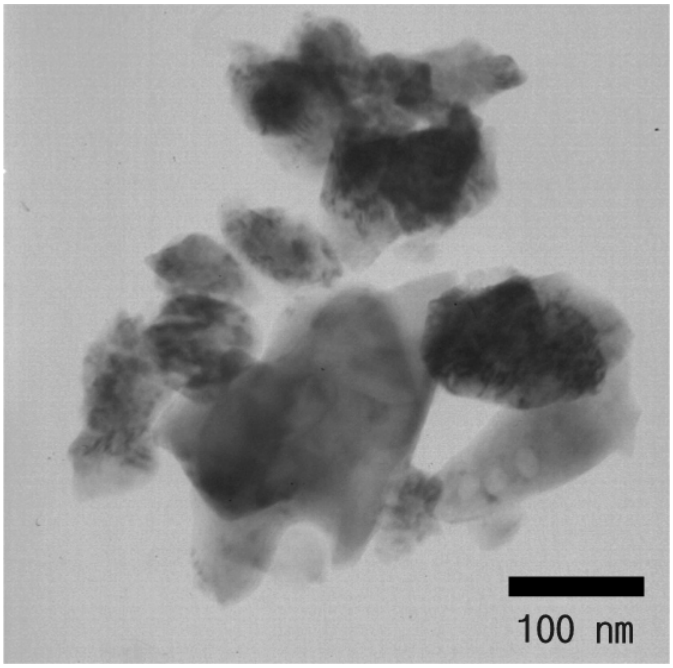

Fig. 1. A transmission electron micrograph showing the UO_2 particles.

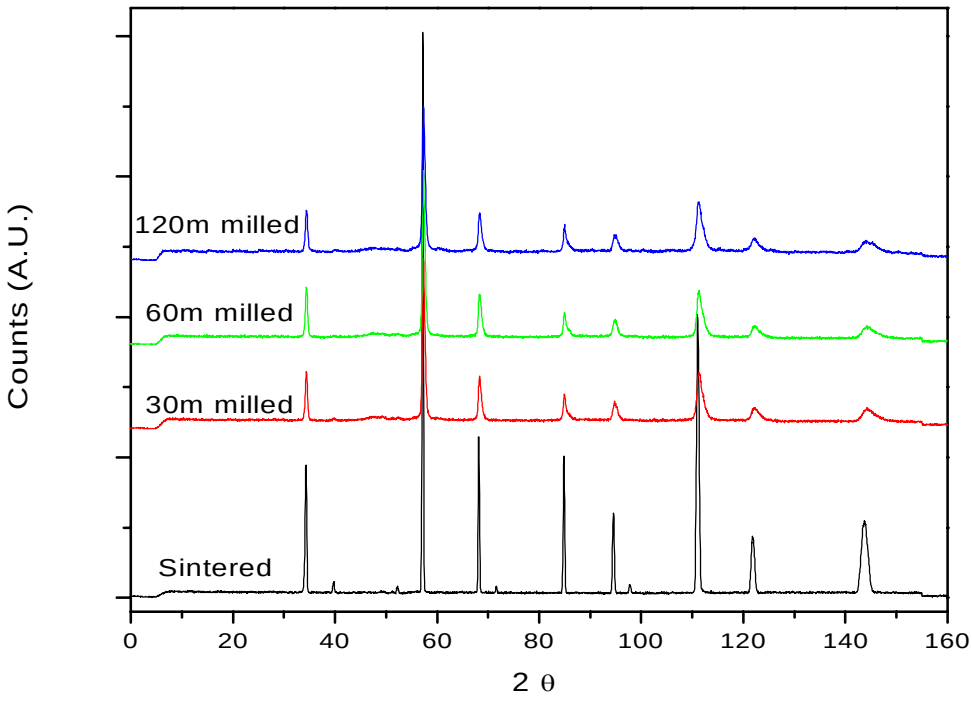

Fig. 2. Neutron diffraction patterns of simulated dry process fuel of sintered pellet and milled powders with varying milling time from 30 min to 120 min.

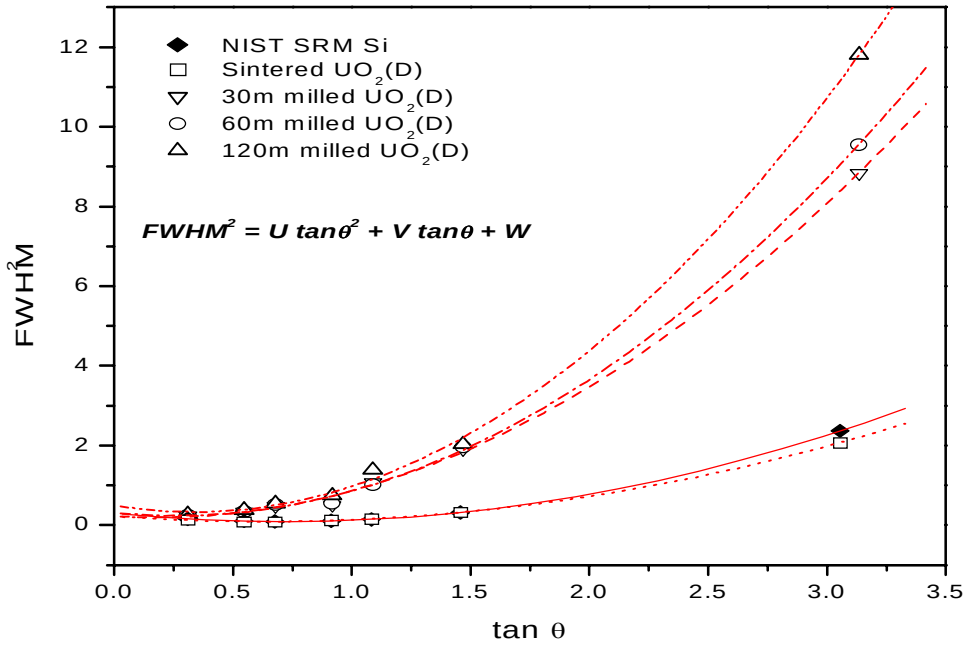

Fig. 3. Line broadening of milled powders and reference materials fitted with Caglioti relation. ($FWHM^2=U\ tan\theta^2 + V\ tan\theta + W$)

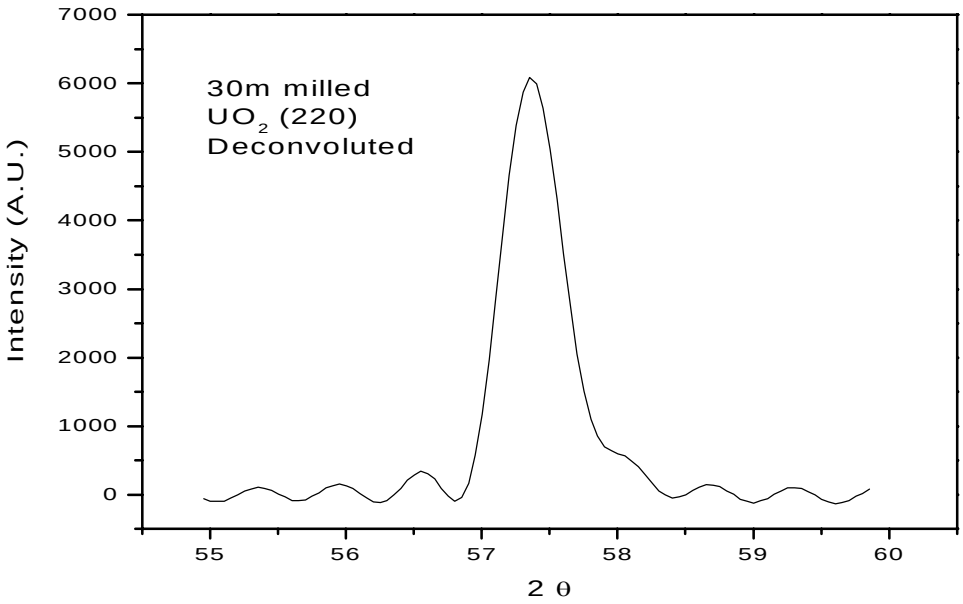

Fig. 4. Microstructural broadening of (220) peak of 30 min milled dry process powder deconvoluted by Stokes' method.

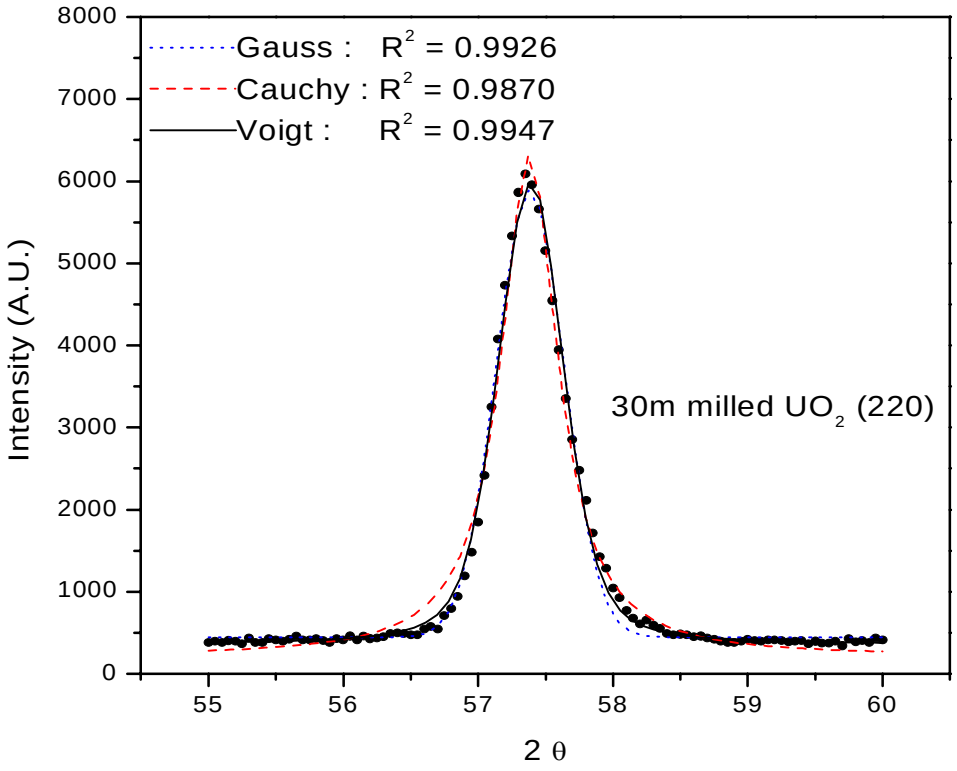

Fig. 5. (220) peak of 30 min milled dry process powder fitted by Gaussian, Cauchy, and Voigt function.

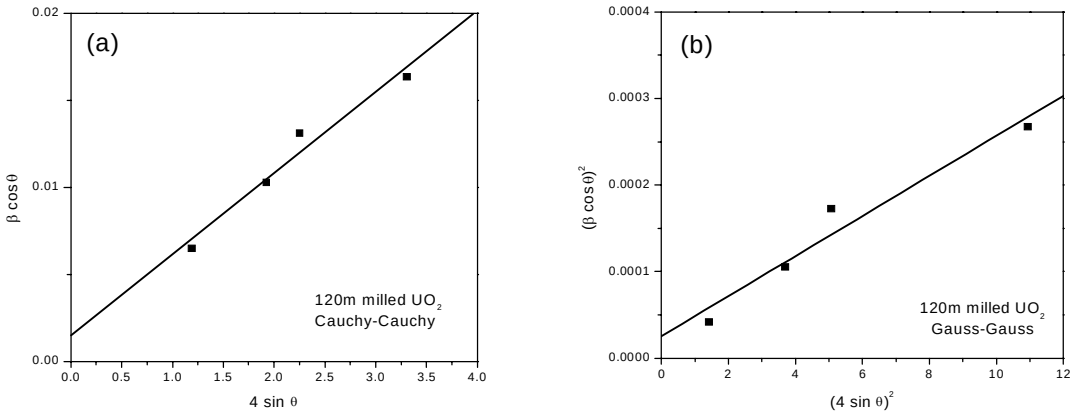

Fig. 6. Hall-Williamson plot of dry process powders milled for 120 min using (a) a Cauchy-Cauchy relation and (b) a Gaussian-Gaussian relation.

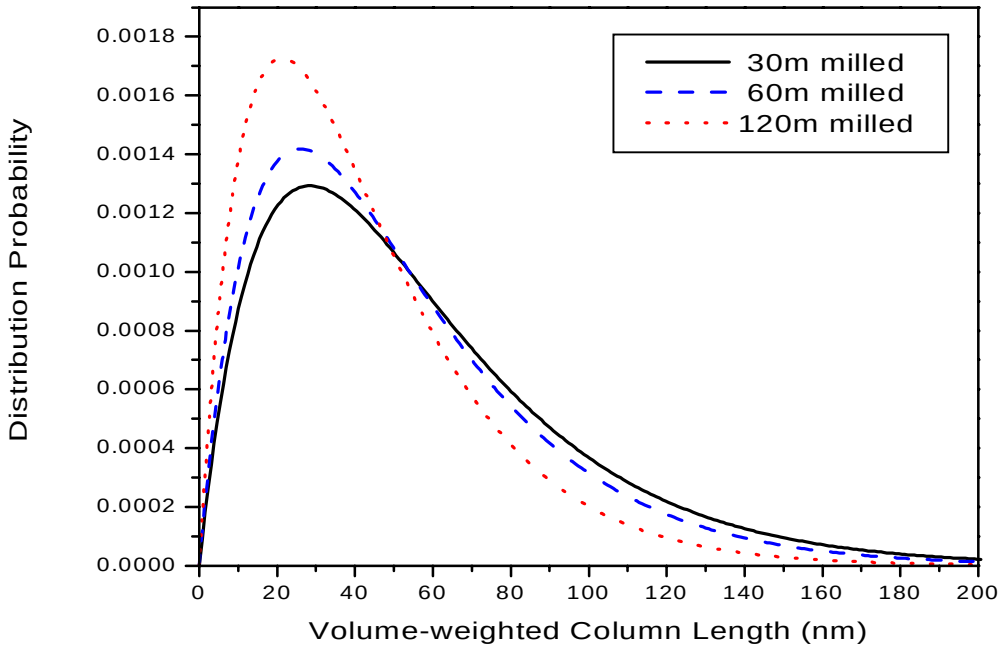

Fig. 7. Volume-weighted column length distribution of attrition milled dry process powders.

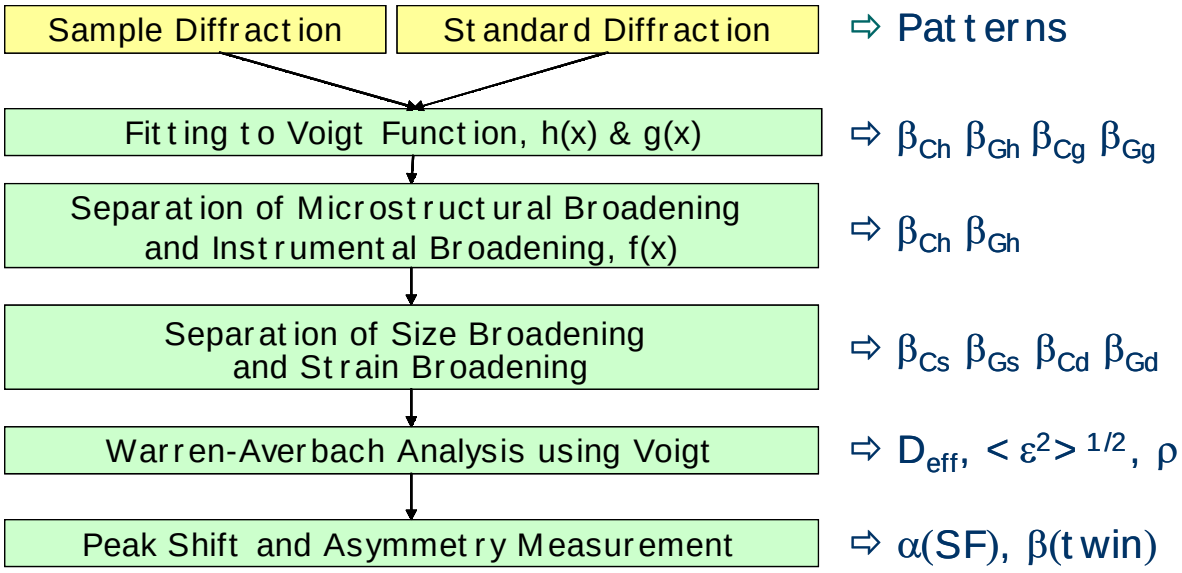

Fig. 8. The flow chart for the measurement of crystallite size of mechanically milled dry process fuel powders by neutron diffraction.