Effect of β-Si₃N₄ starting powder size on elongated grain growth in β-Si₃N₄ ceramics

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Abstract

The microstructural evolution of pressureless sintered silicon nitride ceramics prepared from different particle sizes of β-Si₃N₄ as starting powders, has been investigated. When the specimen prepared from as-received β-powder of 0.66 μm in average size, was sintered at 1850°C, equiaxed β-Si₃N₄ grains were observed. As the size of the initial β-powder went down to 0.26 μm, however, the growth of elongated grains was enhanced, which resulted in a whisker-like microstructure similar to that made from α-starting powder. When the sintering temperature was increased to 2000°C, the elongated grains were also developed even in the specimen made from 0.66 μm β-powder. The observed results were discussed with relation to the two dimensional nucleation and growth theory for faceted crystals. In addition, fracture toughness of the specimen consisting of elongated grains, which was prepared from finer powders, increased. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Aspect ratio; Grain growth; Microstructure-final; Si₃N₄

1. Introduction

Silicon nitride ceramics have been considered to be one of the promising engineering ceramic materials because of their excellent mechanical properties.[1] It is known that the high fracture toughness of Si₃N₄ ceramics is attributed to the rodlike morphology of β-Si₃N₄ grains.[2,3] Therefore, the understanding of the grain growth mechanism of β-Si₃N₄ is very important for controlling the mechanical properties of silicon nitride ceramics.

There are two forms of silicon nitrides: α-Si₃N₄ and β-Si₃N₄.[4] The former is usually used as a starting powder, because this form can give a microstructure with elongated grains.[5,6] In contrast, when the latter is used as a starting powder, it is difficult to obtain the microstructure with elongated grains, even though the final phase after sintering is β-Si₃N₄.[6,7] Therefore, it has been supposed that the α to β transformation is associated with the formation of elongated grains. Although there are many reports on the microstructural evolution of silicon nitride ceramics, the growth mechanism of elongated grains is not well understood, due to its complex relation between α and β phase transformation and grain growth. It was shown that the formation of the large elongated grains was enhanced in pressureless sintering of fine α-Si₃N₄ powder in our previous work.[8] In this case, the influence of starting powder size on the formation of elongated grain was difficult to explain due to the α–β phase transformation during sintering.

In this work, to investigate the grain growth mechanism, β-Si₃N₄ powder was used as a starting material to avoid the effect of α–β phase transformation on the grain growth. The microstructural evolution of sintered materials was characterized with grain size and aspect ratio. Subsequently, the results are discussed in terms of two-dimensional nucleation and growth mechanism. The fracture toughness is also discussed with the resultant microstructure.

2. Experimental procedure

Commercially available β-Si₃N₄ powder (Shin-Etsu, KSN-80 SP, Japan) with more than 85% of β-phase was used as a starting powder. To obtain a fine powder, as-received β-Si₃N₄ was classified by a sedimentation

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technique. Fig. 1 shows the micrographs of as-received (a) and classified (b, c) powders. The size distribution measured by a particle size analyzer (Analysette 22, Fritsch Industries, Germany) is given in Fig. 2. The average size of as-received and classified powders were 0.66, 0.44 and 0.26 μm, respectively. As shown in Fig. 2,

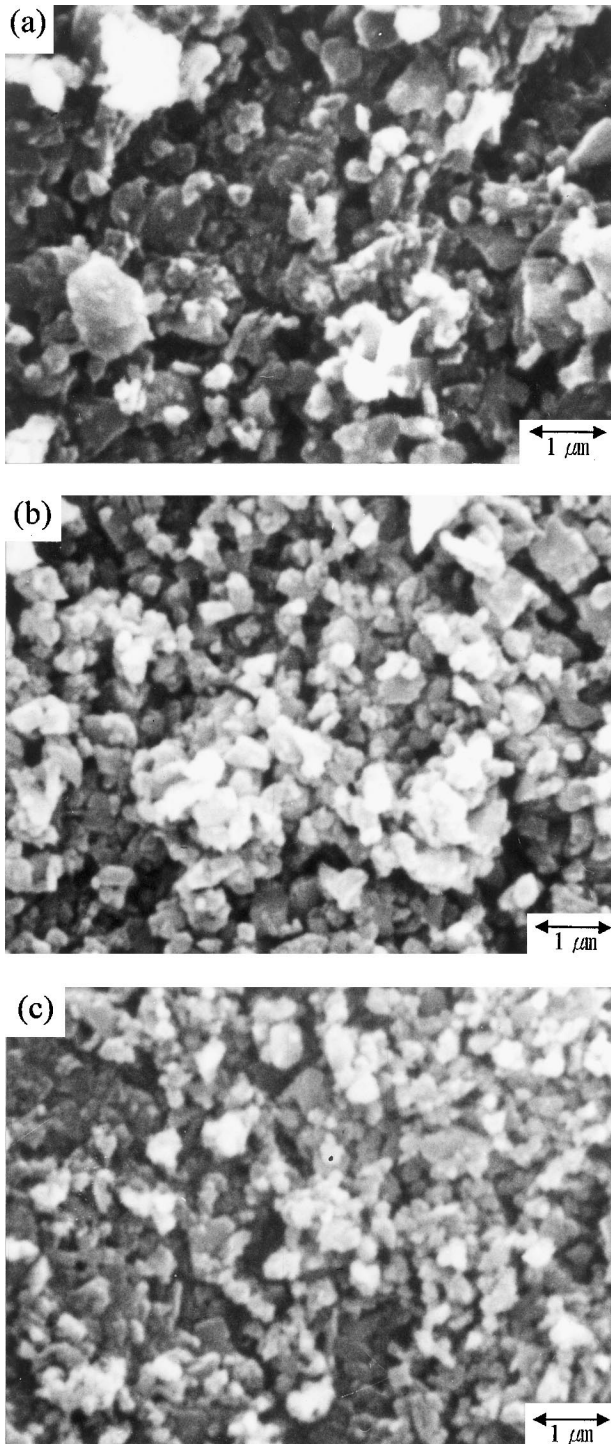Fig. 1. The photographs of the classified and as-received powders: (a) 0.66 μm,(b) 0.44 μm and (c) 0.26 μm.

the shape of each size distribution is similar, i.e. there are no extra peaks in the range of large size.

The powders were mixed with 6 wt% Y_2O_3 (Grade C, H. C. Starck, Berlin, Germany) and 2 wt% Al_2O_3 (AKP30, Sumitomo, Osaka, Japan) and were mixed in isopropyl alcohol using an ultrasonic dispersion method to avoid any change of powder size during the process, and then dried using a rotary vapor evaporation. The mixed powders were pressed into cylindrical pellets of 15 mm in diameter under 100 MPa. The pellets were placed in a graphite crucible coated with BN, packed with Si_3N_4 powder, and then sintered at 1850°C for 5 h under 0.1 MPa nitrogen atmosphere and sintered at 2000°C for 5 h under 4 MPa N_2. Hereafter, the specimens prepared from particle sizes of 0.66, 0.44 and 0.26 μm will be referred to as B6, B4 and B2, respectively.

Sintered materials were sectioned and etched to observe the microstructure using a scanning electron microscope (SEM). An image analyzer (Image Pro-Plus, Media Cybernetics, MD, USA) was used to determine the microstructural characteristics. The shortest diagonal (d) and the longest diagonal (l) of each grain were determined. The characterization of large elongated grains was made by determining the average aspect ratio of the largest 10 grains, $\overline{AR}_{LG}$. More than 1000 grains were observed for each specimen. The fracture toughness was measured by the indentation fracture (IF) method.

3. Results and discussion

Fig. 3 shows the microstructures of B6, B4, and B2 specimen sintered at 1850°C for 5 h. As shown in Fig. 3, the microstructure of the B6 specimen consists of
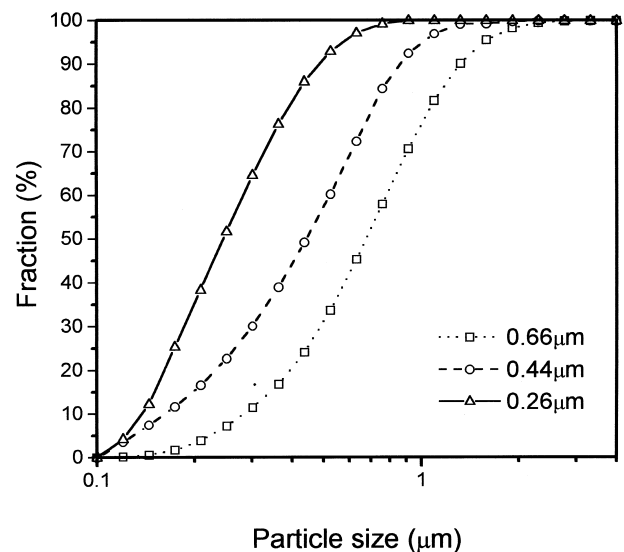

Fig. 2. The particle size distributions of the classified and as-received powders.

mainly equiaxed grains. In B4 and B2 specimens, on the other hand, elongated grains are formed within fine matrix grains. The abnormal growth of β-Si$_3$N$_4$ grains was accelerated with decreased starting powder size. The distributions of grain size and their area fraction determined by microstructure analysis are given in Fig. 4. It can be noted from Fig. 4 that there are high extra

peaks in the range of large grain size for B2 and B4 specimen. This high area fraction suggests that a part of the large grains is more elongated which is consistent with the microstructure as shown in Fig. 3. The average values of d, l, and $\overline{AR}_{LG}$ for each specimen are given in Table 1. The average value of d for the B6-specimen is indeed greater than that of the B2-specimen, but the average aspect ratio of the largest 10 grains for the B2 specimen is about two times larger than that of the B6 specimen. It is interesting to note that the difference in average value of d between B6 and B2 specimen is quite different from that in specimens from α-Si$_3$N$_4$ powders of the previous work,[8] although the starting powder sizes and their distributions in both experiments are similar. For the specimens prepared from α-Si$_3$N$_4$ starting powders in previous work, [8] the average values of d of the specimens prepared from as-received powder (average size : 0.67 μm) and classified powder (average size : 0.25 μm) were 0.53 and 0.46 μm, respectively.

The average values of d after sintering showed only a small difference by 0.07 μm, although the starting powder sizes were quite different from each other. On the other hand, in the specimens prepared from β-starting powders, the difference in the average grain sizes after sintering was great, as much as that of the starting powders. In the case of α-Si$_3$N$_4$ starting powder, it is considered that the difference of the grain sizes was
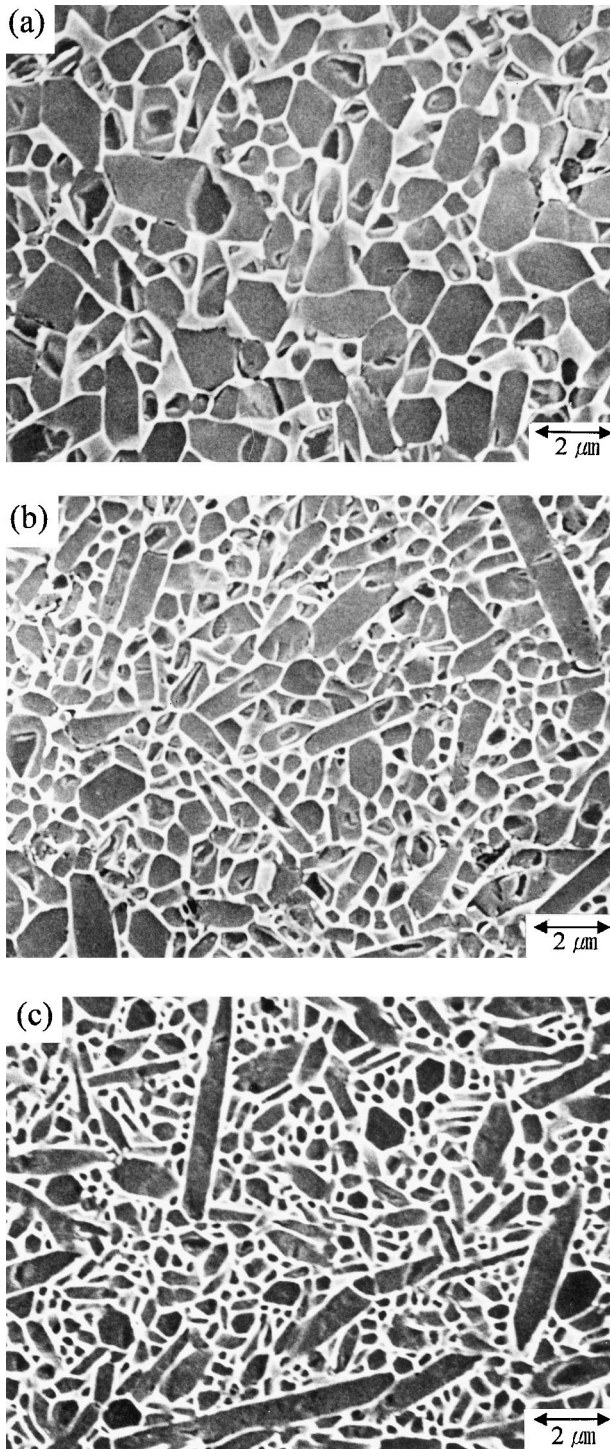

Fig. 3. The microstructures of the B6, B4, and B2 specimens sintered at 1850°C for 5 h: (a) B6, (b) B4 and (c) B2.
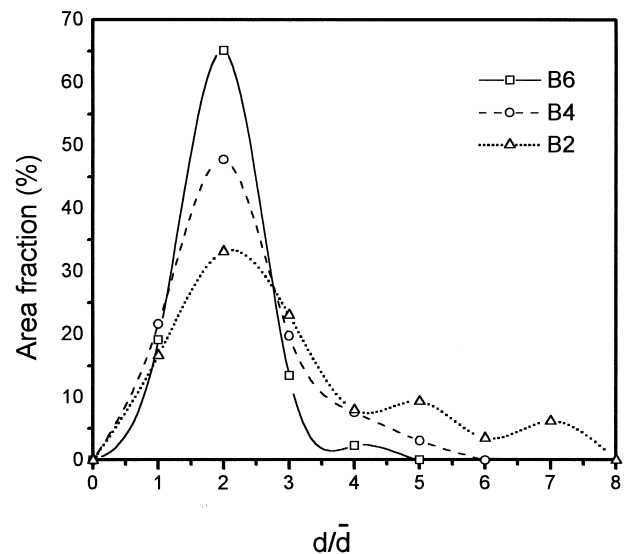

Fig. 4. The grain size distributions of the B6, B4, and B2 specimens sintered at 1850°C for 5 h.

Table 1
Microstructural parameters of the specimens sintered at 1850°C for 5 h

	$\bar{d}$(μm)	$\bar{l}$(μm)	$\overline{AR}_{LG}$
B6-specimen	0.65	1.18	4.92
B4-specimen	0.39	0.77	6.09
B2-specimen	0.23	0.51	10.05

reduced by the grain refinement induced from the phase transformation during sintering. However, when β-Si$_3$N$_4$ was used as a starting powder, the phase transformation did not occur and so they showed significant difference in average values of d after sintering. These facts suggest that the formation of elongated grains in this work is strongly dependent on the β-Si$_3$N$_4$ starting powder size.

The grain growth in β-Si$_3$N$_4$ matrix seems to occur via growth of larger grains and dissolution of smaller ones by material transport through the liquid phase. During the grain growth, the shape of grains varies considerably with the number of growth sites.[9] Numerous growth sites lead to the hindrance of the grain growth by impingement with neighbor β-grains, resulting in equiaxed grains. However, if the number of growth site is few, as frequently observed at abnormal grain growth, the grown grains that consume the matrix grains tend to take the shape of elongated grains. Therefore, it seems that the formation of elongated grains is attributed to the abnormal grain growth.

Recently, it was proposed that the growth of faceted crystals in the liquid matrix occurred by two-dimensional nucleation and growth mechanism and/or screw dislocation mechanism.[10,11] In order for a grain sufficiently larger than the average grain size to grow abnormally, the average grain size should be at least smaller than certain critical value which increases with increasing temperature. Fig. 5 shows the relationship between the minimum radius required for 2-D nucleation and the average radius. The growth by 2-D nucleation will occur in the 2-D nucleation region above the curve in Fig. 5. The value of the average radius required for 2-D nucleation will be slightly smaller than the critical radius. The minimum radius for 2-D nucleation d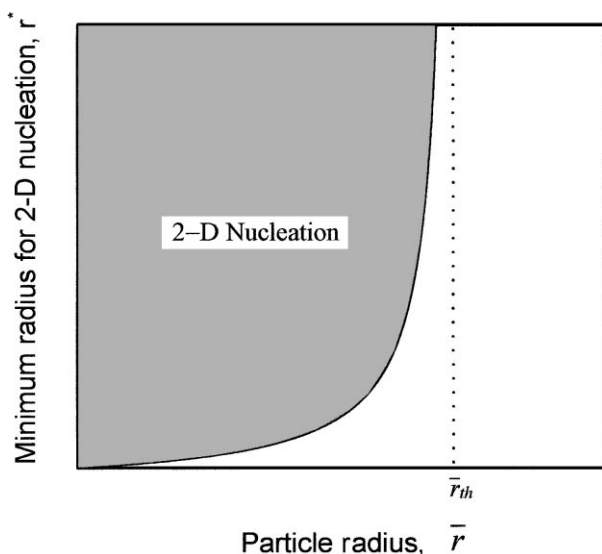ecreases rapidly with decreasing average radius. This means that more grains will grow by 2-D nucleation in the specimen prepared from fine size of the starting powder.

In this study, the observed results can be explained with the prediction of 2-D nucleation and growth theory. The abnormal growth will occur in the grains sufficiently larger than average grain size. As shown in Figs. 1 and 2, the relative fraction of large particles in the starting powders was nearly constant. Hence, it is supposed that the number of growth site in each powder is almost same. However, elongated grains were only observed in B4 and B2 specimen, not in B6 specimen. The starting powder size of B6 specimen is expected to be larger than the critical size so that the abnormal grain growth by the mechanism of 2-D nucleation and growth would not occur. On the contrary, in B4 and B2 specimen, elongated grains, resulting from 2-D nucleation and growth, were observed because the fine starting powders were used. Our results suggest that the average size of starting powder for the formation of elongated grains by 2-D nucleation and growth at 1850°C is smaller than the size of commercially available powders (> 0.5 μm).

In order to investigate the temperature dependence of critical radius required for 2-D nucleation and growth, the B6 specimen was sintered at a high temperature of 2000°C. Fig. 6 shows the microstructure of the B6 specimen which gas pressure sintered at 2000°C for 5 h. It is seen that the elongated grains were more developed as compared to Fig. 2a. As the sintering temperature increased, critical radius required for 2-D nucleation and growth will increase.[11] The average particle size of the B6 specimen, which is out of the 2-D nucleation region at 1850°C, moves into this region at 2000°C by the temperature dependence of critical radius, resulting in the microstructure with more elongated grains. This trend is coincident with the other experimental results in the specimens prepared from β-Si$_3$N$_4$ starting powder, which were sintered at high sintering temperature.[12,13]

Fig. 5. Schematic dependence of the minimum grain radius required for 2-D nucleation on the grain radius.[11]
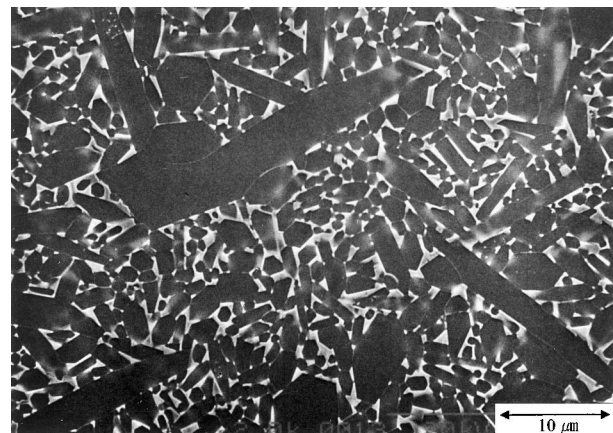

Fig. 6. The microstructure of B6 specimens gas-pressure-sintered at 2000°C for 5 h.
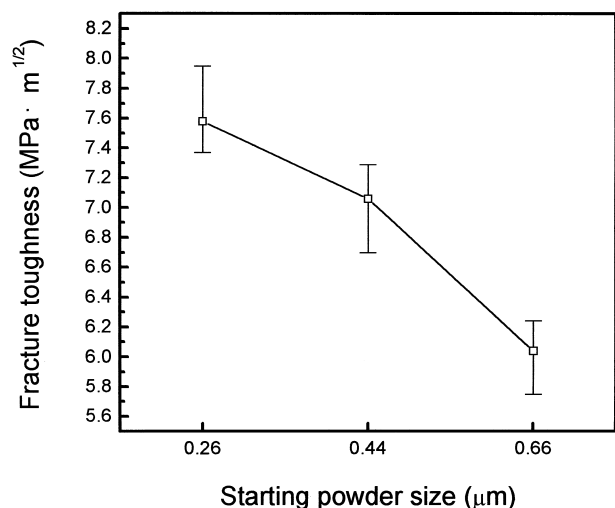
Fig. 7. The fracture toughness of the B6, B4, and B2 specimens sintered at 1850°C for 5 h.

Effect of starting powder size on the fracture toughness is given in Fig. 7. The fracture toughness increased with decreasing the size of starting powder. In Si_3N_4 materials fabricated using α-powder, it is reported that the fracture toughness increase proportionally to the square root of the diameter of the large grains.[14] Although the grain diameter of large grains was smaller in the B2 specimen than B4 and B6, the fracture toughness increased up to 7.6 MPa·m$^{1/2}$. Our result indicates that fracture toughness of Si_3N_4 is not dependent on the grain size. Rather, the elongated grains affect significantly to the improved fracture toughness.

4. Conclusions

The effect of initial β-Si_3N_4 powder size on the microstructural evolution of Si_3N_4 ceramics was investigated. The microstructure of Si_3N_4 ceramics is strongly dependent on the size of starting β-Si_3N_4 powders. The specimen prepared with commercially available β-powder of 0.66 μm in average size showed the microstructure with equiaxed β-Si_3N_4 grains. On the other hand, the growth of elongated grains was enhanced in the specimen prepared with classified β-powder of 0.26 μm average size. Our results suggested that the fine initial powder size was required for the formation of elongated grains by 2-D nucleation and growth mechanism at 1850°C, which should be smaller than the size of commercially available powders (> 0.5 μm). At 2000°C, however, elongated grains could be obtained from as-received β-powder of 0.66 μm average size due to the temperature dependence on the critical size required for 2-D nucleation and growth. Fracture toughness was improved from 6.0 to 7.6 MPa·m$^{1/2}$ with decreasing the size of starting powders from 0.66 to 0.26 μm. It is considered that the formation of elongated grains affected significantly the fracture toughness.

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