

X-Ray Line Profile Analysis of Nanodisperse Silicon Nitride Ceramics

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Keywords: Grain Size Distribution, Nanodisperse Silicon Nitride, X-Ray Diffraction Profile Analysis

Abstract

Nanodisperse silicon nitride powders were produced by different methods of synthesis. The effect of the production routes on the grain-size distribution and the dislocation density in the powders were studied by high-resolution X-ray diffraction. The average grain-size and the dislocation density of the samples were determined by the recently developed *modified* Williamson-Hall and Warren-Averbach procedures from X-ray diffraction profiles. A new numerical method provided log-normal grain-size distributions from the size parameters derived from X-ray diffraction profiles. It was established that the powder produced by silicon nitridation and milling had lower average grain-size and wider size distribution than the sample crystallized from amorphous silicon nitride powder synthesized in plasma reactor. The grain-size distribution and the area-weighted average grain-size obtained by X-rays were in good agreement with those determined by TEM and from the specific surface area, respectively. The dislocation density was found to be between 10^{14} and 10^{15}m^{-2} .

1. Introduction

Dense silicon nitride ceramics are important structural materials because of their good room and high temperature mechanical properties. Silicon nitride ceramics of low porosity are usually densified by liquid-phase sintering [1]. The average grain-size and the grain-size distribution have a great influence on the density, the phase composition and the microstructure, and therefore on the mechanical properties of the resulting ceramics [2]. Consequently, the investigation of the effect of the production routes of silicon nitride powders on the grain-size distribution of these powders has particular relevance.

Krill and Birringer have recently developed a procedure to determine grain-size distribution from the Fourier transform of X-ray diffraction profiles [3]. In this procedure, however, the anisotropic strain broadening has not been accounted for and only the Fourier coefficients of the diffraction profiles were used. It has been shown recently that strain anisotropy can be well accounted for by the dislocation model of the mean square strain [4-7]. The anisotropic contrast caused by dislocations can be summarised in contrast factors, C , which can be averaged over the dislocation population in the crystal. Using the average contrast factors, \bar{C} , in the *modified* Williamson-Hall plot and in the *modified* Warren-Averbach procedure, the different averages of grain-sizes and the dislocation density can be obtained [4]. In a recently published paper a new pragmatical and self-consistent procedure has been proposed for the stable determination of grain-size distribution using the three size parameters obtained from the full widths at half maximum (FWHM), the integral breadths and the Fourier coefficients of the diffraction profiles [8]. The aim of the present paper is to compare the grain-size distribution and the dislocation density in silicon nitride powders produced by different methods of synthesis.

2. Experimental details

2.1. Powder preparation

Four kinds of silicon nitride powders were produced. The first one was synthesized by the vapor-phase reaction of silicon tetrachloride and ammonia in a radiofrequency thermal plasma reactor under conditions given previously (powder SNP) [9]. The resulting powder was predominantly amorphous with a crystalline content of about 20vol%. The plasma powder was heat-treated in a horizontal laboratory furnace in flowing nitrogen at 0.1 MPa, at annealing temperatures of 1350°C (SNP1350) and 1500°C (SNP1500) for 2 h. The fourth powder was produced by nitridation of silicon and post-milling (SNM).

2.2. X-ray diffraction technique

The crystalline phases were identified by X-ray diffraction using a Guinier-Hagg focusing camera and $\text{CuK}\alpha_1$ radiation. The diffraction profiles were measured by a special double crystal diffractometer with negligible instrumental broadening [4]. A fine focus rotating cobalt anode (Nonius FR 591) was operated as a line focus at 36 kV and 50 mA ($\lambda=0.1789$ nm). The symmetrical 220 reflection of a Ge monochromator was used in order to have wavelength compensation at the position of the detector. The $\text{K}\alpha_2$ component of the Co radiation was eliminated by an 0.16 mm slit between the source and the Ge crystal. The profiles were registered by a linear position sensitive gas flow detector.

Transmission electron microscopy (TEM, JEOL JEM200CX) has been used for direct measurement of the grain-size distribution. The specific surface areas of the powders were determined from the nitrogen adsorption isotherms by the BET (Brunauer-Emmett-Teller) method. Assuming that the grains have spherical shape, the area-weighted average grain-size (t) in nanometers was calculated as $t=6000/qS$ where q is the density in g/cm^3 and S is the specific surface area in m^2/g .

3. Evaluation of the X-ray diffraction profiles

3.1. The modified Williamson-Hall and Warren-Averbach methods

Assuming that strain broadening is caused by dislocations the full widths at half maximum (FWHM) of diffraction profiles can be given by the *modified* Williamson-Hall plot as [8]:

$$\Delta K = \gamma / D + \alpha (K\bar{C}^{1/2})^2 + O(K^4\bar{C}^2), \quad (1)$$

where D is a size parameter characterising the column lengths in the specimen, γ equals to 0.9, α is a constant depending on the effective outer cut-off radius, the Burgers vector and the density of dislocations, \bar{C} is the average contrast factor of dislocations depending on the relative positions of the diffraction vector and the Burgers and the line vectors of the dislocations [4, 5-7] and O stands for higher order terms in $K^2\bar{C}$. $K=2\sin\theta/\lambda$, where θ is the diffraction angle and λ is the wavelength of X-rays. $\Delta K=\cos\theta [\Delta(2\theta)]/\lambda$, where $\Delta(2\theta)$ is the FWHM of the diffraction peak. The size parameter corresponding to the FWHM, D , is obtained from the intercept at $K=0$ of a smooth curve according Eq. (1) [4]. The *modified* Williamson-Hall procedure was also applied for the integral breadths of the profiles. In this case γ was taken as 1 and the obtained size parameter denoted by d .

It has been shown that the average dislocation contrast factor, \bar{C} , in an untextured hexagonal polycrystalline specimen is the following function of Miller indices hkl [10]:

$$\bar{C} = \bar{C}_{hkl} \left[1 + \frac{[A(h^2 + k^2 + (h+k)^2) + Bl^2]l^2}{[h^2 + k^2 + (h+k)^2 + \frac{3}{2}(\frac{a}{c})^2 l^2]} \right], \quad (2)$$

where \bar{C}_{hk0} is the average dislocation contrast factor for the $hk0$ reflections, A and B are parameters depending on the elastic constants and on the character of dislocations in the crystal and c/a is the ratio of the two lattice constants of the hexagonal crystal. Inserting Eq. (2) into Eq. (1) the latter one was solved for D, α , A and B by the method of least squares. $\bar{C}_{hk0}=0.0279$ was calculated numerically for both α - and β -Si₃N₄ assuming elastic isotropy because of the lack of the knowledge of anisotropic elastic constants.

The *modified* Warren-Averbach equation is [4]:

$$\ln A(L) \cong \ln A^S(L) - \rho B L^2 \ln(R_e/L) (K^2 \bar{C}) + O(K^4 \bar{C}^2), \quad (3)$$

where $A(L)$ is the absolute value of the Fourier coefficients of the diffraction profiles, A^S is the size Fourier coefficient, ρ is the dislocation density, $B=\pi b^2/2$ (b is the length of the Burgers vector), R_e is the effective outer cut-off radius of dislocations, L is the Fourier length and O stands for higher order terms in $K^2 \bar{C}$. The average dislocation contrast factors \bar{C} determined from the *modified* Williamson-Hall plot of FWHM were also used in Eq. (3). The size parameter corresponding to the Fourier coefficients is denoted by L_0 . It is obtained from the size Fourier coefficients, A^S , by taking the intercept of the initial slope at $A^S=0$ [11]. Assuming that the grains are spherical, the area-weighted average grain-size of the crystalline phases ($\langle x \rangle_{\text{area}}^c$) was calculated from L_0 as follows: $\langle x \rangle_{\text{area}}^c = 3L_0/2$ [3,12].

Assuming that the surface area of the entire powder equals to the sum of the surface areas of the crystalline and the amorphous fractions, the area-weighted average grain-size of the amorphous phase was calculated from those of the entire powder (t) and the crystalline fraction ($\langle x \rangle_{\text{area}}^c$) and from the ratio of the volumes of the amorphous and the crystalline fractions, V_a/V_c as follows [13]

$$\langle x \rangle_{\text{area}}^a = \frac{V_a}{V_c} \cdot \left[\frac{1}{t} \left(1 + \frac{V_a}{V_c} \right) - \frac{1}{\langle x \rangle_{\text{area}}^c} \right]^{-1}. \quad (4)$$

3.2. Determination of grain-size distribution from X-ray diffraction

In a recent work a pragmatical and self-consistent numerical procedure has been worked out to relate the experimentally determined D, d and L_0 values to the parameters of a grain-size distribution function, $f(x)$ [8]. A brief description of this procedure is given below. It was observed by many authors that the grain-size distribution of nanocrystalline materials is log-normal [3,14]:

$$f(x) = \frac{1}{\sqrt{2\pi \ln \sigma}} \cdot \frac{1}{x} \exp \left\{ -\frac{[\ln(x/m)]^2}{2 \ln^2 \sigma} \right\}, \quad (5)$$

where x is the grain-size, σ is the variance and m is the median of the size distribution function $f(x)$. If the crystallites are distortion free the intensity distribution can be described as [14]:

$$I(s) = \int_0^\infty M \cdot \frac{\sin^2(\pi Ms)}{2(\pi s)^2} \cdot \text{erfc} \left[\frac{\ln(M/m)}{\sqrt{2 \ln \sigma}} \right] dM, \quad (6)$$

where $s=A(2\theta)/\lambda$, M is the length of the columns in the direction of the diffraction vector, *erfc* is the complementary error function. The parameters σ and m corresponding to our samples were determined from Eq. (6) by a computer program satisfying the condition that the sum of the squares of the difference between the D, d and L_0 of the numerically calculated $I(s)$ function and the experimental values of these parameters is minimum.

4. Results and discussion

The phase composition of the silicon nitride powders can be seen in Table 1. It can be established that the as-synthesized plasma powder (SNP) is predominantly amorphous with 20vol% crystalline phase content. After the heat-treatment at temperature of 1350°C (SNP1350) α -Si₃N₄ crystallized from the predominantly amorphous silicon nitride powder while the amount of β -Si₃N₄ did not change. At 1500°C the crystalline phase content of the sample became very high (80vol%) and both α - and β -Si₃N₄ crystallized from the amorphous phase (SNP1500). The powder produced by silicon nitridation and milling (SNM) has very high α -Si₃N₄ content (97vol%). The average grain-size and the grain-size distribution calculated for the major α -Si₃N₄ phase are taken as characteristic parameters for the entire crystalline fraction of each sample because the amount of β -Si₃N₄ phase is small compared to that of α -Si₃N₄.

Table 1: The phase composition of the silicon nitride powders.

sample	amorphous (vol%)	α -Si ₃ N ₄ (vol%)	β -Si ₃ N ₄ (vol%)
SNP	80	17	3
SNP1350	65	32	3
SNP1500	20	67	13
SNM	-	93	7

The three size parameters obtained from the X-ray line profile analysis for the silicon nitride powders are listed in Table 2. The area-weighted average grain-size calculated for the crystalline fraction ($\langle x \rangle_{\text{area}}^c$) and that of the entire powder (t) can be also seen in Table 2. The area-weighted average grain-size of the amorphous phase ($\langle x \rangle_{\text{area}}^a$) was calculated from Eq. (4) for the powders having high amorphous fraction. The values of the amorphous average grain-size are 31 and 49 nm for the as-synthesized plasma powder (SNP) and for the sample heat-treated at 1350°C (SNP1350), respectively. It can be established that in these samples the average grain-size of the amorphous phase is lower than that of the crystalline fraction. The average size of the crystalline grains decreased slightly at temperature 1350°C because of the crystallization of the smaller amorphous grains, while it significantly increased during heat-treatment at 1500°C because of the extensive grain-coarsening in the sample (see Table 2). For the powders having high amount of crystalline phases (SNP1500 and SNM) the average grain-size of the crystalline fraction obtained by X-rays agrees well with that of the entire powder calculated from the specific surface area.

Table 2: The three size parameters, D , d , L_0 obtained by X-rays; the area-weighted average grain-size of the crystalline fraction ($\langle x \rangle_{\text{area}}^c$) determined by X-rays and that of the entire powder (t) calculated from the specific surface area; the two parameters, m and σ , characterizing the log-normal grain-size distribution function of the crystalline fraction; and the dislocation density (ρ) in silicon nitride powders.

sample	D [nm]	d [nm]	L_0 [nm]	$\langle x \rangle_{\text{area}}^c$ [nm]	t [nm]	m [nm]	σ	ρ [m ⁻²]
SNP	87±5	72±4	49±3	74±5	35±2	36±3	1.67±0.07	4.9 × 10 ¹⁴
SNP1350	84±4	62±3	40±3	60±5	52±3	20±2	1.88±0.08	1.8 × 10 ¹⁴
SNP1500	81±4	70±4	62±4	93±6	94±5	73±7	1.30±0.07	5.7 × 10 ¹⁴
SNM	74±4	57±4	41±3	62±5	71±4	27±3	1.71±0.08	7.7 × 10 ¹⁴

Log-normal particle size distribution functions were determined for the crystalline fraction of the powders by the procedure described in section 3.2. As the result of this calculation the two parameters, σ and m corresponding to the log-normal size distribution are obtained and listed in Table 2. Fig. 1 shows the grain-size distribution function, $f(x)$, corresponding to the calculated m and σ values for the silicon nitride powders. It can be established that for the powder crystallized at 1350°C the median (m) of the size distribution decreased and the variance (σ) increased because of the crystallization of the smaller amorphous grains. After the heat-treatment at 1500°C the median of the size distribution increased and the variance decreased because of the extensive grain-coarsening in the sample. The entirely crystalline powder produced by silicon nitridation and milling (SNM) has lower median and higher variance than the plasma powder having very high crystalline phase content (SNP1500). The log-normal size-distribution function corresponding to the σ and m values for the powder SNM is shown as solid line in Fig. 2. The size distribution obtained from the TEM micrographs is shown as bar-graph in Fig. 2. (The scales of the bar-diagram and the size-distribution function are on the left- and the right hand side of the figure.) In the TEM measurements 300 particles were chosen at random in different areas in the powder. The agreement between the bar-diagram and the size-distribution function is good. The small quantitative difference between the X-ray and the TEM results is probably due to the fact that the bar-diagram was obtained from a relatively small number of grains. The dislocation density has been determined from the *modified* Warren-Averbach plot [4] and are listed in Table 2. The dislocation densities were found to be between 10^{14} and 10^{15}m^{-2} .

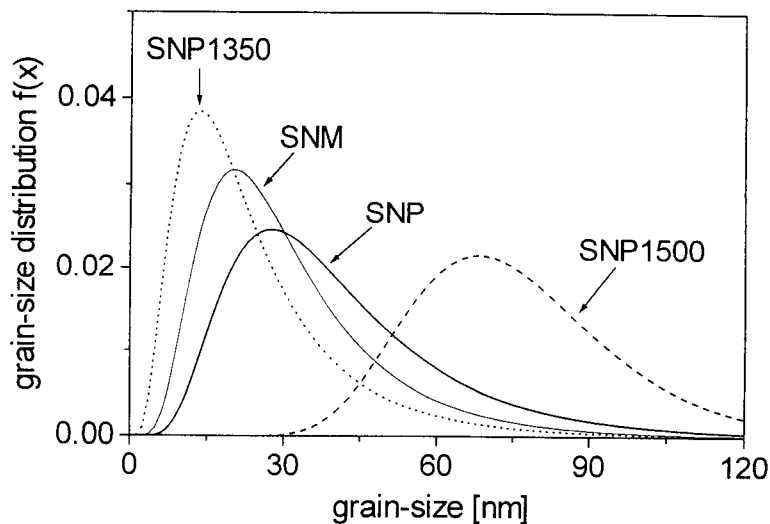


Figure 1: The grain-size distribution function, $f(x)$, of the crystalline fraction of the silicon nitride powders.

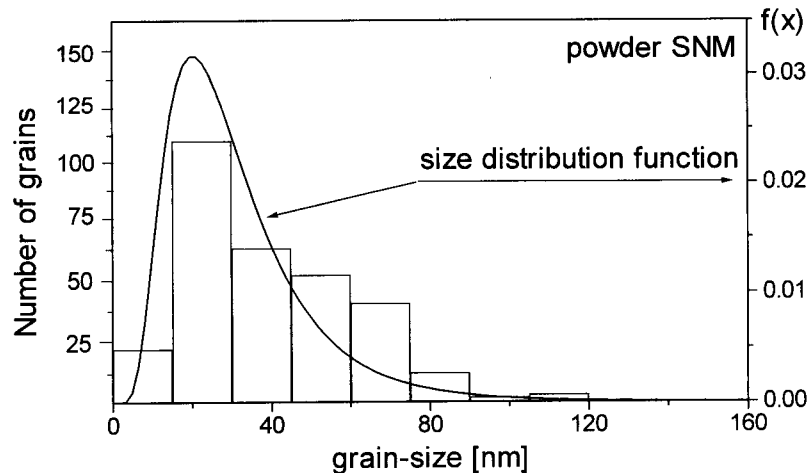


Figure 2: Bar-diagram of the size distribution obtained from TEM micrographs and the size distribution function, $f(x)$ (solid line), determined by X-rays for the powder produced by silicon nitridation and milling (SNM).

5. Conclusions

The effect of the production methods of silicon nitride powders on the grain-size distribution and the dislocation density was studied. It was established that during the heat-treatment of the plasma powder at 1350°C the average grain-size decreased and the width of the size distribution increased because of the crystallization of the smaller amorphous particles. After the heat-treatment at 1500°C the average grain-size increased and the width of the size distribution decreased. The powder produced by silicon nitridation and milling had lower average grain-size and wider size distribution than the sample crystallized from amorphous plasma silicon nitride powder (SNP1500). For the powders having high amount of crystalline phases the grain-size distribution and the average grain-size obtained by X-rays were in good agreement with those determined by TEM and from the specific surface area, respectively.

Acknowledgements

The authors are grateful for the financial support of the Hungarian Scientific Research Fund, OTKA, Grant Nos. D-29339 and T-031786.

References

1. J. Szépvölgyi and I. Mohai, *Ceram. Int.* **25** (1999), p. 711.
2. G. Ziegler, J. Heinrich and G. Wötting, *J. Mat. Sci.* **22** (1987), p. 3041.
3. C. E. Krill and R. Birringer, *Phil. Mag. A*, **77** (1998), p. 621.
4. T. Ungár and A. Borbély, *Appl. Phys. Lett.* **69** (1996), p. 3173.
5. T. Ungár, I. Dragomir, Á. Révész and A. Borbély, *J. Appl. Cryst.* **32** (1999), p. 992.
6. M. Wilkens, *phys. stat. sol. (a)* **104** (1987) K1.
7. R. Kuzel Jr. and P. Klimanek, *J. Appl. Cryst.* **21** (1988), p. 363.
8. T. Ungár, J. Gubicza and G. Ribárik, *J. Appl. Cryst.* in preparation
9. J. Szépvölgyi, F. L. Riley, I. Mohai, I. Bertoti and E. Gilbert, *J. Mater. Chem.* **6** (1996), p. 1175.
10. T. Ungár and G. Tichy, *phys. stat. sol. (a)* **171** (1999), p. 425.
11. B. E. Warren, *Progr. Metal Phys.* **8** (1959), p. 147.
12. A. J. C. Wilson, *X-ray Optics*, Methuen, London 1962.
13. J. Gubicza, J. Szépvölgyi, I. Mohai, G. Ribárik and T. Ungár, *J. Mat. Sci.* to be submitted
14. Ch. D. Terwilliger and Y. M. Chiang, *J. Am. Ceram Soc.* **78** (1995), p. 2045.