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Control and Characterization of Abnormally Grown Grains in Silicon Nitride Ceramics

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Abstract

The intrinsic grain growth behavior of β-Si_3N_4 was investigated by annealing fine-grained β-Si_3N_4 ceramics with 0–30 wt% β-nuclei. The development of bimodal microstructures was observed in annealed materials with 0·1–10 wt% nuclei, caused by the abnormal grain growth of nuclei due to the large driving force. This driving force was related to the difference in nuclei and matrix grain solubility in the liquid phase. The driving force for abnormal grain growth was also related to the stable morphology of β-grains of about 4 in aspect ratio. The fact that the driving force was constant in materials with 0·1–3 wt% nuclei is explained by the constant diffusion space for nuclei. Nuclei addition exceeding 10 wt% decreased the driving force because of nuclei interaction. A unimodal microstructure was developed with 30 wt% nuclei addition. © *1997 Elsevier Science Limited. All rights reserved.*

1 Introduction

The fracture toughness of sintered silicon nitride ceramics must be improved if they are to be used as engineering materials. Tough ceramics have been prepared by developing bimodal microstructures, which have abnormally grown grains in fine and uniform matrices. Increased fracture toughness is attributed to crack deflection and crack bridging by abnormally grown grains.[1–4]

α-Si_3N_4 powders are usually used as starting powders when developing bimodal microstructures. In liquid-phase sintering of α-Si_3N_4, α-grains dissolve in the liquid phase and precipitate as β-grains. The abnormal grain growth of large β-nuclei is assumed to be accelerated by α/β phase transformation.[5–8]

Reproducible microstructures are very difficult to obtain during α-powder sintering, however, because the relationship between microstructure development and phase transformation is very complex. In other words, it is not possible to control microstructures during such sintering.[9]

Bimodal microstructures have also been obtained in the sintering of β-powders with a wide particle-size distribution. In this case, particle-size distribution is the main factor enabling the development of a bimodal microstructure.[10]

Recent work on β-powder sintering and grain growth has obtained very stable microstructures after annealing at 1800°C when fine-grained, uniform silicon nitride ceramics were prepared by the low-temperature hot-pressing of very fine powders. This result is assumed to be produced by the low driving force for grain growth.[11,12]

Fine-grained ceramics containing small numbers of large grains have also developed bimodal microstructures due to the selective growth of large grains. These results support the assumption that the driving force of β-grain growth is based on the difference in particle size, and abnormal grain growth occurs only when the particle-size difference exceeds a critical value. Adding large β-nuclei in fine, uniform β-grains yields reproducible bimodal microstructures in the absence of α/β phase transformation.[13,14]

An important aspect of engineering materials is the wide distribution of mechanical properties, particularly strength. Fracture sources in ceramics include defects such as pores, inclusions, and large grains generated during processing, as well as surface cracks produced during surface finishing. The failure of a specimen originates in the largest defect.[15] Silicon nitride ceramics with a bimodal microstructure show *R*-curve behavior, in which fracture resistance increases with crack growth. In such materials, the fracture source is a large grain, meaning that reliable materials should be obtainable by controlling grain size and distribution.[11,13]

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Given this, adding large β-nuclei to fine-grained β-ceramics may enable the fabrication of tough, highly reliable ceramics.

Microstructure development by adding nuclei remains poorly understood. The present study explores grain growth behavior in fine-grained and dense β-Si_3N_4 ceramics containing various amounts of β-nuclei in annealing at 1800°C to clarify the effect of nuclei addition. The presence of residual pores has been reported to inhibit grain growth.[16] In the present work, high-density materials were obtained by hot-pressing to exclude the effect of pores. This report describes the range of nuclei addition for developing a bimodal microstructure and its effect on the number and size of abnormally grown grains.

2 Experimental Procedure

Commercially available submicrometer β-Si_3N_4 powders (Denki Kagaku Kogyo Co., Tokyo, Japan, SN-P21FC grade; α-phase content: 6·7 wt%, average particle size: 0·56 μm) were separated into fine and coarse powders through centrifugal sedimentation. The particle size distribution was determined by laser diffraction (CILAS Granulometer 1064, CILAS Co., Orleans Cedex, France). Fine powder with coarse powder as nuclei was mixed with 5 wt% Y_2O_3 (Shin-Etsu Chemical Co., Tokyo, Japan, 99·9% pure) and 2 wt% MgO (Wako Chemical Co., Osaka, Japan, high-purity grade) in *n*-hexane using a silicon nitride ball mill. Nuclei in the amounts of 0, 0·1, 0·3, 1, 3, 10, and 30 wt% were added to Si_3N_4.

The powder mixture was then hot-pressed at 20 MPa in a N_2 atmosphere. The temperature was raised at a rate of 30°C/min to 1700 or 1750°C and cooled immediately. The relative densities of hot-pressed materials were determined from the size and weight.

The grain-growth behavior of the hot-pressed materials was investigated by annealing at 1800°C for 1 h in 1 MPa of N_2. Annealed materials were cut, polished, and plasma-etched by CF_4 containing 7·8% O_2. Microstructures were observed using scanning electron microscopy (SEM). Grain diameters (d) and apparent lengths (L) of two-dimensionally exposed grains were evaluated using an image analyzer (Luzex III, Nireco Co., Tokyo, Japan).[17] The diameter and length of each grain were determined from the shortest and the longest diagonal. The grain size distribution was evaluated by plotting fractional area against grain diameter. Plots represented the boundary value of the matrix and abnormally grown grains in bimodal microstructures, enabling us to determine the volume fraction of the matrix and large grains. The average aspect ratio was cited as the mean value of the 10% highest observed apparent aspect ratio (L/d), and the average grain diameters and aspect ratios of both the matrix and abnormally grown grains were determined. The number of evaluated matrix grains was 1000 to 2000 and the number of evaluated abnormally grown grains 50 to 500.

3 Results and Discussion

SEM micrographs showed the average particle size of the fine powder to be about 0·2 μm and the size distribution to be very narrow because of the elimination of large particles (>0·5 μm) (Fig. 1 and Table 1). The average particle size of the coarse powder is about 0·8 μm, which is about four times larger than that of the fine powder. Although the particle-size distribution of coarse powder obtained using the particle-size analyzer is broad, it is relatively uniform insofar as can be seen in SEM micrographs, but fine particles have not been completely eliminated.

In the hot-pressing of fine powder without nuclei, a maximum of 1700°C is high enough to produce high-density material (>97% relative density), which is about 100°C lower than that for original submicrometer powder,[9] and the densifi-

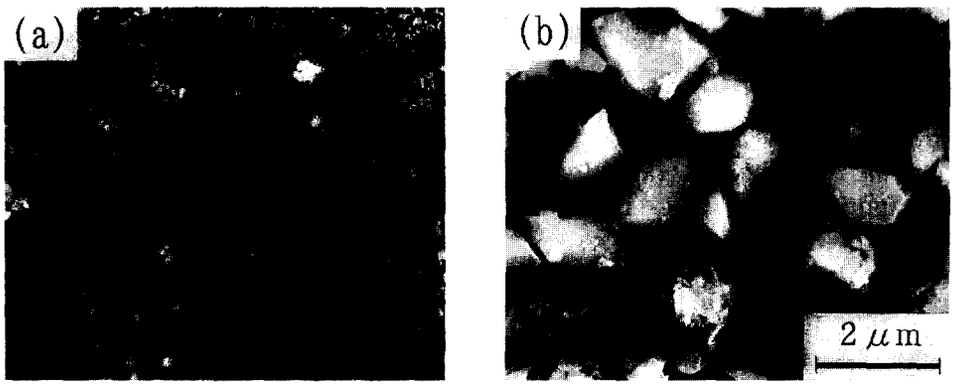

Fig. 1. SEM micrographs of (a) fine powder and (b) coarse powder (nuclei).

Table 1. Characteristics of starting powders

Powder	*Fine*	*Coarse*
Particle size (μm)		
10%	< 0·10	0·19
50%	0·20	0·83
90%	0·46	2·22
Specific surface area (m^2/g)	26·0	7·2

cation behaviors of fine powders with 0·1–10 wt% nuclei were similar to that of fine powder without nuclei (Fig. 2). Fine powder with 30 wt% nuclei showed different densification behavior, and a maximum hot-pressing temperature of about 50°C higher than that of fine powder without nuclei was needed to obtain high-density material. In the present work, we used a maximum hot-pressing temperature of 1700°C for 0–10 wt% and 1750°C for 30 wt% nuclei addition.

The microstructure of the hot-pressed material without nuclei is very fine and uniform. The average grain diameter is 0·18 μm and grains are spherical.[12] Grain elongation was observed in the annealed material, but the rate of diameter increase was very small. The grain diameter averaged 0·30 μm after heating at 1800°C for 1 h. The stable microstructure of this material was further shown by little grain growth even after annealing for 4 h (average grain diameter: 0·33 μm).[12]

The growth kinetics of β-Si_3N_4 grains in silicon nitride ceramics containing a liquid phase have been reported by a few authors,[17–19] who demonstrated that grain growth followed the empirical grain growth law, $D^n - D_0^n = Kt$, where D is the grain size, D_0 is the grain size at time zero, K is the rate constant, t is time, and n is the growth exponent. Hwang[18] and Mitomo *et al.*[17] reported $n = 3$ in the direction of both length and width. Lai *et al.*[19] reported $n = 3$ for length and $n = 5$ for

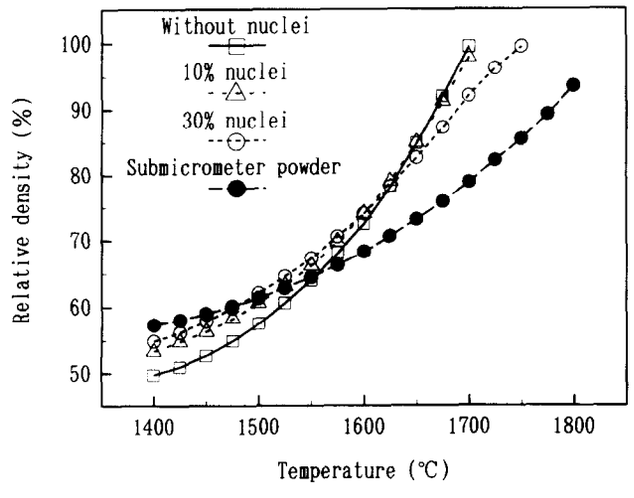

Fig. 2. Densification behaviors of fine powder without and with nuclei compared to that of submicron powder.

width. Regarding the stability of this material, at an early stage of annealing, faceted hexagonal rod-like grains may be formed, reflecting the crystalline structure. In subsequent stages of annealing, the grain growth driving force is thought to be very small because the interfacial energy between faceted grains and a liquid phase may be very small and grain-size distribution very narrow. It has been determined theoretically that the narrow grain size distribution caused normal grain growth in a steady state.[20,21]

In annealing at 1800°C for 1 h, a bimodal microstructure having abnormally grown grains in fine matrix grains developed in materials with 0·1–10 wt% nuclei (Figs 3 and 4). Since the grain-size difference between nuclei and matrix grains is large, the grain growth driving force for nuclei may be high, causing nuclei to grow selectively.[20] Interestingly, the effect of nuclei addition to the very fine, stable matrix in the microstructure occurs even with only 0·1 wt% addition, and nuclei seem to have no influence on the grain growth behavior of matrix grains as seen from particle-size distributions.

The unimodal microstructure developed with 30 wt% nuclei addition is similar to material made from commercial submicrometer powder,[9] presumably due to nuclei interaction.

We evaluated the bimodal microstructure by determining the average diameter and aspect ratio of matrix grains and abnormally grown grains using image analysis. The critical diameter for the definition of matrix and abnormally grown grains is about 0·8 μm (Fig. 4). All grains in material with 30 wt% nuclei are regarded as abnormally grown grains due to the unimodal microstructure. The mean diameters and aspect ratios of matrix grains are independent of the amount of nuclei and equal to that of material without nuclei (Figs 5 and 6). Quantitatively, nuclei seem to have no influence on the grain growth behavior of matrix grains. Similarly, the mean diameters of abnormally grown grains are fixed up to a 10 wt% nuclei addition, but a decrease in diameter is observed with 30 wt% addition. In contrast, the mean aspect ratios of abnormally grown grains are also nearly constant and larger than those of matrix grains up to 3 wt% addition. The aspect ratio decreases with higher addition. In the material with 10 wt% nuclei, the driving force for width is unchanged, but that for length direction decreases due to contact among abnormally grown grains, reflecting the elongated shape of these grains. In the material with 30 wt% nuclei, the nuclei driving force in both length and width decreases markedly because distances among abnormally grown grains are very short.

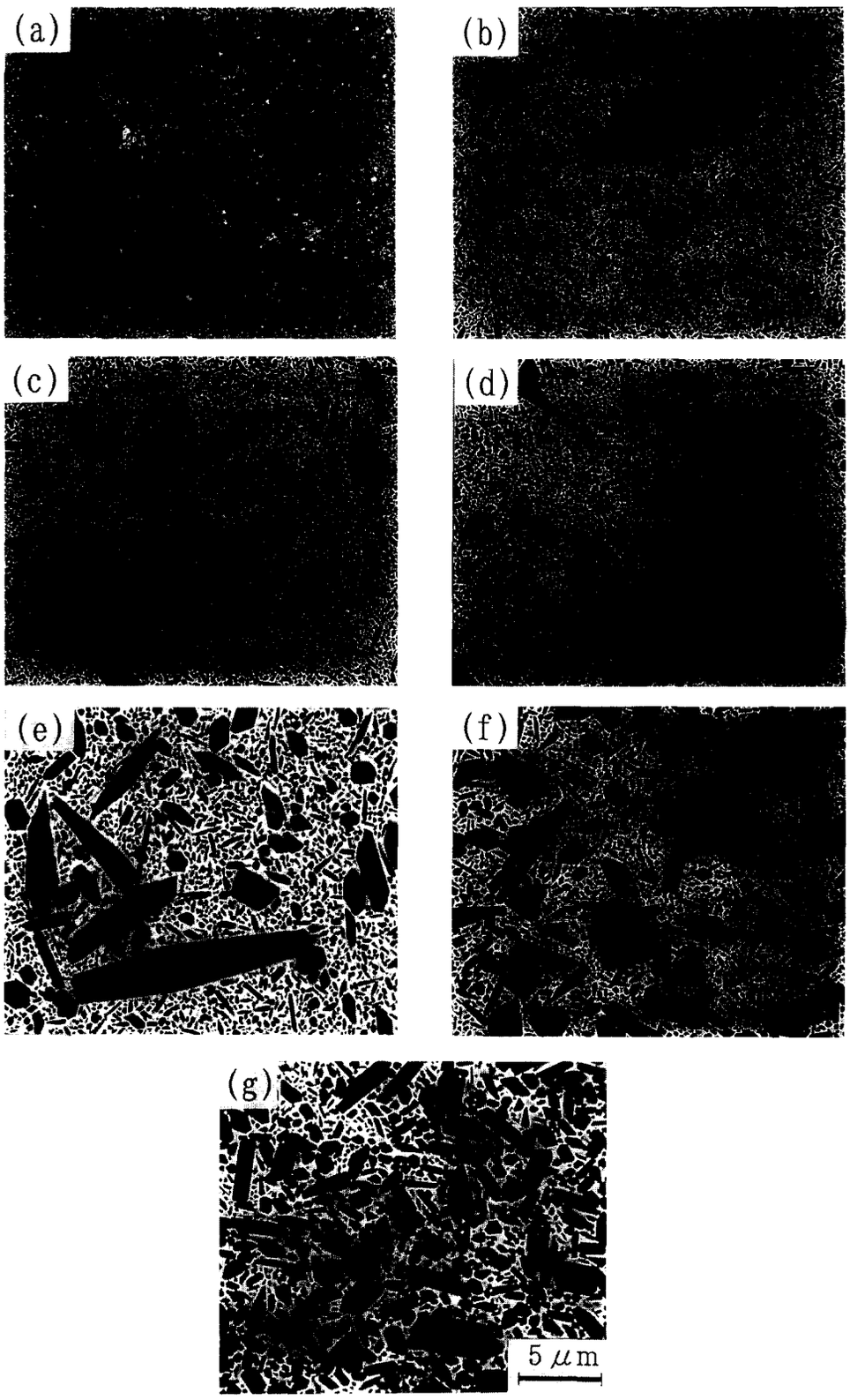

Fig. 3. SEM micrographs after heat treatment at 1800°C of materials containing (a) 0%, (b) 0·1%, (c) 0·3%, (d) 1%, (e) 3%, (f) 10%, and (g) 30% nuclei.

To confirm the effect of nuclei on grain growth, we plotted the number of abnormally grown grains per unit area (1 mm^2) against the amount of nuclei (Fig. 7) using image analysis. We found that the number of abnormally grown grains is proportional to the amount of nuclei except for 30 wt% addition, in which all grains are regarded as abnormally grown grains due to the unimodal microstructure. This result indicates that only additive coarse grains operate as nuclei for abnormal grain growth.

The effect of abnormally grown grains on toughening can be analyzed in terms of the volume fraction of abnormally grown grains as well as size and shape.[2] The volume fraction of abnormally grown grains reportedly corresponds to the

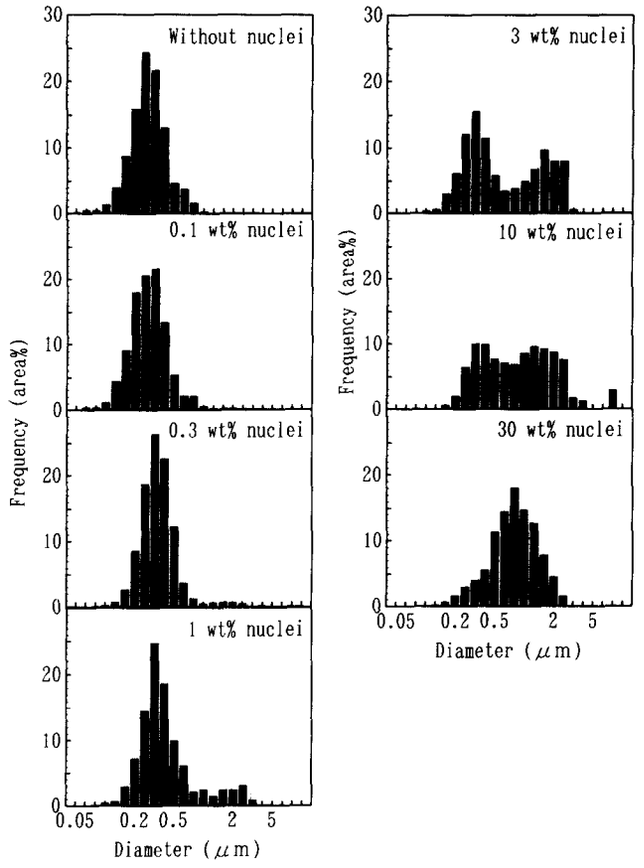

Fig. 4. Grain-size distributions after heat treatment at 1800°C.

area fraction obtained from the two-dimensional cross-section area.[22] The area fraction of abnormally grown grains is then plotted against the amount of nuclei (Fig. 8). The area fraction of abnormally grown grains increases proportionally with the amount of nuclei at 0·1–3 wt% nuclei addition, but the plot of 10 wt% nuclei addition differs from the correlation. This result is consistent with the change of the mean diameter and aspect ratio of abnormally grown grains with the amount of nuclei (Figs 5 and 6).

Dressler *et al.*[23] explained grain growth behavior during α-Si_3N_4 powder sintering using a model based on the relationship between the equilibrium concentrations of α- and β-particles in solvent and grain size. The α-phase concentration is higher than that of the β-phase and decreases with increasing grain size. The smaller particles dissolve in the liquid phase and precipitate on nuclei, which causes both α/β-transformation and grain growth. This model was derived by assuming particles to be spherical, and shows that the concentration gradient in the liquid phase was induced by the difference in grain size and crystal phase. The model explains the effect of α/β-transformation and nuclei addition on grain growth.

Yet another important grain growth driving force, however, is induced by the difference in the interfacial energy between crystallographic planes.

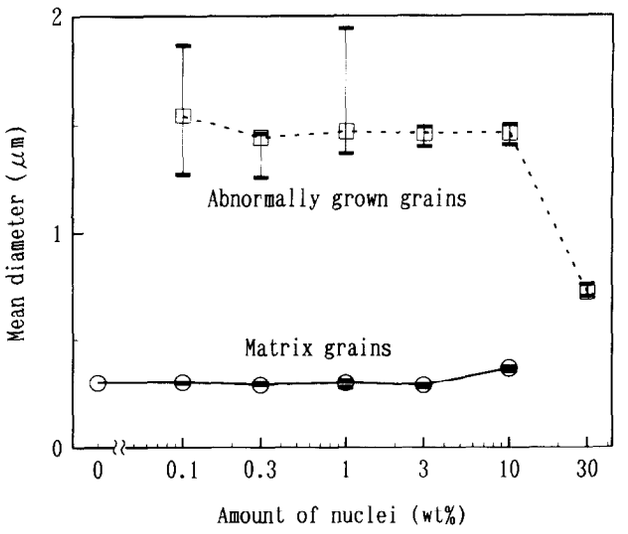

Fig. 5. Mean diameter of matrix and large grains as a function of nuclei amounts.

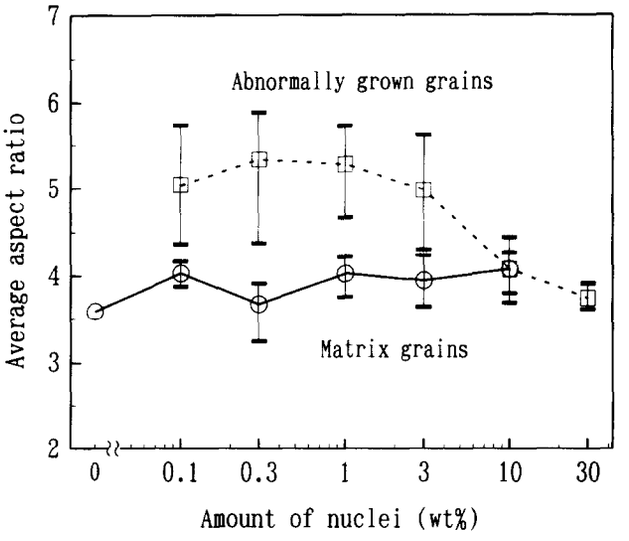

Fig. 6. Aspect ratios of matrix and large grains as a function of nuclei amounts.

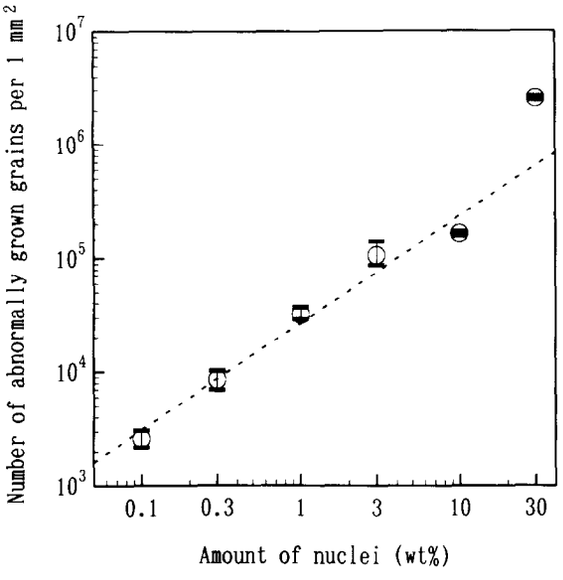

Fig. 7. The number of large grains as a function of nuclei amounts.

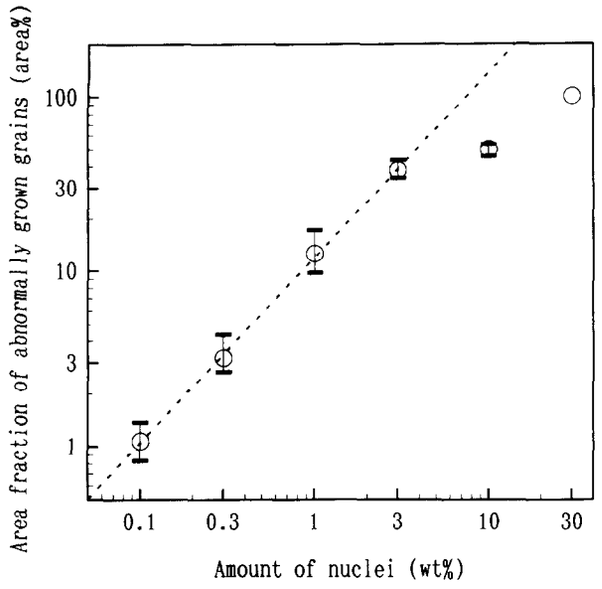

Fig. 8. The area fraction of large grains as a function of nuclei amounts.

Si_3N_4 grains grow isothermally in a preferential direction, i.e. [001], because of the anisotropy of interfacial energy, through which hexagonal rod-like grains develop. The solubility of faceted grains in the liquid phase must be lower, therefore, than that of spherical grains. We can modify the above model by considering the effect of interfacial energy (Fig. 9) on the intrinsic nature of β-Si_3N_4 grain growth.

The difference in the solubility of particles in the liquid phase, ΔC, corresponding to the grain-growth driving force can be expressed as

$$\Delta C = \Delta C_r + \Delta C_p + \Delta C_i \qquad (1)$$

where ΔC_r is the difference in solubility based on particle size (the solubility of a smaller spherical grain is higher than that of a larger one of the same phase), ΔC_p, crystal phase (the solubility of a spherical α-grain is higher than a β-grain of the same size and shape) and ΔC_i, interfacial energy (the solubility of a spherical grain is higher than that of a faceted one of the same phase and volume). This modified model explains the grain growth behavior in previous and present work. The microstructure of low-temperature hot-pressed material from fine β-powder is composed of uniform, fine, and spherical grains (average grain diameter, d: 0·18 μm; average aspect ratio, $R95$: 1·4). Annealing this material at 1800°C for 0·5 h, increases d and $R95$ (d: 0·29 μm, $R95$: 3·5). After prolonged annealing at 1800°C for 4 h, changes of d and $R95$ were very small (d: 0·35 μm, $R95$: 3·7).[12] After annealing for 0·5 h, grains tended to facet. After prolonged annealing, grain growth was slight and the faceted shape (aspect ratio) unchanged. The aspect ratio of grains could be related to the anisotropy of interfacial energy. In this case, it is assumed that grains with an aspect ratio of about 4 are most stable energy-wise and have the lowest equilibrium concentration. The equilibrium concentration of grains with higher aspect ratios must be higher (Fig. 9). In the initial stage, grain shape change may be caused by the driving force based on ΔC_r and ΔC_i. Once a microstructure composed of the most stable faceted grains develops, only ΔC_r contributes to grain growth, but the effect of ΔC_r is small, reflecting the narrow size distribution of the starting powder, i.e. $\Delta C_i > \Delta C_r$. Thus, the microstructure composed of uniform and faceted grains was very stable after prolonged annealing.[24]

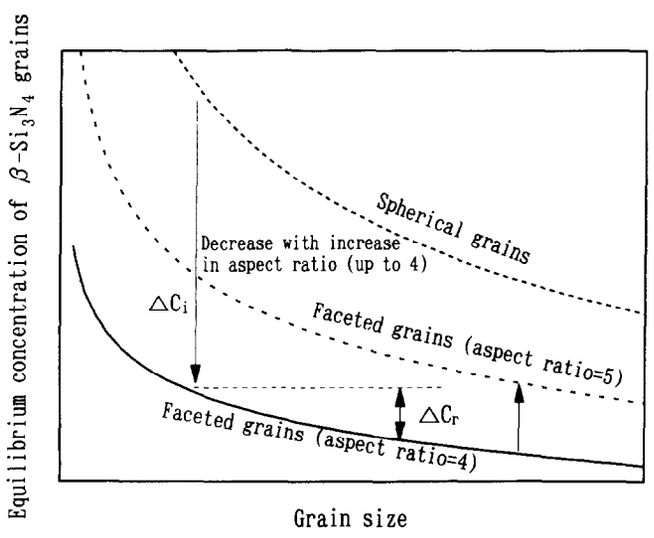

Fig. 9. Dependence of equilibrium concentrations of spherical and faceted β-grains on grain size.

A difference in solubility exceeding a critical value, ΔC_{crit}, is thought to cause abnormal grain growth because the rapid dissolution of highly soluble grains results in a supersaturated liquid phase.[25,26] Grain-growth behavior can therefore be divided into two types:

$\Delta C > \Delta C_{crit}$: abnormal grain growth

$\Delta C \leq \Delta C_{crit}$: normal grain growth

Bimodal microstructures develop in α-Si_3N_4 powder sintering because abnormal grains grow due to local supersaturation caused by the contribution of ΔC_p (eqn (1)). Since we cannot control the position of supersaturation, it is not possible to control abnormal grain growth and resulting bimodal microstructures during α-powder sintering. The present work showed that large β-nuclei added to fine β-powder are supersaturated by a liquid phase with matrix grains. In other words, abnormally grown grains originate only from nuclei, which is supported by the fact that the number of abnormally grown grains corresponds to the amount of nuclei (Fig. 7). As mentioned above,

the hexagonal prismatic shape of β-grains is more stable energy-wise, meaning that the liquid phase in contact with the basal plane has higher supersaturation, which is why abnormally grown grains have higher aspect ratios than equilibrium values (Fig. 6). When α-Si_3N_4 powders were used, the rather higher supersaturation caused by the contribution of ΔC_p resulted in a rather higher aspect ratio.

To explain microstructure development in this work, we studied the relationship between the abnormal grain growth driving force and the amount of nuclei (Fig. 10). Each nucleus has a supersaturated effective space around a grain, in which smaller grains transport to nuclei through the liquid phase. The abnormal grain growth driving force may depend on the situation of effective space. In a small amount of nuclei (less than 3 wt%), each nucleus had an independent effective space due to the long distance from each other. Therefore, all abnormally grown grains from nuclei have the same size and shape. In this work, if only one nucleus exists in the matrix, one abnormally grown grain appears. This idea is supported by the fact that a bimodal microstructure developed with only 0·1 wt% nuclei addition and the size of each abnormally grown grain is unrelated to the amount of nuclei in 0·1–3 wt% nuclei addition. This shows that materials without nuclei addition have uniform microstructures and no detected nuclei. This uniform microstructure has not been prepared from α-Si_3N_4 powder or commercial β-Si_3N_4. In 10 wt% nuclei addition, individual effective spaces begin to come in. The diffusing materials in overlapped effective spaces are shared by each nucleus, decreasing the grain growth driving force due to decreased supersaturation. When the amount of nuclei increases further (30 wt%), the interaction of each nucleus increases, resulting in the transition from abnormal to normal grain growth. It leads to the unimodal microstructure, which is nearly consistent with the microstructure obtained from original β-powder with a broad grain size distribution,[9] i.e. there are many nuclei in the original β-powder. Matrix grains isolated from the effective space of abnormal grain growth, however, are in equilibrium, leading to normal grain growth.

Two limits exist in nuclei addition for bimodal microstructure development: a lower limit at about 0·1 wt% nuclei addition and an upper limit at about 10 wt% nuclei addition. The sizes and shapes of abnormally grown grains were nearly constant at 0·1–3 wt% nuclei addition. The effect of nuclei appeared with only 0·1 wt% nuclei addition using fine, uniform β-starting powder as a matrix. Unimodal microstructures developed below

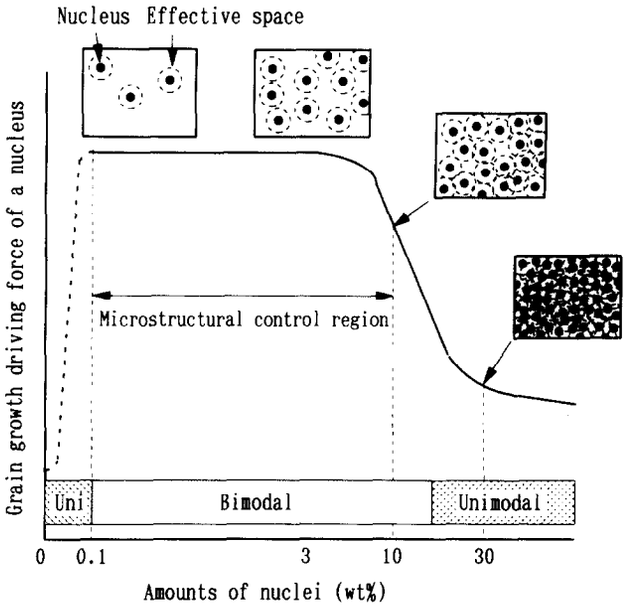

Fig. 10. Variations in grain-growth driving force based on the amount of nuclei addition.

and above these limits. The present study showed that it is possible to control the bimodal microstructure by adding 0·1–10 wt% nuclei to a homogeneous, fine matrix. The region is related to the distance among nuclei, i.e. the effective space of the grain-growth driving force for a nucleus. Further work will be needed to clarify the relationship between the controlled microstructure and mechanical properties such as fracture toughness, strength, and Weibull modulus.

4 Conclusion

The grain growth behavior of fine-grained β-Si_3N_4 ceramics with varying amounts of nuclei (0–30 wt%) was investigated in annealing at 1800°C for 1 h. Fine-grained β-Si_3N_4 ceramics without nuclei had a homogeneous, stable microstructure and showed no abnormal grain growth. When 0·1–10 wt% nuclei were introduced in fine-grained β-Si_3N_4 ceramics, they grew abnormally, consuming neighboring fine grains which resulted in the development of a bimodal microstructure. A unimodal microstructure developed without nuclei addition or with 30 wt% nuclei addition. The difference in microstructural development is explained in terms of effective space around nuclei.

Acknowledgments

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References

1. Huebner, G. & Knoch, H., Mechanical properties of hot-pressed silicon nitride with different grain structures. *J. Am. Ceram. Soc.*, **62** (1979) 29–32.
2. Becher, P. F., Microstructural design of toughened ceramics. *J. Am. Ceram. Soc.*, **74** (1991) 255–269.
3. Wotting, G., Kanka, B. & Ziegler, G., Microstructural development, microstructural characterization and relation to mechanical properties of dense silicon nitride. In *Non-oxide Technical and Engineering Ceramics*, ed. S. Hampshire. Elsevier Applied Science, London, 1986, pp. 83–96.
4. Sajglik, P., Dusza, J. & Hoffmann, M. J., Relationship between microstructure, toughening mechanisms, and fracture toughness of reinforced silicon nitride ceramics. *J. Am. Ceram. Soc.*, **78** (1995) 2619–2624.
5. Lee, D., Kang, S. L., Petzow, G. & Yoon, D. N., Effect of α to $\beta(\beta')$ phase transition on the sintering of silicon nitride ceramics. *J. Am. Ceram. Soc.*, **73** (1990) 767–769.
6. Shuttor, D. & Fishman, G. S., Densification and sintering kinetics in sintered silicon nitride. *J. Am. Ceram. Soc.*, **75** (1992) 1063–1067.
7. Wotting, G., Gugel, E., Schwier, G., Starck, H. C. & Lange, H., Processing for improved fracture toughness of dense silicon nitride. In *Ceramics Science IV, Ceramics Transactions, Vol. 22*, ed. S. Hirano, G. L. Messing & H. Hausner. Am. Ceram. Soc., Ohio, 1991, pp. 647–655.
8. Lange, F. F., Fracture toughness of Si_3N_4 as a function of the initial α-phase content. *J. Am. Ceram. Soc.*, **62** (1979) 428–430.
9. Hirotsuru, H., Mitomo, M. & Nishimura, T., Influence of phase transformation on densification behavior and grain growth of fine silicon nitride powder. *J. Ceram. Soc. Japan*, **104** (1996) 23–27.
10. Mitomo, M., Hirotsuru, H., Suematsu, H. & Nishimura, T., Fine-grained silicon nitride ceramics prepared from β-powder. *J. Am. Ceram. Soc.*, **78** (1995) 211–214.
11. Mitomo, M., Hirosaki, N. & Hirotsuru, H., Microstructural design and control of silicon nitride ceramics. *MRS Bull.*, **20** (1995) 19–22.
12. Mitomo, M., Nishimura, T. & Hirotsuru, H., Fabrication and grain growth behavior of fine-grained silicon nitride ceramics. *Eur. J. Solid State Inorg. Chem.*, **32** (1995) 693–700.
13. Hirosaki, N., Akimune, Y. & Mitomo, M., Effect of grain growth of β-silicon nitride on strength, Weibull modulus, and fracture toughness. *J. Am. Ceram. Soc.*, **76** (1993) 1892–1894.
14. Hirosaki, N., Akimune, Y. & Mitomo, M., Microstructure characterization of gas-pressure-sintered β-silicon nitride containing large β-silicon nitride seeds. *J. Am. Ceram. Soc.*, **77** (1994) 1093–1094.
15. Evans, A. G., Structural reliability: a processing-dependent phenomenon. *J. Am. Ceram. Soc.*, **65** (1982) 127–137.
16. Mitomo, M., Yang, N., Kishi, Y. & Bando, Y., Influence of powder characteristics on gas pressure sintering of Si_3N_4. *J. Mater. Sci.*, **23** (1988) 3413–3419.
17. Mitomo, M. & Uenosono, S., Microstructure development during gas-pressure sintering of α-silicon nitride. *J. Am. Ceram. Soc.*, **75** (1992) 103–108.
18. Hwang, C. J. & Tien, T. Y., Microstructural development in silicon nitride ceramics. *Materials Science Forum*, **47** (1988) 84–109.
19. Lai, K. R. & Tien, T. Y., Kinetics of β-Si_3N_4 grain growth in Si_3N_4 ceramics sintered under high nitrogen pressure. *J. Am. Ceram. Soc.*, **76** (1993) 91–96.
20. Hillert, M., On the theory of normal and abnormal grain growth. *Acta Metall.*, **13** (1965) 227–238.
21. Thompson, C. V., Frost, H. J. & Spaepen, F., The relative rates of secondary and normal grain growth. *Acta Metall.*, **35** (1987) 887–890.
22. Hirosaki, N., Akimune, Y. & Mitomo, M., Quantitative analysis of microstructure of self-reinforced silicon nitride ceramics. *J. Ceram. Soc. Japan*, **101** (1993) 1239–1243.
23. Dressler, W., Kleebe, H. J., Hoffmann, M. J., Ruhle, M. & Petzow, G., Model experiments concerning abnormal grain growth in silicon nitride. *J. Eur. Ceram. Soc.*, **16** (1996) 3–14.
24. Warren, R. & Waldron, M. B., Microstructural development during the liquid-phase sintering of cemented carbides. *Powder Metall.*, **15** (1972) 166–201.
25. Schreiner, M., Schmitt, Th., Lassner, E. & Lux, B., On the origins of discontinuous grain growth during liquid phase sintering of WC–Co cemented carbides. *Powder Metall. Int.*, **16** (1984) 180–183.
26. Hennings, D., Janssen, R. & Reynen, P., Control of liquid-phase-enhanced discontinuous grain growth in barium titanate. *J. Am. Ceram. Soc.*, **70** (1987) 23–27.