Journal of the European Ceramic Society **19** (1999) 2183–2187

PII: S0955-2219(99)00030-8
0955-2219/99/$ - see front matter

Effect of Seeding on the Thermal Conductivity of Self-reinforced Silicon Nitride

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(Received 10 November 1998; accepted 30 December 1998)

Abstract

Thermal conductivity of Si_3N_4 containing large β-Si_3N_4 particles as seeds for grain growth was investigated. Seeds addition promotes growth of β-Si_3N_4 grains during sintering to develop the duplex microstructure. The thermal conductivity of the material sintered at 1900°C improved up to 106 $W m^{-1} K^{-1}$, although that of unseeded material was 77 $W m^{-1} K^{-1}$. Seeds addition leads to reduction of the sintering temperature with developing the duplex microstructure and with improving the thermal conductivity, which benefits in terms of production cost of Si_3N_4 ceramics with thermal conductivity. © 1999 Elsevier Science Limited. All rights reserved

Keywords: grain growth, microstructure-final, thermal conductivity, Si_3N_4, seeding.

1 Introduction

Silicon nitride ceramics have been investigated over many years for their potential application as structural materials because of their excellent mechanical properties at room and elevated temperatures. Many researchers have investigated mechanical properties such as strength, fracture toughness, reliability, creep, and wear resistance, and chemical stabilities such as oxidation, but less attention has been paid to thermal properties. Controlling the thermal conductivity of silicon nitride ceramics is important when this material is used for engine components. Lower thermal conductivity is required for the application of heat insulation components to reduce fuel consumption. On the other hand, higher thermal conductivity is necessary for improving thermal shock resistance.

Thermal conductivity of polycrystalline silicon nitride was reported to be 20–70 $W m^{-1} K^{-1}$ at room temperature before 1995.[1–4] These values are considerably lower than those of other non-oxide ceramics such as SiC (270 $W m^{-1} K^{-1}$)[5] and AlN (260 $W m^{-1} K^{-1}$).[6] So silicon nitride has not been considered as the candidate material for high thermal conductivity. Concerning the thermal conductivity of nonmetallic crystals in which phonons transport heat, Slack[7] has shown that ceramics with (1) small atomic mass, (2) strong interatomic bonding, (3) simple crystal structure, and (4) low anharmonicity of lattice vibration have high thermal conductivity. Ceramics having high thermal conductivity satisfy these four conditions. Considering silicon nitride, the characteristics of crystal are not so far from those of AlN or SiC except the third one; the crystal structure of Si_3N_4 is more complex than that of AlN or SiC. Haggerty *et al.*[8] suggested that the complexity in crystal structure of silicon nitride is not a disqualifying factor for high thermal conductivity and predicted that its thermal conductivity should be up to 200 $W m^{-1} K^{-1}$.

The authors[9,10] have experimentally succeeded in improving the thermal conductivity of silicon nitride ceramics up to 122 $W m^{-1} K^{-1}$. The key processing conditions for higher thermal conductivity are (1) selecting an appropriate additive composition which does not make a solid solution, (2) reducing the additive amount to as small as possible, and (3) promoting grain growth by the heat treatment at a markedly high temperature of 2200°C. The composition and amount of grain boundary phases affect the thermal conductivity of silicon nitride ceramics because the thermal conductivity of the silica base glass is considerably lower than that of Si_3N_4 crystals. A solid solution also degrades the thermal conductivity because point

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defects in crystals scatter the phonons which mainly transfer the heat in silicon nitride. Grain growth of β-Si_3N_4 crystals in polycrystalline ceramics improves thermal conductivity because of purification of the grains and decreasing the two-grain junction films.

This heat treatment condition is unfavorable for industrial production because the applied temperature, 2200°C, is considerably higher than that of conventional sintering for Si_3N_4, though higher temperature significantly promotes grain growth and improves the thermal conductivity. Thus, the new processing which promotes grain growth at lower heat-treatment temperature is strongly required. The method of adding large β-Si_3N_4 grains to the raw Si_3N_4 powder has been proposed as an effective method to promote grain growth of self-reinforced silicon nitride.[11,12] Rod-like seeds addition control the anisotropy of the microstructure and the thermal conductivity of silicon nitride ceramics.[13–15] The object of this report is to investigate the effect of addition of large β-Si_3N_4 particles as seeds on the grain growth behavior and thermal conductivity of sintered silicon nitride.

2 Experimental Procedure

Two types of β-Si_3N_4 powder, fine powder (Powder F, Grade SN-P21FC, Denki Kagaku Kogyo, Tokyo, Japan) and coarse powder (Powder C, Special grade, Denki Kagaku Kogyo, Tokyo, Japan), which were made by nitridation of pure silicon, were used as raw materials. Powder F was used for fabricating fine matrix grains and powder C was added to act as seeds for grain growth. These powders mainly consisted of β-Si_3N_4 and were similar in purity to common α-type raw powders, as shown in Table 1. To prepare a powder composition without seeds, 97·9 wt% powder F, 1·2 wt% Nd_2O_3, 0·8 wt% Y_2O_3 (99·9% pure, Shin-etsu Chemical, Tokyo, Japan), and 0·1 wt% MgO (Grade HP-30, Konoshima Chemical, Japan) were ball milled in ethanol for 94 h. To prepare a powder composition containing seeds, 97.4 wt% powder F, 1·2 wt% Nd_2O_3, 0·8 wt% Y_2O_3, and 0·1 wt% MgO were ball milled in ethanol for 94 h, after which 0·5 wt% powder C was added, and the mixture was milled for 4 h. After they were dried, the powder mixtures were die pressed under 20 MPa and isostatically pressed under 200 MPa. The resultant disk specimens were 13 mm in diameter and 4 mm thick. Sintering was performed in a graphite resistance furnace. The specimens were fired at a heating rate of 500°C h^{-1} and maintained for 4 h at 1900°C in 10 MPa N_2. Then, some of the specimens were heat-treated for 4 h at 2000°C in 10 MPa N_2. High N_2 gas pressure was required to prevent the thermal decomposition of Si_3N_4 at high temperatures.

Table 1. Properties of raw silicon nitride powders

	Powder F	*Powder C*
α-Phase content (wt%)	7	< 1
Fe impurity (wt%)	0.002	0.004
Al impurity (wt%)	0.015	0.004
Ca impurity (wt%)	0.015	0.012
O impurity (wt%)	1.63	0.26
Average particle size (μm)	0.49	5.3

Microstructural features of the sintered materials were evaluated quantitatively by digital processing and analysis. The sintered material was cut and polished, and then plasma-etched in CF_4 gas containing 8% O_2. The microstructure was observed by scanning electron microscopy (SEM). Outlines of the grains were traced manually and the length, diameter, and area of each grain were measured digitally using the VIDAS-plus system (Carl Zeiss, Aalen, Germany). Grain length and diameter were defined as the maximum grain projection and minimum grain projection, respectively.

Thermal diffusivity at room temperature was measured by the laser flash method using a ruby laser and InSb for the infrared detector. Disk samples were ground to 10 mm in diameter and 2 mm thick. Black carbon layers were applied on both sides of the disk samples to enhance absorption of the flash energy. Specific heat at room temperature was measured by the laser flash method using a Pt-PtRh13% thermocouple. A graphite plate (11 mm in diameter and 0·25 mm thick) was attached to the front surface of the disk samples. Thermal conductivity (κ) was calculated according to the equation

$$\kappa = \alpha \cdot C_p \cdot \rho \qquad (1)$$

where α is thermal diffusivity, C_p is the specific heat, and ρ is the density.

3 Results and Discussion

Figure 1 shows the microstructure of Si_3N_4 added with 0·5 wt% seeds (S19) or without seeds (N19), and sintered at 1900°C. The relative densities of these materials were > 98% of the theoretical density. Two distinct SEM images were employed for one sample: Fig. 1(A) and (C) are observed at low magnification of 400× to evaluate relatively large grains (≥2 μm) and Fig. 1(B) and (D) are observed at high magnification of 2000× to evaluate smaller matrix grains. Both specimens had a duplex microstructure consisting of a lot of fine matrix grains (< 2 μm) and a few large elongated grains (≥2 μm). These microstructures are typical of self-reinforced

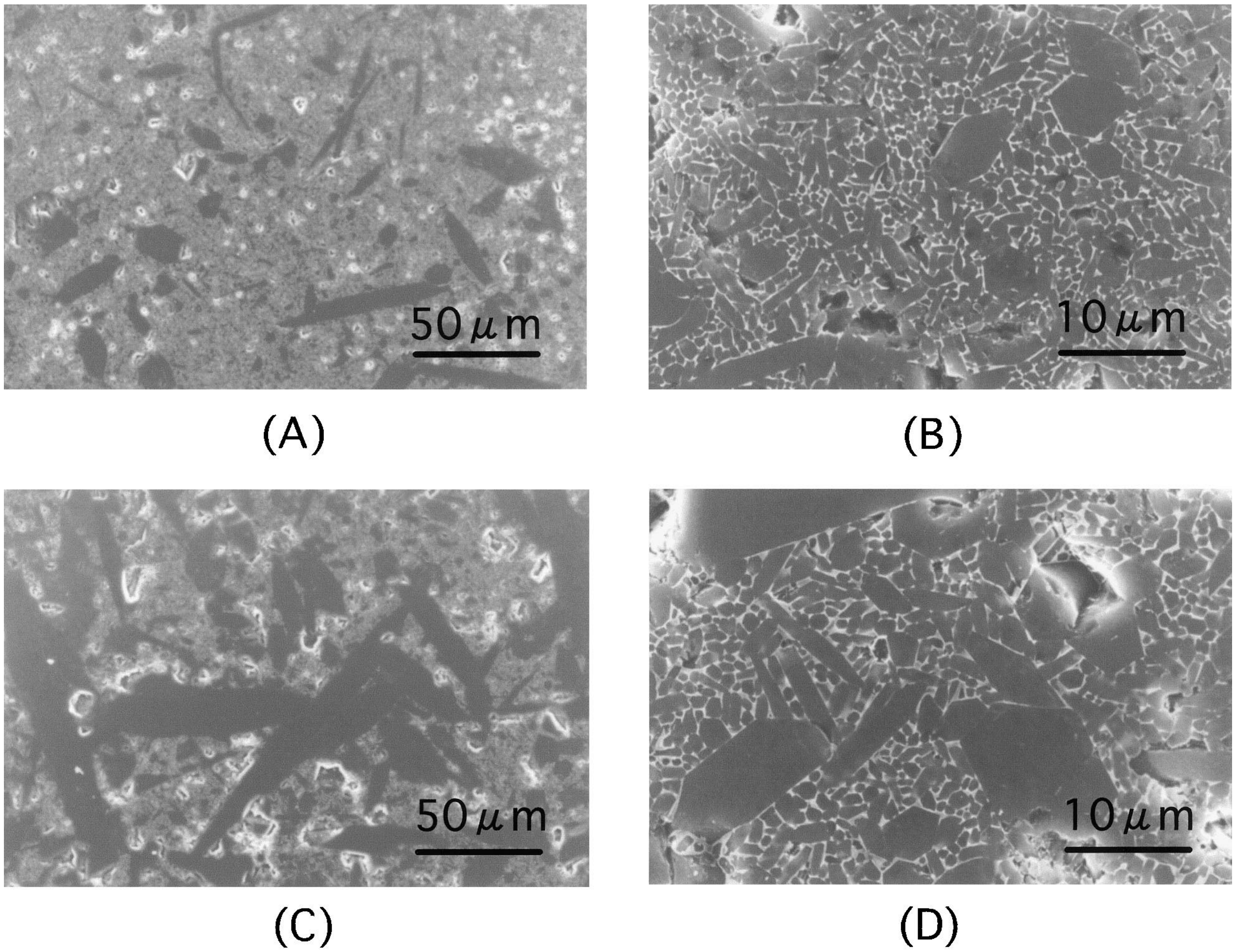

Fig. 1. Microstructure of Si_3N_4 sintered at 1900°C: (A) and (B) without seeds, and (C) and (D) containing seeds.

silicon nitride materials, whose liquid-phase sintered silicon nitride ceramics are heat-treated at higher temperature. Both specimens had similar matrix grains, but the large grains were substantially different in size and number.

Digital processing and analysis were conducted to quantitatively evaluate the microstructure with the wide-ranged grain size distribution. Two SEM images with a different magnification for one sample were analyzed by image processor to measure length, diameter, and area of each grains, then synthesized into one distribution. Details of this procedure were described in the literature.[16] Figure 2 shows the grain size distribution of (A) N19 and (B) S19. The self-reinforced microstructure was also confirmed by the grain size distribution; two peaks with the grain size of $<2\,\mu$m and $\geq 2\,\mu$m were clearly observed. The lower peak corresponds to the matrix grains and the upper peak corresponds to elongated grains in the self-reinforced microstructure. These figures also confirm that N19 contains less elongated grains than S19.

Figure 3 shows the microstructure of Si_3N_4 added with 0·5 wt% seeds (S20) or without seeds (N20), sintered at 1900°C, and heat-treated at 2000°C. These photographs were observed at low magnification of 400×. Observation at high magnification of 2000× was also carried out and the microstructures were similar to Fig. 1(B) and (D). Figure 4 shows the grain size distribution of these specimens. Both specimens had a similar grain size distribution and microstructure. Under the condition of heat-treatment at 2000 °C, seeds addition did not affect the microstructure.

Introducing large β-Si_3N_4 particles as seeds into fine Si_3N_4 raw powder is effective in controlling the microstructure. During firing, fine Si_3N_4 dissolves and precipitates on the large β-Si_3N4 particles. Seeds addition accelerates grain growth because the driving force for grain growth is the difference in grain size.[17] These results indicate that seeds, when added to the raw Si_3N_4 powder, are effective in developing large grains at 1900°C; at this temperature, mass transport is too small for pronounced grain growth in the unseeded powder. Temperatures at $\geq$2000°C are required for such grain growth when seeds are not used.

Figure 5 shows the effects of seeds addition and heat treatment temperature on the thermal conductivity of sintered materials. Thermal conductivity of S19 was $77\,W\,m^{-1}\,K^{-1}$, rather a low value. Seeds addition increased the thermal

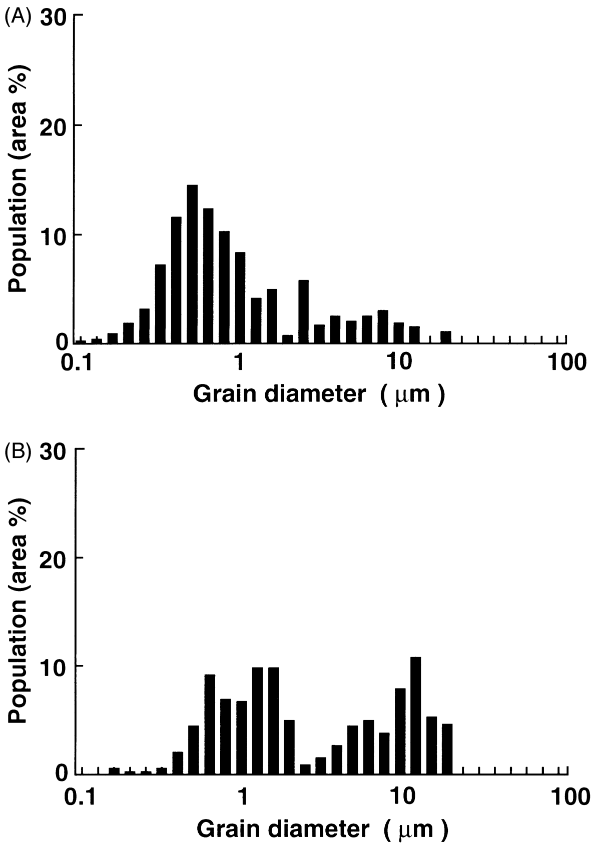

Fig. 2. Grain size distribution of Si_3N_4 sintered at 1900°C: (A) without seeds, and (B) containing seeds.

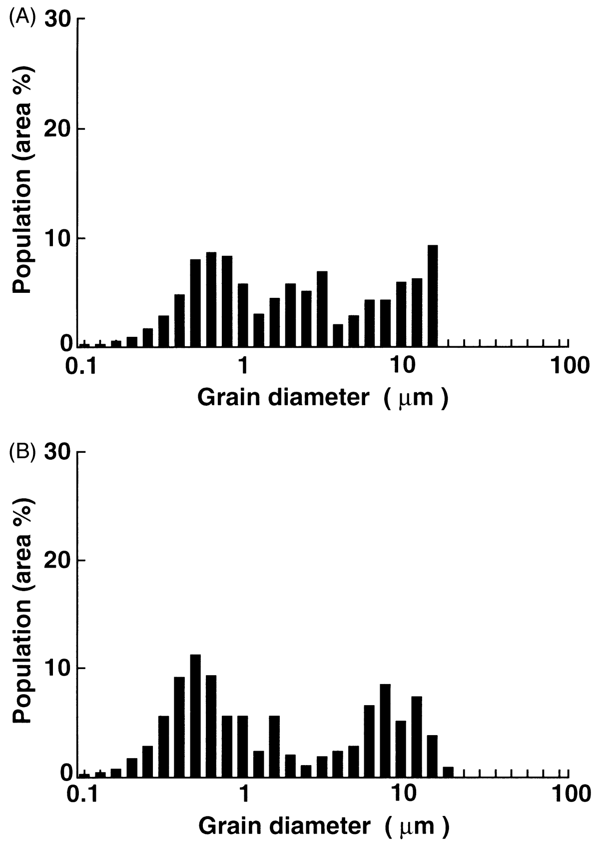

Fig. 4. Grain size distribution of Si_3N_4 heat-treated at 2000°C: (A) without seeds, and (B) containing seeds.

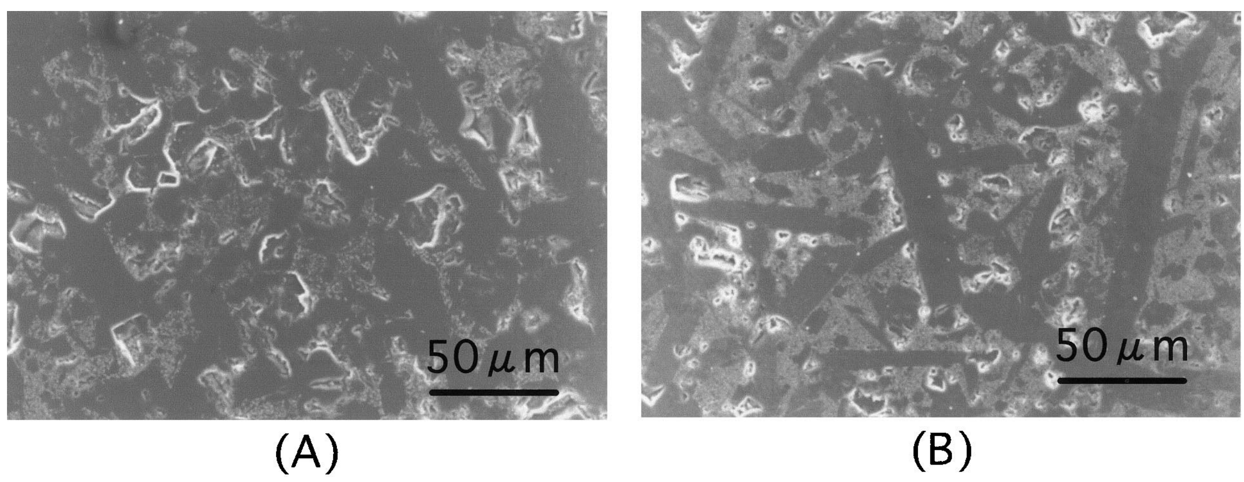

Fig. 3. (A) without seeds, and (B) containing seeds. Microstructure of Si_3N_4 heat-treated at 2000°C.

conductivity up to 106 W m^{-1} K^{-1}, notwithstanding sintering at the same temperature. Under the condition of heat-treatment at 2000°C, seeds addition did not affect the thermal conductivity as much as the microstructure: 122 W m^{-1} K^{-1} for N20 and 120 W m^{-1} K^{-1} for S20. These values are at a similar level to the previously reported ones of the material sintered at 2200°C.

As noted in the introduction, thermal conductivity in polycrystalline ceramics is lowered by the phonon scattering at grain boundary phase, solid solution or impurities in the crystal, crystal defects, and so on. Grain boundary films and multi-grain junction phases in silicon nitride ceramics consist of oxynitride glass with the thermal conductivity of 0·5–1 W m^{-1} K^{-1}.[9] Both films and junctions reduce thermal conductivity, but films affect more strongly than junctions because of their morphology.[9] The grain boundary films are swept out into the multi-grain junction during the grain growth, thus higher thermal conductivity was obtained in the sample with large grain size. Grain growth not only decreases the amount of films, but also purifies the impurities and defects in the Si_3N_4

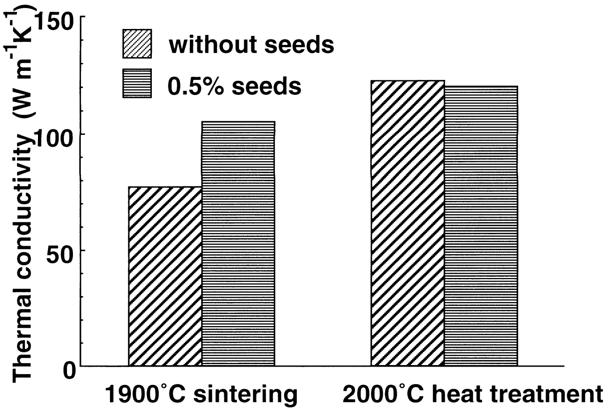

Fig. 5. Effect of seeds addition and sintering temperature on the thermal conductivity of Si_3N_4 ceramics.

grain. Silicon nitride raw powders contain impurities and crystal defects in the grain. The grown parts of Si_3N_4 grain have a lower amount of impurities and defects than the raw Si_3N_4 powder because most of impurities and defects in the raw powder are removed by the segregation phenomena at the precipitation step during the liquid phase sintering in which smaller Si_3N_4 grains dissolve to the liquid, diffuse in the liquid, and reprecipitate onto the larger grains. Therefore, the material with large grain size has higher thermal conductivity.

4 Conclusion

Silicon nitride containing Y_2O_3–Nd_2O_3–MgO additive was seeded with or without β-Si_3N_4 large particles and gas-pressure sintered and heat treated. Seeds addition promotes growth of elongated β-Si_3N_4 grains in duplex microstructure. The thermal conductivity improved up to $106\,W\,m^{-1}\,K^{-1}$, although that of unseeded material was $77\,W\,m^{-1}\,K^{-1}$. Seeds addition leads to reducing the sintering temperature with developing the duplex microstructure and with improving the thermal conductivity, which benefits in terms of production cost of Si_3N_4 ceramics with thermal conductivity.

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