FULL PAPER

Anisotropic sintering shrinkage and microstructural evolution of *c*-axis-oriented Si₃N₄ ceramics

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High-thermal-conductivity Si₃N₄ ceramics are desired for substrates in SiC power devices. We successfully fabricated highly *c*-axis-oriented Si₃N₄ ceramic by casting in a rotating-magnetic field and then sintered using a conventional gas pressure. As a result, the *c*-axis orientation of Si₃N₄ grains effectively improves the thermal conductivity. The sintering behavior of *c*-axis-oriented Si₃N₄ ceramics was investigated. The linear shrinkage ratio in the *c*-axis-oriented direction was smaller than that in the direction normal to the *c*-axis-oriented direction. Fine *c*-axis-oriented structures resulted from the orientation of β-Si₃N₄ seeds during the casting because they played as templates controlling the grain growth of β-Si₃N₄ nuclei and inducing the anisotropic sintering shrinkage.

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1. Introduction

Silicon nitride (Si₃N₄) is a typical engineering ceramic because of its good mechanical properties such as high strength, hardness, toughness, and good chemical and thermal stabilities.^{1)–11)} Substrates with high thermal conductivities in the thickness direction are urgently needed for silicon carbide power devices.¹²⁾ Silicon nitride (Si₃N₄) ceramics are expected to be applied as substrates because they have better mechanical properties than conventional aluminum nitride ceramics. Si₃N₄ itself exhibits anisotropic thermal conductivity, i.e., the thermal conductivity of Si₃N₄ in the *c*-axis direction is higher than that in the *a*-axis direction,^{13),14)} which means that having the *c*-axis of Si₃N₄ as the thickness direction should be effective in making Si₃N₄ a high-thermal-conductivity substrate.

In previous works, *c*-axis-oriented Si₃N₄ ceramics were fabricated via moulding processes in which external fields were applied. Hirao et al. reported Si₃N₄ ceramics with anisotropic microstructures fabricated by tape-casting and hot-pressing processes.¹⁵⁾ Watari et al. also reported that crystal-oriented Si₃N₄ ceramics were fabricated using the tape-casting method, followed by hot isostatic pressing.¹⁶⁾ Because the shape of the β-Si₃N₄ seed particles is rod-like and they are easily oriented in the in-plane direction by shear stress in the tape-casting process, the *c*-axes of β-

Si₃N₄ grains cannot be oriented in the thickness direction of the substrate. *c*-axis-oriented Si₃N₄ ceramics were fabricated by applying stress fields and magnetic fields. In this process, the orientation of ceramic particles is not restricted by the moulding process and geometry of the component, which means that a substrate in which the *c*-axis of Si₃N₄ is oriented in the thickness direction is possibly obtained. Li et al. reported the first fabrication of *c*-axis-oriented Si₃N₄ ceramics using a magnetic field.¹⁷⁾ Zhu et al. reported the fabrication of *c*-axis-oriented Si₃N₄ ceramics using a rotating magnetic field.^{18),19)} In their work, 5 wt % β-Si₃N₄ whiskers were added to the powder mixture as seeds.¹⁸⁾ Fine near-equiaxed 5 wt % β-Si₃N₄ particles were also used.¹⁹⁾ These seeds were highly oriented using a rotating magnetic field of 12 T in green bodies. Because of sintering the green bodies, *c*-axis-oriented Si₃N₄ ceramics were successfully obtained. Particularly, the *c*-axis-oriented Si₃N₄ ceramics containing fine near-equiaxed particles exhibited very high thermal conductivities.¹⁹⁾ Recently, Takahashi et al. reported the fabrication of *c*-axis-oriented Si₃N₄ ceramics via a very low magnetic field orientation process using multilayered-graphene-coated β-Si₃N₄ seed particles prepared by mechanical treatment.²⁰⁾

The anisotropic sintering shrinkage behaviour has often been reported in *c*-axis-oriented Si₃N₄ ceramics.^{18),21),22)} Teshima et al. reported the anisotropic shrinkage of *c*-axis-oriented Si₃N₄ ceramics fabricated by extrusion moulding and gas pressure sintering.²¹⁾ In their report, the sintering

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shrinkage ratios were 21% in the extrusion direction and 7% in the radial direction. Zhu et al. also reported anisotropic sintering shrinkages 22% in the parallel and 7% in the normal directions relative to an applied rotating magnetic field.¹⁸⁾ Park et al. reported a model based on the anisotropic sintering shrinkage of Si₃N₄ containing oriented β -Si₃N₄ whiskers.²²⁾ In their report, the anisotropy of shrinkage became larger as the whiskers content increased. In these reports, only the property and microstructure of the final product were shown; the densification and microstructure evolution mechanism were not clarified. Densification of Si₃N₄ ceramics resulted from particle rearrangement, α - β phase transformation, and Ostwald ripening of β -Si₃N₄ grains.²³⁾ The grain growth of β -Si₃N₄ grains in the *c*-axis direction is faster than in the *a*-axis direction. As a result, elongated β -Si₃N₄ grains are developed during densification of Si₃N₄ ceramics. Therefore, a green body having oriented Si₃N₄ seeds should exhibit anisotropic shrinkage and microstructure development.

It has been reported that densification and grain growth progress anisotropically in crystal oriented ceramics.^{24)–27)} The anisotropic sintering shrinkage completely depends on the preferential direction of grain growth and the packing structure of green compact. Patwardhan et al. examined the anisotropic sintering shrinkage of roughly oriented aluminium oxide (Al₂O₃) ceramics fabricated using ellipsoidal particles by the doctor blade technique.²⁴⁾ Shui also examined the anisotropic sintering shrinkage of *c*-axis-oriented Al₂O₃ ceramics fabricated by applying a magnetic field.²⁵⁾ Tanaka et al. reported *c*-axis-oriented zinc oxide (ZnO) powder compacts prepared using a high magnetic field orientation process.²⁶⁾ Takahashi et al. examined the anisotropic sintering shrinkage and microstructural evolution of *c*-axis-oriented strontium barium niobate (SBN) powder compacts prepared by applying a high magnetic field.²⁷⁾ In these reports, the mechanisms of anisotropic sintering shrinkage and microstructural evolution differ depending on the material. Although the anisotropic sintering shrinkage and microstructural evolution during solid phase sintering have been reported above, details of the anisotropic sintering shrinkage and microstructural evolution of *c*-axis-oriented Si₃N₄ via liquid phase sintering and phase transformation have not been investigated. In this work, the anisotropy of sintering shrinkage and microstructure evolution of *c*-axis-oriented Si₃N₄ ceramics were investigated.

Green compacts with *c*-axis-oriented β -Si₃N₄ seeds were prepared by casting in a magnetic field at 10 T. Specimens for measuring the sintering shrinkage normal and parallel to the applied magnetic field were prepared by cutting out from the green compact after dewaxing.

2. Experimental procedures

β -Si₃N₄ (NP-500, Denka Co., Ltd., Japan) and α -Si₃N₄ powders (SN-E10, Ube Industries Ltd., Japan) were used as raw materials. **Figure 1** presents the morphology of β -Si₃N₄ seed particles observed using a scanning electron microscope (SEM, JSM-6390LV, JEOL, Japan). The aver-

Fig. 1. Morphologies of β -Si₃N₄ seed particles.

age particle size (d_{50}) measured by laser diffraction/scattering (SALD-7000, Shimadzu Co., Japan) was 0.6 μ m. The average particle size was also measured from image analysis using Fig. 1, and was the same as the d_{50} measured by the laser diffraction/scattering method. The average aspect ratio calculated from image analysis was 1.5. Sintering aids are needed to fabricate dense Si₃N₄ ceramics. Li et al. have been reported that Y₂O₃-HfO₂-SiO₂ system can improve not only enhancement of the densification of Si₃N₄ but also formation of cubic HfO₂ crystalline phases to reduce grain boundary glassy phase.²⁸⁾ Therefore, the Si₃N₄-Y₂O₃-HfO₂-SiO₂ system should be expected to achieve high thermal conductivity. Y₂O₃ (RU-P, Shin-etsu Chemical Co., Ltd., Japan), HfO₂ (HF001PB, Kojundo Chemical Laboratory Co., Ltd., Japan), and SiO₂ (SO-C2, Admatechs Co., Ltd., Japan) were added as sintering aids. The starting composition was fixed at β -Si₃N₄: α -Si₃N₄:Y₂O₃:HfO₂:SiO₂ = 10:82:2.5:5:0.5 by weight. These powders were mixed and dispersed by ultrasonic radiation with polyethyleneimine (M_w = 10000) dispersant in distilled water, with solid loading of 20 vol %. The slurry was loaded in a plastic mould 25 mm in diameter and placed in a rotating magnetic field at 10 T. After drying, a green compact was obtained, which was calcined at 500°C for 3 h in air to burn the polymer dispersant. The dewaxed green body was fired at 1700–1900°C for 5 min or 6 h in 0.9 MPa N₂.

Relative density was measured by the Archimedes method. Phases and crystal orientations of the Si₃N₄ ceramics were estimated by X-ray diffraction (XRD, Multiflex 2kW, Rigaku Co., Japan). The Lotgering factor (*L.F.*), as the orientation degree, was calculated from the XRD profiles by the following equation: $L.F. = (\rho - \rho_0) / (1 - \rho_0)$, where $\rho_0 = \Sigma I_0(00l) / \Sigma I_0(hkl)$ and $\rho = \Sigma I(00l) / \Sigma I(hkl)$, where I_0 and I are the diffraction peak intensities of non-oriented and oriented samples, respectively. The linear shrinkage ratio was evaluated from sample geometry. The plasma-etched surface was observed by SEM. A thin film sample for transmission electron microscopy observation was prepared by Ar ion milling and specimens were observed using a transmission electron microscope (TEM, JEOL-2100F, JEOL, Japan). The compositions of the specimens were measured by energy dispersive

X-ray spectrometry in scanning TEM (STEM-EDS). The β ratio was calculated by the Rietveld method using RIETAN-FP.²⁹⁾

3. Results and discussion

3.1 Density and sintering shrinkage

Table 1 lists the relative density and sintering shrinkages of Si_3N_4 ceramics prepared with and without a rotating magnetic field. The relative densities of Si_3N_4 ceramics prepared with and without a rotating magnetic field were almost the same: 99 and 96%, respectively, which were estimated using the true density calculated from the raw powder composition. The thermal conductivity in the c -axis orientation direction was $100 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (the non-oriented ceramics had $65 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). The anisotropic linear shrinkage ratio showed the same tendency as reported in previous studies; that is, the linear shrinkage ratio along the direction parallel to the rotational axis of the sample in the magnetic field was smaller than that in the direction normal to the rotational axis.

Figure 2 shows the densification and anisotropic sintering shrinkage behaviours of c -axis-oriented Si_3N_4 ceramics. The horizontal axis shows the sintering condition and the vertical axis shows the relative density and linear shrinkage ratio parallel and normal to the applied magnetic field. Increase in the firing temperature and soaking time increased the relative densities of the sintered bodies. Although the relative density obtained with a rotating magnetic field was the same as that without a magnetic field, the sintering shrinkage ratio strongly depended on the direction of the applied magnetic field, i.e., the linear shrinkage ratio normal to the rotational axis of the sample in the magnetic field was larger than that parallel to the rotational axis of the sample in the magnetic field. This anisotropic sintering shrinkage increased markedly with an increasing sintering temperature above 1800°C . The linear shrinkage ratios in the directions parallel and normal to the rotational axis of the sample in the magnetic field were 9 and 16%, respectively, at 1900°C . Finally, the linear shrinkage ratio in the direction parallel to the rotational axis of the sample in the magnetic field decreased to 3%, which means that the sample expanded in the direction normal to the applied magnetic field at 1900°C . Although the anisotropic shrinkage ratios of Si_3N_4 ceramic in final products have been reported previously,^{18),21),22)} this strange anisotropic sintering shrinkage behaviour was discovered in the present study. The reason for the anisotropic sintering shrinkage should be related to the microstructural evolution of Si_3N_4 ceramic.

Table 1. The relative density, linear shrinkage ratio and thermal conductivity of Si_3N_4 ceramics sintered at 1900°C for 6 h

Magnetic field /tesla	Relative density /%	Linear shrinkage ratio /%	κ / $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
0	99	19	65
10	96	Normal direction 22 Parallel direction 3	100

3.2 Phases present

Figures 3 and 4 show XRD patterns of the green compact and sintered bodies prepared with and without a rotating magnetic field (10 T). The plane parallel to the magnetic field was measured as shown in Fig. 4. A strong (002) peak of $\beta\text{-Si}_3\text{N}_4$ was observed in the pattern of the green compact prepared with a rotating magnetic field, but not in that of the green compact prepared without the magnetic field. This result indicates that the c -axes of the $\beta\text{-Si}_3\text{N}_4$ seed particles were oriented normal to the direction of the applied magnetic field. After firing at 1900°C for 6 h, the peaks of $\alpha\text{-Si}_3\text{N}_4$ disappeared and the (002) peak of $\beta\text{-Si}_3\text{N}_4$ increased. The orientation degree calculated using the Lotgering method was 0.70 after densification. It was confirmed that $\alpha\text{-}\beta$ phase transformation and orientation of $\beta\text{-Si}_3\text{N}_4$ occurred in association with densification.

Figure 5 shows the β ratio changes of Si_3N_4 ceramics prepared with and without the magnetic field during sintering. The β ratio change showed the almost same trend between the non-oriented and c -axis-oriented Si_3N_4 ceramics. As shown in Fig. 3, the relative density was also the same, independent of orientation. From these results, the driving force for sintering due to the $\alpha\text{-}\beta$ phase transformation was unchanged; that is, the $\alpha\text{-}\beta$ phase transition is not the principal factor causing the anisotropic sintering shrinkage behaviour.

Fig. 2. Densification and anisotropic sintering shrinkage behavior of c -axis oriented Si_3N_4 ceramics ($\triangle$: c -axis oriented, $\circ$: non-oriented Si_3N_4 ceramics).

Fig. 3. XRD patterns of non-oriented Si₃N₄ ceramics sintered at (a) 1700°C for 5 min (b) 1800°C for 5 min (c) 1900°C for 5 min (d) 1900°C for 6 h.

Fig. 4. XRD patterns of *c*-axis oriented Si₃N₄ ceramics sintered at (a) 1700°C for 5 min (b) 1800°C for 5 min (c) 1900°C for 5 min (d) 1900°C for 6 h.

3.3 Microstructural evolution

Figures 6(d) and 7(d) show the microstructures of sintered bodies prepared with and without the rotating magnetic field and which were fired at 1900°C for 6 h. The observed plane was parallel to the rotational axis of the sample in the magnetic field. In the sintered body prepared with the magnetic field, the *c*-axes of the prismatic Si₃N₄

Fig. 5. $\beta/(\alpha + \beta)$ change during sintering (Δ : *c*-axis oriented, $\circ$: non-oriented Si₃N₄ ceramics).

grains were dominantly along the direction normal to the applied magnetic field. In contrast, a non-oriented structure was observed in the sintered body prepared without magnetic field. These results are consistent with previous reports.^{15)–20)}

The densification of Si₃N₄ ceramics is related to the α - β phase transformation and the development of rod-like β -Si₃N₄ grains. Figures 4 and 7 present the XRD patterns and microstructures of *c*-axis-oriented Si₃N₄ ceramics fired at various conditions. As observed in Fig. 4, an α - β phase transformation occurred and the intensities of the (002) and (101) peaks increased with firing temperature and soaking time. During the initial sintering stage [Figs. 4(a) and 7(a)], the oriented β -Si₃N₄ seed particles grew with the α - β phase transformation via liquid phase sintering. Here, although the microstructures of the non-oriented and *c*-axis-oriented bodies were completely different [shown in Figs. 6(a) and 7(a)], their relative densities were the same at 66%. **Figure 8** shows the grain size distributions of ceramics fired at 1700°C for 5 min, as shown in Figs. 6(a) and 7(a). The *y*-axis is the quantity of grain per unit area and the *x*-axis is the equivalent circle diameter. The grain size distribution in Fig. 8 is almost the same and it can be considered that the β -Si₃N₄ seeds grew individually. This result means that the effect of seeds on the formation of microstructure was the same during the initial stage of sintering in both the non-oriented and *c*-axis-oriented bodies. That is, in the *c*-axis-oriented Si₃N₄ ceramics, β -Si₃N₄ nuclei produced from the α - β phase transformation contributed to form the highly oriented microstructure via their orientation. In Figs. 4(b) and 7(b), the α - β phase transformation was completed and the β -Si₃N₄ nuclei produced from the α - β phase transformation grew between elongated β -Si₃N₄ grains. In particular, the intensity of the (101) plane increased. In Figs. 4(c) and 7(c), smaller β -Si₃N₄ grains with the same direction as the larger elongated β -Si₃N₄ grains grew preferentially, and the intensity of the (002) plane increased. Finally, the (002) plane peak remained [as shown in Fig. 4(d)], the oriented β -Si₃N₄

Fig. 6. Microstructures of non-oriented Si_3N_4 ceramics sintered at (a) 1700°C for 5 min (b) 1800°C for 5 min (c) 1900°C for 5 min (d) 1900°C for 6 h.

Fig. 7. Microstructures of *c*-axis-oriented Si_3N_4 ceramics sintered at (a) 1700°C for 5 min (b) 1800°C for 5 min (c) 1900°C for 5 min (d) 1900°C for 6 h.

grains grew markedly, and the oriented structure was completely formed, as shown in Fig. 7(d).

The microstructures were evaluated in more detail using TEM. **Figure 9** presents the high-angle annular dark-field scanning transmission electron microscopy (HAADF-

STEM) images of non-oriented and *c*-axis-oriented Si_3N_4 ceramics. The observed plane was normal to the rotational axis of the sample in the magnetic field. The bright area is an intergranular glassy phase consisting of SiO_2 and sintering aids. Comparing the HAADF-STEM images, the

thicknesses of the intergranular glassy phases were clearly different. The *c*-axis-oriented Si₃N₄ ceramics had very thin glassy phases between hexagonal grains. In contrast, the non-oriented Si₃N₄ ceramics had thick glassy phases around the grains. The difference in thickness of the glassy phase might result from the liquid phase being squeezed out from between the *c*-axis-oriented β -Si₃N₄ grains. On the other hand, if β -Si₃N₄ grains grow randomly, the glassy phase seems thicker because the space between β -Si₃N₄ grains was only infilled by the liquid phase. **Table 2** presents an analysis of the orientation direction of β -Si₃N₄ grains using Fig. 9(a). The degree of the tilt angle φ from the basis [000] axis was calculated using the following equations.³⁰⁾

$$\varphi = \cos^{-1}(\cos x \cdot \cos y) \quad (1)$$

$$\theta = \tan^{-1}\left(\frac{\tan y}{\sin x}\right) \quad (2)$$

φ of most of the oriented β -Si₃N₄ grains was small. High-integrity adjacent grains had similar and smaller φ (for example, the φ values between the β -Si₃N₄ grains Nos. 1 and 3 were 2.19 and 2.26, respectively). The grain boundary was round in such high-integrity β -Si₃N₄ grains.

Fig. 8. Grain size distribution of ceramics sintered at 1700°C for 5 min.

In contrast, the grain boundary was straight for low-integrity β -Si₃N₄ grains (for example, the φ values between the β -Si₃N₄ grains Nos. 5 and 10 were 2.41 and 13.13, respectively).

3.4 Mechanism of anisotropic sintering shrinkage and microstructure evolution

In oriented Al₂O₃ ceramics, the linear shrinkage ratio along the direction with higher necking among particles per unit length in the powder compact was larger during the initial stage of sintering than that along the other direction. In addition, during the middle and final stages of sintering, the difference in shrinkage decreased gradually with densification and grain growth.^{24),25)} This result indicates that the anisotropic sintering shrinkage of oriented Al₂O₃ ceramic depends on the packing structure of the powder compact. The anisotropic sintering shrinkage behaviour of Al₂O₃ ceramic is not the same as that of *c*-axis-oriented Si₃N₄ ceramics. Shrinkage occurred regardless of direction during the initial stage of sintering in the case of *c*-axis-oriented Si₃N₄ ceramics, which means that the packing structure of the powder compact is not dominant. Densification and grain growth occurred isotropically during the initial stage of sintering in *c*-axis-oriented ZnO ceramics. Anisotropic shrinkage and grain growth occurred simultaneously during the middle and final stages of sintering. The linear shrinkage ratio along

Table 2. Evaluation of orientation of β -Si₃N₄ grains in (00*l*) plane of *c*-axis oriented Si₃N₄ ceramics

Grain No.	<i>x</i>	<i>y</i>	Tilt angle $\varphi/^\circ$	Tilt direction $\theta/^\circ$
1	1.5	1.6	2.19	46.9
2	1.4	4	4.24	70.7
3	-2.2	0.5	2.26	167.2
4	9.2	-2.5	9.53	-15.3
5	1.6	-1.8	2.41	-48.4
6	-4.6	2.9	5.44	147.7
7	0.1	9.5	9.50	89.4
8	-5.7	-3.4	6.63	-149.1
9	-6.4	2.5	6.87	158.6
10	9	-9.6	13.13	-47.2

Fig. 9. HAADF-STEM images of (a) (00*l*) plane of *c*-axis oriented and (b) non-oriented Si₃N₄ ceramics.

Fig. 10. Schematic illustrations of formation mechanism for *c*-axis-oriented Si_3N_4 ceramic.

the direction of grain growth was larger than that normal to its direction.²⁶⁾ That is, the grain growth of ZnO is strongly related to anisotropic sintering. For SBN, neck formation (densification) and grain growth along the *c*-axis direction dominated the anisotropic sintering shrinkage. The linear shrinkage ratios of the *c*-axis direction during initial and final sintering were larger than those of the *a*-axis direction.²⁷⁾ It was the same as the behaviour of Si_3N_4 : the anisotropy of sintering shrinkage in ZnO and SBN increased markedly in the final stage. However, in the case of Si_3N_4 , the mechanism of anisotropic sintering shrinkage and microstructure development should be completely different from the above cases because densification and grain growth occur via liquid phase reaction.

This anisotropic sintering behaviour and formation process of the *c*-axis-oriented structure in Si_3N_4 ceramics can be considered as in Fig. 10. Initially, the $\beta\text{-Si}_3\text{N}_4$ seed particles grew markedly along the direction normal to the applied magnetic field. Therefore, sintering shrinkage was limited by the remarkably elongated grain growth of $\beta\text{-Si}_3\text{N}_4$; shrinkage along the direction parallel to the applied magnetic field (ΔL_a) was larger than that along the normal direction (ΔL_c). During hot pressing of Si_3N_4 ceramics, it has been reported that elongated grain growth occurred in the direction normal to the applied stress.¹⁶⁾ In this work, although external stress was not applied during sintering, internal stress should result from anisotropic grain growth of the $\beta\text{-Si}_3\text{N}_4$ seed particles, which means a higher sintering stress along the parallel direction than the normal direction. The anisotropic sintering stress from the seeds and nuclei formed by the $\alpha\text{-}\beta$ phase transformation enhanced the grain growth of $\beta\text{-Si}_3\text{N}_4$ in the direction parallel to the applied magnetic field. Therefore, the intensities of the (101) and (200) peaks increased during the middle stage of sintering. The reason for the higher (101) peak fired at 1800°C for 5 min [Fig. 4(b)] is that the grain growth rate of $\beta\text{-Si}_3\text{N}_4$ nuclei was higher than that of $\beta\text{-Si}_3\text{N}_4$ seed particles.

In the final stage, grains oriented in the (101) direction disappeared because of the anisotropic sintering stress and the strongly oriented microstructure of the elongated $\beta\text{-Si}_3\text{N}_4$ grains developed. This anisotropic sintering stress probably resulted in squeezing liquid phase from grain boundaries, as shown in Fig. 9. It is apparent that the dominant factor was a small quantity of oriented $\beta\text{-Si}_3\text{N}_4$ seed particles, which acted as a template and caused the anisotropic sintering stress with grain growth, leading to the orientation of $\beta\text{-Si}_3\text{N}_4$ grains originating from the nuclei by $\alpha\text{-}\beta$ phase transformation. This phenomenon appears as the “self-organization” of *c*-axis-oriented Si_3N_4 ceramics.

4. Conclusion

Highly *c*-axis-oriented Si_3N_4 ceramics were fabricated using magnetic field orientation and gas pressure sintering. Although the densification behaviours were almost identical, the sintering shrinkage behaviours differed depending on the *c*-axis orientation; the linear sintering shrinkage ratio in the *c*-axis direction was smaller than that in the direction normal to the *c*-axis. The $\alpha\text{-}\beta$ phase transformation occurred similarly without relation to the *c*-axis orientation. Fine *c*-axis-oriented structures resulted from the orientation of $\beta\text{-Si}_3\text{N}_4$ seeds during the casting because they played as templates controlling the grain growth of $\beta\text{-Si}_3\text{N}_4$ nuclei and inducing the anisotropic sintering shrinkage.

Reference

- 1) G. C. Deeley, J. M. Herbert and N. C. Moore, *Powder Metall.*, **4**, 145–151 (1961).
- 2) K. Komeya and F. Noda, SAE Technical Paper, 740237 (1974).
- 3) M. Mitomo, *J. Mater. Sci.*, **11**, 1103–1107 (1976).
- 4) G. R. Terwillinger and F. F. Lange, *J. Mater. Sci.*, **10**, 1169–1174 (1975).

- 5) K. Komeya, M. Komatsu, T. Kameda, Y. Goto and A. Tsuge, *J. Mater. Sci.*, **26**, 5513–5516 (1991).
- 6) M. Matsuoka, J. Tatami, T. Wakihara, K. Komeya and T. Meguro, *J. Asian Ceram. Soc.*, **2**, 199–203 (2014).
- 7) I. W. Chen and A. Rosenflanz, *Nature*, **389**, 701–704 (1997).
- 8) S. G. Guo, N. Hirotsaki, Y. Yamamoto, T. Nishimura and M. Mitomo, *J. Am. Ceram. Soc.*, **85**, 1607–1609 (2002).
- 9) C. H. Lin, K. Komeya, T. Meguro, J. Tatami, Y. Abe and M. Komatsu, *J. Ceram. Soc. Jpn.*, **111**, 452–456 (2003).
- 10) J. Tatami, I. W. Chen, Y. Yamamoto, M. Komatsu, K. Komeya, D. K. Kim, T. Wakihara and T. Meguro, *J. Ceram. Soc. Jpn.*, **114**, 1049–1053 (2006).
- 11) J. Tatami, E. Kodama, H. Watanabe, H. Nakano, T. Wakihara, K. Komeya, T. Meguro and A. Azushima, *J. Ceram. Soc. Jpn.*, **116**, 749–754 (2008).
- 12) D. Kusano, G. Tanabe and S. Sato, *Nikkei Technical Journal*, **1**, 1–4 (2011).
- 13) N. Hirotsaki, S. Ogata and C. Kocer, *Phys. Rev. B*, **65**, 1–11 (2002).
- 14) B. Li, L. Pottier, J. P. Roger, D. Fournier, K. Watari and K. Hirao, *J. Eur. Ceram. Soc.*, **19**, 1631–1640 (1999).
- 15) K. Hirao, K. Watari, M. E. Brito, M. Toriyama and S. Kanzaki, *J. Am. Ceram. Soc.*, **79**, 2485–2488 (1996).
- 16) K. Watari, K. Hirao, M. E. Brito, M. Toriyama and S. Kanzaki, *J. Mater. Res.*, **14**, 1538–1541 (1999).
- 17) S. Q. Li, K. Sassa and S. Asai, *J. Am. Ceram. Soc.*, **87**, 1384–1387 (2004).
- 18) X. W. Zhu, Y. Sakka, T. S. Suzuki, T. Uchikoshi and S. Kikkawa, *Acta. Mater.*, **58**, 146–161 (2010).
- 19) X. W. Zhu, Y. Sakka, Y. Zhou, K. Hirao and K. Itatani, *J. Eur. Ceram. Soc.*, **34**, 2585–2589 (2013).
- 20) T. Takahashi, M. Sado, N. Sugimoto, J. Tatami, M. Iijima, S. Inagaki, Y. Kubota, I. Yamamoto and S. Tanaka, *Adv. Pow. Tech.*, **27**, 2005–2011 (2016).
- 21) H. Teshima, K. Hirao, M. Toriyama and S. Kanzaki, *J. Ceram. Soc. Jpn.*, **107**, 1216–1220 (1999).
- 22) D. S. Park and C. W. Kim, *J. Am. Ceram. Soc.*, **82**, 780–782 (1999).
- 23) M. Mitomo, “Proceedings of the 1st International Symposium of the Science on Engineering Ceramics”, Ed. by S. Kimura and K. Niihara, Ceram. Soc. Japan (1991) pp. 101–107.
- 24) J. S. Patwardhan and W. R. Cannon, *J. Am. Ceram. Soc.*, **89**, 3019–3026 (2006).
- 25) A. Shui, L. Zeng, Y. Liu, A. Makiya and K. Uematsu, *Ceram. Trans.*, **198**, 211–217 (2011).
- 26) S. Tanaka, Y. Nagashima, R. Furushima and K. Uematsu, *Mater. Sci. Eng.*, **21**, 012008 (2011).
- 27) T. Takahashi, S. Tanaka, Z. Kato and K. Uematsu, *J. Ceram. Soc. Jpn.*, **121**, 411–415 (2013).
- 28) H. Li, K. Komeya, J. Tatami, T. Meguro, Y. Chiba and M. Komatsu, *J. Ceram. Soc. Jpn.*, **100**, 342–346 (2001).
- 29) F. Izumi and K. Momma, *Solid State Phenom.*, **130**, 15–20 (2007).
- 30) H. Nakano, H. Nakano and K. Watari, *Adv. Technol. Mater. Mater. Process. J.*, **8**, 67–72 (2006).