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Fabrication of Silicon Nitride–Silicon Oxynitride *in-situ* Composites

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Abstract

Fine-grained β-Si_3N_4 *ceramics were fabricated from fine and uniform* β-*powder by hot-pressing at 1700–1750°C using different sintering aids (cordierite,* Y_2O_3–MgO, *and* Y_2O_3–Al_2O_3*). The microstructural development of hot-pressed bodies was studied in annealing at 1750°C for 0·5 to 8 h. When* Y_2O_3–MgO *and* Y_2O_3–Al_2O_3 *were used as sintering aids, fine and uniform microstructures were maintained because of the low driving force for grain growth of* β-Si_3N_4. *When cordierite was used as an aid,* β-Si_3N_4 *reacted with the* SiO_2 *in the additive and developed a bimodal microstructure with large* Si_2N_2O *grains in fine* β-Si_3N_4 *matrix grains after annealing. Local segregation of* β-Si_3N_4 *grains was observed after hot-pressing. Nucleation of* Si_2N_2O *occurred at a part of the segregation surface in the early stage of annealing.* Si_2N_2O *grains grew selectively with annealing time, resulting in improved fracture toughness.* © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

The fracture toughness of sintered silicon nitride ceramics must be improved if these ceramics are to be used as engineering materials. Tough silicon nitride ceramics have been prepared by developing bimodal microstructures, i.e. *in-situ* composites, which are composed of fine matrix grains and a small number of elongated grains.[1] Increased fracture toughness is attributed to crack deflection and crack bridging by elongated grains.[2,3]

Silicon nitride *in-situ* composites have been developed by α/β phase transformation during sintering[4,5] or by seeding large β-nuclei in fine powders.[6–8] Selective abnormal grain growth is assumed to be accelerated by α/β phase transformation or the large difference in particle size. This way of producing *in-situ* composites is based on grain-growth kinetics, which are not easy to control.[9]

The β'-O′ sialon ceramics are thought to be Si_3N_4-based composite materials, enabling microstructures to be tailored that combine the oxidation resistance of O′-sialon (Si_2N_2O solid solution) and the strength of β'-sialon (β-Si_3N_4 solid solution).[10,11] Yabuta *et al.* reported that β'-O′ sialon ceramics with large O′-grains in fine β'-grains are produced by sintering the mixture of α-Si_3N_4, SiO_2, and Al_2O_3, which can be regarded as an *in-situ* composite produced by the chemical reaction in starting powders during sintering.[12,13] Hot isostatic pressing is required to get dense composite sialon ceramics due to their low sinterability. The microstructural development in β'-O′ sialon ceramics, not studied as comprehensively as oxidation resistance, and the role in improving the mechanical properties of β'-O′ sialon ceramics remain poorly understood.

'*In-situ* composites' are used to develop composite or composite-like microstructures during sintering. The processing methodology can be divided into three categories: (1) the development of composite microstructures by the abnormal grain growth of small number of grains in Si_3N_4[4–8] and SiC ceramics,[14,15] (2) the formation of reinforcing grains through chemical reaction,[16–18] and (3) phase change based on temperature[19,20] or pressure change.[21] The reinforcing grains form during sintering or in subsequent heat treatment which avoid sacrificing sinterability as in usual composite processing. Our work focused on the second of these three categories.

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We explored the possibility of controlling microstructures of β-Si_3N_4–Si_2N_2O *in-situ* composites by using the reaction between Si_3N_4 and sintering aids. We studied optimum conditions for composite microstructures by annealing fine-grained dense β-Si_3N_4 monolithic ceramics. Fine β-Si_3N_4 powder was used as the starting powder to inhibit α/β phase transformation and abnormal grain growth of β-Si_3N_4.

2 Experiments

Specially prepared fine β-Si_3N_4 powder[7] was used because of its high purity, fineness, and very narrow particle size distribution (grains larger than 0·5 μm were eliminated). The average particle size was 0·20 μm, the specific surface area was 26·0 $m^2 g^{-1}$, and oxygen content was 1·8 wt%. Sintering aids used were cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}\ 5SiO_2$; Marusu-yuyaku Co., Nagano, Japan, SS600), Y_2O_3 (Shin-etsu Chemical Co., Tokyo, Japan, 99·9% pure), MgO (Wako Chemical Co., Osaka, Japan, high-purity grade), and Al_2O_3 (Taimei Chemicals Co., Nagano, Japan, TM-D grade, 99·99% pure). Fine β-Si_3N_4 powder was mixed with different sintering aids (Table 1) in *n*-hexane using a silicon nitride ball mill.

The powder mixture was then hot-pressed at 20 MPa in a N_2 atmosphere. The temperature was raised at 30°C min^{-1} to 1700–1750°C, then cooled immediately. Hot-pressed materials were annealed at 1750°C for 0·5–8 h in a N_2 atmosphere to determine Si_2N_2O formation and grain growth behavior. Hot-pressing and annealing conditions are also shown in Table 1.

Bulk densities of both as-hot-pressed and annealed materials were measured by the Archimedes method. X-ray diffraction (XRD) was used to identify crystalline phases and to determine Si_2N_2O content using calibration lines.[22] Elemental distributions in selected materials were analyzed with an electron probe microanalyzer (EPMA). Microstructures were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM samples were prepared by cutting, polishing, and plasma-etching with CF_4 containing 7·8 wt% O_2. TEM samples were prepared by cutting thin sections, followed by mechanical thinning, dimpling, and argon-ion-beam thinning to perforation. When β-Si_3N_4–Si_2N_2O composites were obtained, diameter (d) and apparent length (L) of Si_2N_2O grains in some SEM micrographs were measured with an image analyzer (Luzex III, Nireco Co., Tokyo, Japan). The diameter and apparent length of each grain were determined from the shortest and longest diagonal. The average aspect ratio was cited as the mean value of the 10% highest observed apparent aspect ratio (L/d).[23] The number of evaluated Si_2N_2O grains was 100 to 200 for each specimen. The fracture toughness was measured by Vicker's indentation under 98 N.[24]

3 Results and Discussion

The relative densities and phase compositions of as-hot-pressed and annealed materials are shown in Table 1. In hot-pressing, all samples could be sintered to high density (> 95% relative density) and only β-Si_3N_4 was detected by XRD as a crystalline phase. After annealing, they had achieved nearly full density (> 97% relative density). The presence of Si_2N_2O was detected as a secondary crystalline phase in the cordierite sample, although no secondary phase was present in the sample with Y_2O_3–Al_2O_3 and Y_2O_3–MgO. Si_2N_2O was reportedly formed by the reaction between Si_3N_4 and SiO_2 in a liquid phase containing Al_2O_3 or Y_2O_3.[22,25–27] In this work, all samples contained Y_2O_3 and/or Al_2O_3, so two possibilities exist for the SiO_2 reactant for Si_2N_2O formation: (1) oxide present on the surface of Si_3N_4 starting powder (SiO_2 content in the powder was estimated to be 3·4 wt% from the 1·8 wt% of oxygen content); and (2) SiO_2 present in cordierite. Since Si_2N_2O was only detected in the annealed material with cordierite, SiO_2 in cordierite must be a main reaction source for Si_2N_2O formation, whereas the lower

Table 1. Experimental conditions and characterization of hot-pressed and annealed materials

Sintering aids	*Hot-pressed (20 MPa)*				*Annealed (1750°C)*			
	Temp. (°C)	*Density (%)*	*Content (wt%)*		*Holding time (h)*	*Density (%)*	*Content (wt%)*	
			β-Si_3N_4	Si_2N_2O			β-Si_3N_4	Si_2N_2O
7 wt% Cordierite					0.5	97·5	96	4
($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$)	1750	96·1	100	0	1	97·9	88	12
					4	98·3	86	14
					8	97·9	84	16
5 wt% Y_2O_3 + 2 wt%MgO	1700	95·5	100	0	1	99.5	100	0
5 wt%Y_2O_3 + 2 wt%Al_2O_3	1750	95·4	100	0	1	99·1	100	0

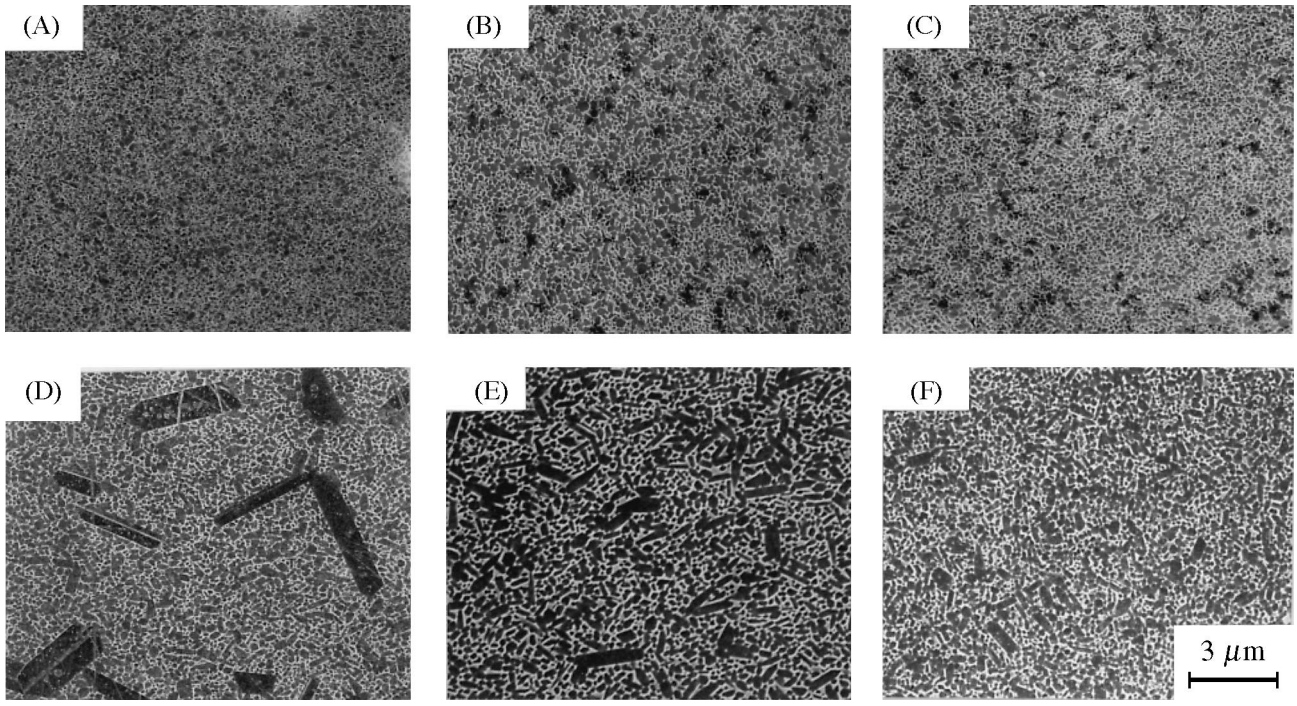

Fig. 1. SEM micrographs of (A)–(C) as-hot-pressed and (D)–(F) annealed materials. Sintering aids: (A),(D) cordierite, (B),(E) Y_2O_3–MgO, and (C),(F) Y_2O_3–Al_2O_3.

reactivity of SiO_2 on Si_3N_4 powder might be due to its uniform distribution.

Microstructures of as-hot-pressed materials were very fine and uniform, with grain sizes almost the same as the starting powder [Fig. 1(A)–(C)]. This means that the hot-pressing process should be effective in densification without appreciable grain growth. The microstructures of the annealed materials were divided into two types, one observed in samples with Y_2O_3–Al_2O_3 and Y_2O_3–MgO, in which fine and uniform microstructures were maintained, and the other observed in the sample with cordierite, in which a bimodal microstructure with large elongated grains in fine matrix grains developed [Fig. 1(D)–(F)]. The driving force for the growth of β-Si_3N_4 grains in silicon nitride ceramics containing a liquid phase is thought to be α/β phase transformation and the difference in particle size.[7,28] Here the driving force for grain growth should be very small, because Si_3N_4 starting powder is almost β-phase and its particle size distribution is very narrow. Fine and uniform microstructures were therefore maintained in samples with Y_2O_3–Al_2O_3 and Y_2O_3–MgO.

Silicon, oxygen, magnesium, and aluminum distributions in both as-hot-pressed and annealed materials with cordierite were determined by EPMA analysis (Fig. 2). Nitrogen was not easily detected because of its low sensitivity. Silicon was abundant because it was included in both Si_3N_4 starting powder and the sintering aids. Si_3N_4-rich regions free of oxygen, magnesium, and aluminum, which were assumed not to be large grains but

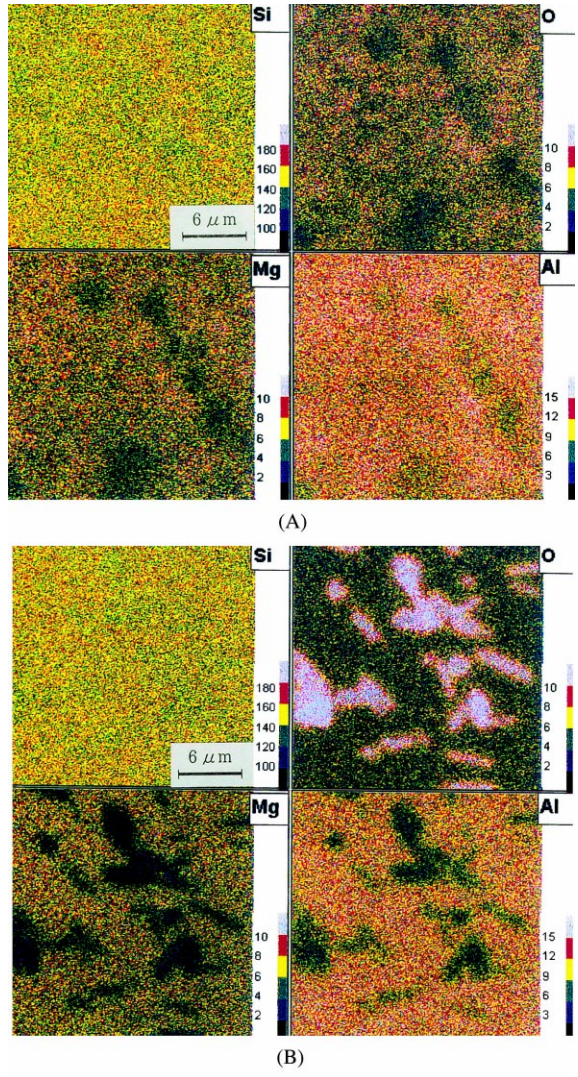

Fig. 2. EPMA analysis of (A) as-hot-pressed and (B) annealed materials using cordierite as a sintering aid.

segregations of fine β-Si_3N_4 grains [Fig. 1(A)], were observed in the as-hot-pressed material [Fig. 2(A)]. In the annealed material [Fig. 2(B)], regions with a large amount of oxygen and free of magnesium and aluminum were observed, and corresponded to large elongated grains in a bimodal microstructure [Fig. 1(D)]. XRD and EPMA analysis confirmed that large elongated grains were Si_2N_2O. Although Si_2N_2O grains were not observed by XRD and SEM in the as-hot-pressed material, embryos for Si_2N_2O nuclei (Si_3N_4-rich regions in Fig. 2(A) may have already been formed in the hot-pressing process. Si_2N_2O nucleation and grain growth are thought to have been caused by a surface reaction at the segregate during annealing through selective adsorption of SiO_2 from surrounding region.[29]

Detailed TEM studies (Fig. 3) of the microstructures of the annealed material with cordierite showed large elongated grains of Si_2N_2O and fine β-Si_3N_4. TEM analysis also shows that Si_2N_2O grains grow selectively parallel to [010], which may be related to the anisotropic nature of the crystal structure, and contain stacking faults.[29] Small α-Si_3N_4 particles reportedly act as heterogeneous nucleation sites for Si_2N_2O in α-Si_3N_4–SiO_2–Al_2O_3 system.[30] In this study, only a portion of the β-Si_3N_4 particles at the surface of the segregates can serve as Si_2N_2O nucleation site because special crystallographic orientation is necessary between β-Si_3N_4 and Si_2N_2O.[29] Grain growth occurs by diffusion of SiO_2 from surrounding matrix to β-Si_3N_4/Si_2N_2O interfaces. The rapid grain growth in the [010] direction results in the entrapment of fine β-Si_3N_4 grains.

The microstructural development of silicon nitride ceramics with a liquid phase containing SiO_2 and Al_2O_3 and/or Y_2O_3 such as cordierite and Y_2O_3–SiO_2 has been reported,[31–35] but the formation of Si_2N_2O was not extensively discussed. In such experiments, α-Si_3N_4 powders were used as starting powders and α/β-phase transformation occurs in liquid-phase sintering. In other words, α-grains dissolve in a liquid phase and precipitate as β-grains. Abnormal grain growth of β-Si_3N_4 is known to be accelerated kinetically by α/β phase transformation, meaning that a bimodal microstructure having abnormally grown β-Si_3N_4 grains should develop, possibly hiding or suppressing the formation of large elongated Si_2N_2O grains. Here the abnormal grain growth of β-Si_3N_4 should not occur, yielding a bimodal microstructure with large elongated Si_2N_2O grains in β-Si_3N_4 matrix grains.

The effect of annealing time on the microstructures of materials with cordierite was investigated. The materials were annealed at 1750°C for 0, 0·5, 1, 4, and 8 h (Fig. 4). A bimodal microstructure with large Si_2N_2O grains in β-Si_3N_4 fine grains developed in materials annealed for more than 0·5 h. SEM micrographs make it easy to distinguish between Si_2N_2O and β-Si_3N_4 grains because of the difference in size and contrast. We quantified the number, diameter, apparent length and area of Si_2N_2O grains using an image analyzer. To confirm Si_2N_2O nucleation behavior, we plotted the number of Si_2N_2O grains per unit area (1 mm^2) against annealing time (Fig. 5). It was shown that the number of Si_2N_2O grains increased markedly in the early stage of annealing (up to

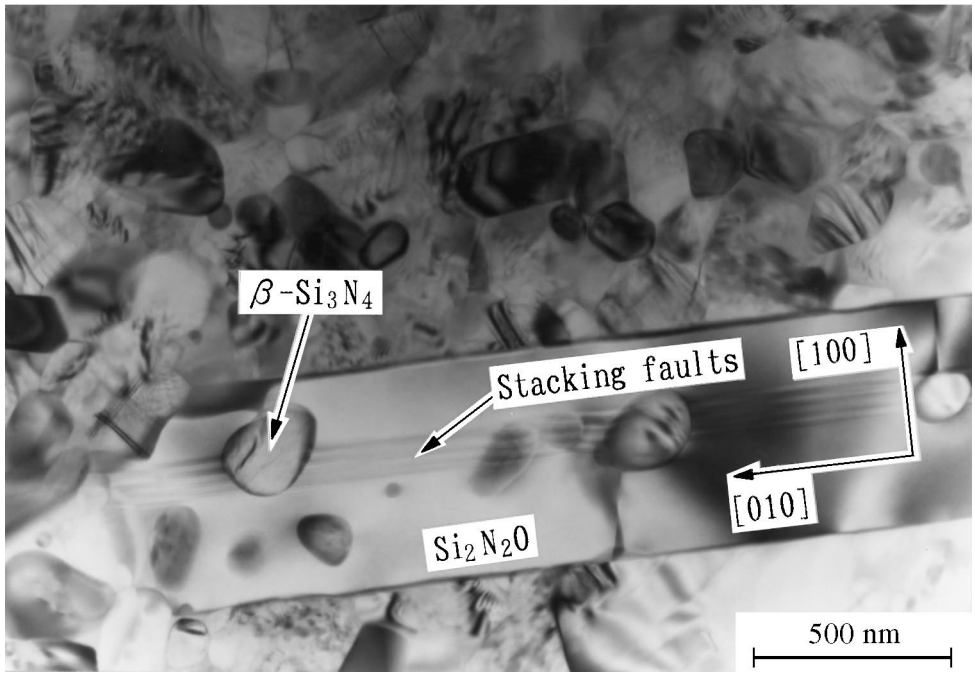

Fig. 3. TEM micrograph of annealed material with cordierite.

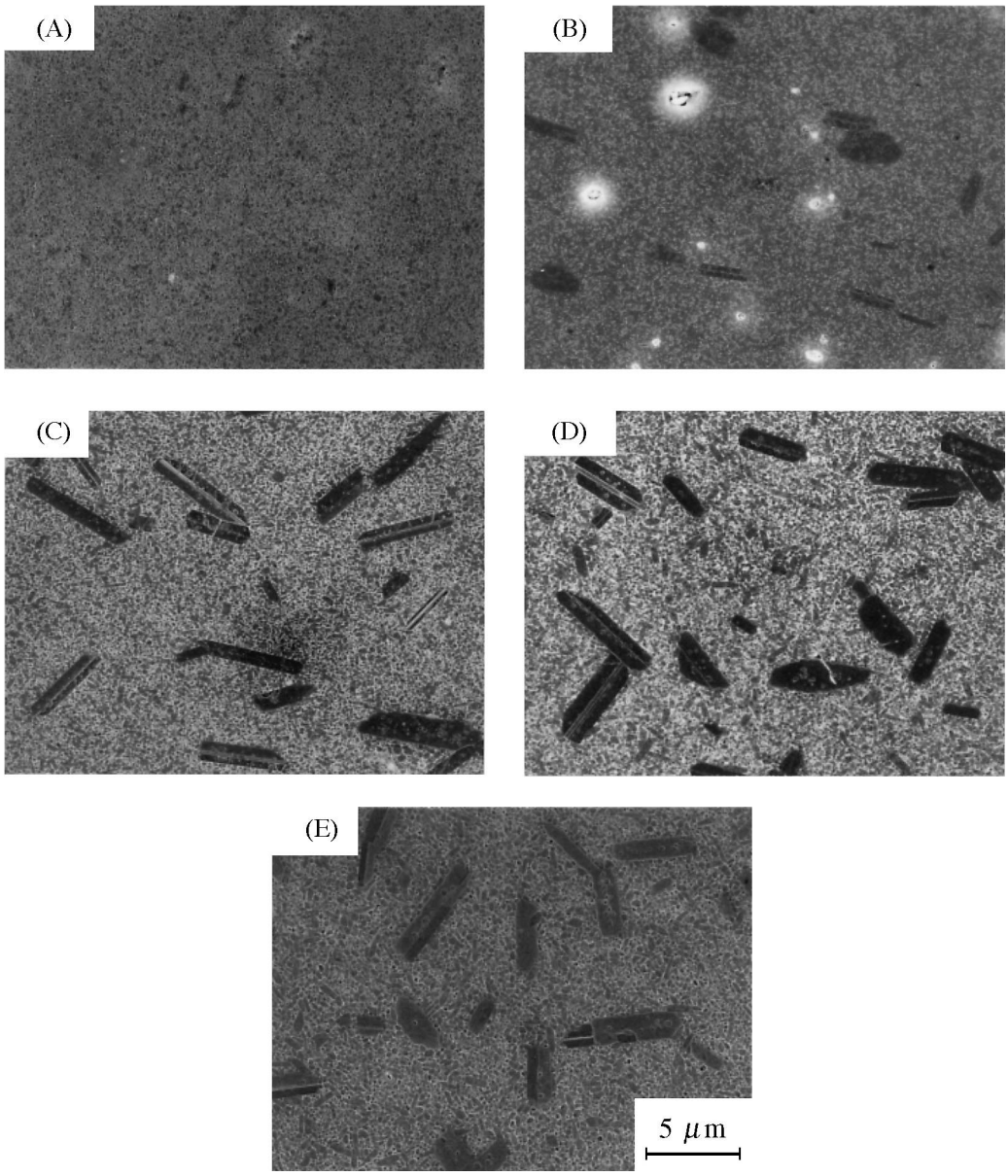

Fig. 4. SEM micrographs of Si_3N_4 materials with cordierite: (A) hot-pressing, and annealing at 1750°C for (B) 0·5 h, (C) 1 h, (D) 4 h, and (E) 8 h.

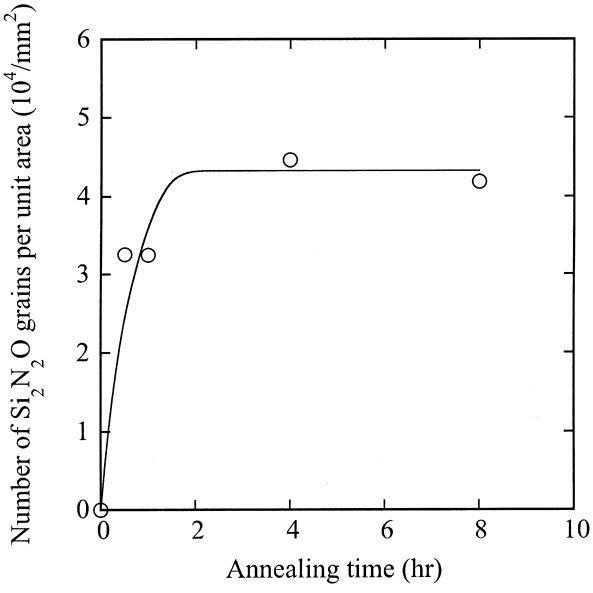

Fig. 5. The number of Si_2N_2O grains in materials with cordierite as a function of annealing time.

~1 h), after which it was constant, regardless of annealing time. This result strongly suggests that the Si_2N_2O nucleation occurs only at the early stage of annealing. The segregation of the Si_3N_4-rich region surrounded by additives, which was observed in the as-hot-pressed material [Fig. 2(A)], is assumed to be the nucleation sites.[29] There might be a low probability for a specific orientation between β-Si_3N_4 grains in the segregates and Si_2N_2O grains, which is a possible reason for the small number of nuclei. This topotaxial orientation occurs only in small regions at the surface of Si_3N_4 grains. On the other hand, Si_2N_2O grain-growth rate is very high because of the fast diffusion of nitrogen and oxygen atoms in the liquid phase. Therefore, as soon as one nucleus appears, it grows rather quickly, indicated by a sharp drop of (N, O) in the surrounding liquid and hence prevention of further nucleation in that area. Initial high Si_2N_2O

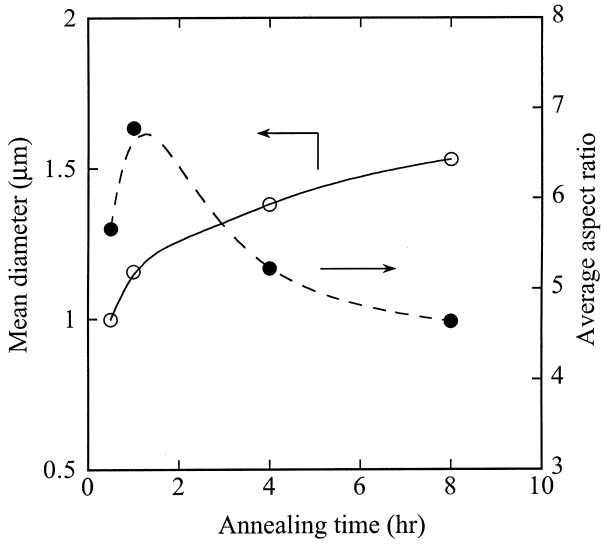

Fig. 6. Mean diameter and average aspect ratio of Si_2N_2O grains in materials with cordierite as a function of annealing time.

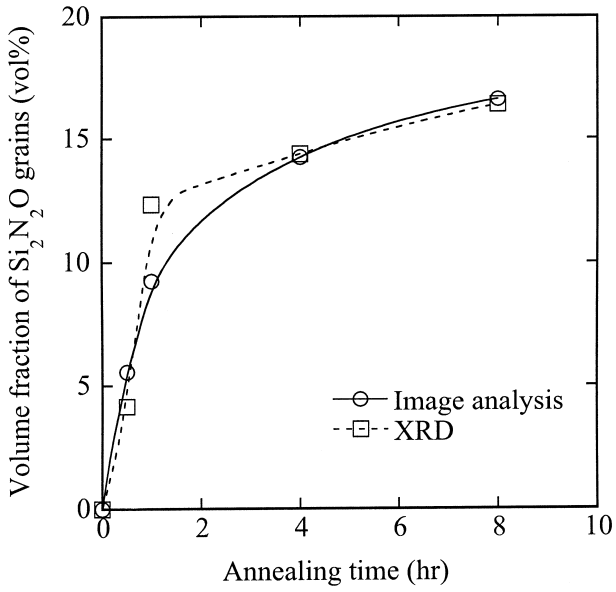

Fig. 7. Volume fraction of Si_2N_2O grains in materials with cordierite as a function of annealing time.

grain-growth rate and slight misorientation between β-Si_3N_4 and Si_2N_2O might cause stacking faults.[29]

To confirm Si_2N_2O grain growth behavior, we plotted the mean diameter and average aspect ratio of Si_2N_2O grains against annealing time (Fig. 6). Mean diameter increases with the annealing time. The aspect ratio becomes largest after 1 h of annealing, suggesting that Si_2N_2O grains grew both in length and width in the early stage of annealing (< 1 h) and only in width in later stage (> 1 h).

The effect of large grains in a bimodal microstructure on toughening was analyzed in terms of the volume fraction, size and shape. The volume fraction of large grains, which corresponds to the area fraction obtained from a two-dimensional cross-section, is plotted against the annealing time, together with the results determined by XRD

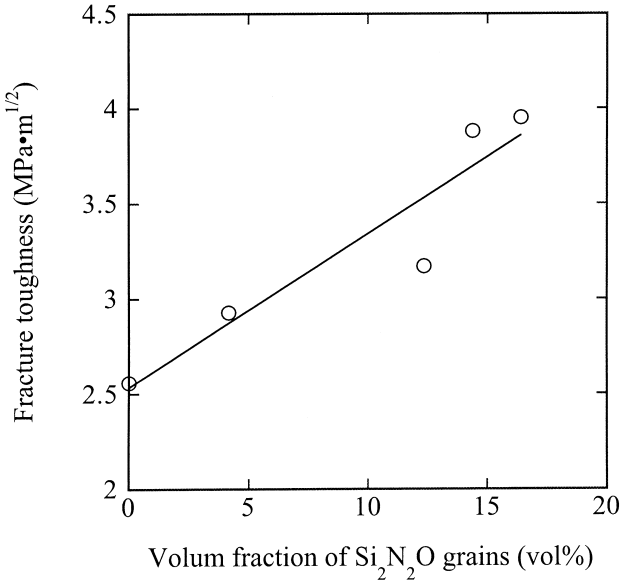

Fig. 8. Fracture toughness of materials with cordierite as a function of volume fraction of Si_2N_2O grains.

(Fig. 7). The result obtained by image analysis is similar to that by XRD. The volume fraction of large grains (Si_2N_2O) increases sharply in the early stage of annealing, but gradually thereafter. This is consistent with Si_2N_2O nucleation and grain growth behavior expected from the change in number, mean diameter, and aspect ratio of Si_2N_2O grains with annealing time (Figs 5 and 6). The fracture toughness of cordierite-doped materials increases with volume fraction of Si_2N_2O grains (Fig. 8), and is related to bimodal microstructural development resulting from Si_2N_2O formation. Although the determination of mechanical properties is still preliminary, our experiments suggest that microstructural control using chemical reaction between Si_3N_4 and SiO_2 through a liquid phase containing Al_2O_3 may effectively improve fracture toughness.

4 Conclusion

The microstructural development of fine-grained β-Si_3N_4 ceramics using different sintering additives such as cordierite, Y_2O_3–MgO, and Y_2O_3–Al_2O_3 was studied in annealing at 1750°C for 1 h. Fine β-Si_3N_4 ceramics with Y_2O_3–MgO or Y_2O_3–Al_2O_3 had a homogeneous, stable microstructure and showed no abnormal grain growth. When cordierite was used as a sintering additive, β-Si_3N_4 reacted with the SiO_2 in a liquid phase that resulted in a bimodal microstructure with large elongated Si_2N_2O grains in fine β-Si_3N_4 matrix grains. This behavior was clarified by the use of fine β-Si_3N_4 starting powder with a relatively low driving force for grain growth. Si_2N_2O nucleation occurred only

in the early stage of annealing and Si_2N_2O grew selectively after prolonged annealing because of the low nucleation rate and a fast grain-growth rate. A bimodal microstructural development resulted from Si_2N_2O formation improved the fracture toughness.

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