MICROSTRUCTURAL CONTROL OF β-SILICON NITRIDE CERAMICS TO IMPROVE THERMAL CONDUCTIVITY

K. Furuya[1], F. Munakata[1], K. Matsuo[2], Y. Akimune[2], J. Ye[3] and A. Okada[1]*

[1]Materials Research Laboratory, Nissan Motor Company, Ltd., 1 Natshushima-cho, Yokosuka 237-8523, Japan
[2]Smart Structure Research Center, National Institute for Advanced Industrial Science and Technology, 1-1-1, Umezono, Tsukuba 305-8568, Japan
[3]Research Department, NISSAN ARC, Ltd., 1 Natsushima-cho, Yokosuka 237-0061, Japan

Abstract

An advanced silicon nitride material with high isotropic thermal conductivity (149 W m^{-1} K^{-1}) has been developed. This high thermal conductivity was achieved with a process that combines high-quality seed crystals with a suitable additive system to promote grain growth. In this process, the addition of β-Si$_3$N$_4$ seed crystals was found to be effective in improving thermal conductivity due to their low defect and impurity concentrations. The seed crystals seem to work as nuclei for controlling grain growth during the sintering process. Controlling the growth of elongated grains so that they do not interact with each other seems important for suppressing the generation of new defects inside the grains.

Keywords: β-Si$_3$N$_4$ seed crystal, selective grain growth sintering, thermal conductivity

Introduction

Silicon nitride is a candidate material for use in harsh environments. For application to automotive engines, improvements in thermal and mechanical properties are necessary to meet strict requirements for thermal shock resistance. The thermal conductivity of silicon nitride has been reported to be 20 to 70 W m^{-1} K^{-1} [1–4], which is rather low compared with other non-oxide ceramics such as AlN (260 W m^{-1} K^{-1}) [5] and SiC (270 W m^{-1} K^{-1}) [6]. However, high thermal conductivity can be expected for silicon nitride due to its small atomic mass and strong interatomic bonding, properties that are desirable for obtaining high thermal conductivity [7]. Thermal conduction in silicon nitride primarily results from the transport of phonons that are scattered by lattice imperfections [8], impurities forming solid solutions, precipitations [9], and

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* Author for correspondence: E-mail: furuyak@nrc.nissan.co.jp

grain boundaries. Therefore, the thermal conductivity of silicon nitride is affected by the crystal structure, additive composition and the microstructure.

Previously, we reported a new process for improving the thermal conductivity of β-Si_3N_4 up to 120 W m^{-1} K^{-1} at room temperature by promoting grain growth and selecting suitable additive systems [10]. The addition of silicon nitride whiskers was investigated as a way of introducing nuclei for controlling grain growth during sintering. The resultant material exhibited high thermal conductivity of 162 W m^{-1} K^{-1} parallel to the grain alignment direction and 84 W m^{-1} K^{-1} perpendicular to the alignment [11]. It was thought that the thermal conductivity of silicon nitride ceramics might be improved further through the use of high-quality β-Si_3N_4 crystals with low defect and impurity concentrations as seed crystals due to the possible reduction in phonon scattering inside the elongated grains. We subsequently reported the successful synthesis of large β-Si_3N_4 whisker-like single crystals of several mm in length and 0.2 mm in diameter by using a silicon-melt technique [12].

In the present study, synthesized β-Si_3N_4 crystals with low defect and impurity concentrations were employed as nuclei for three-dimensional random seeding to develop an isotropic material with high thermal conductivity.

Experimental

Crystal growth of β-Si_3N_4 seeds

Seed crystals of β-Si_3N_4 were grown using a silicon-melt technique. Details of this technique [12], as well as the crystal separation procedure [13], have been described elsewhere. The silicon powder (99.999% pure) was melted in a reaction bonded silicon nitride (RBSN) crucible in an argon atmosphere at the melting point of silicon (1687 K) for an hour, after which the temperature was raised to 1873 K. Nitrogen gas was then introduced into the furnace at a flow rate of 4 mL min^{-1} and the crucible was held at 1873 K for 1 h. Finally, the furnace was slowly cooled down at a rate of 46 K h^{-1} to room temperature. The β-Si_3N_4 crystals thus formed were separated using an aqueous hydrofluoric acid (HF) treatment followed by a H_2SO_4 treatment. After drying, the β-Si_3N_4 crystals were meshed to a dimension smaller than 20 μm and employed as seed crystals.

Selective grain growth sintering

A raw β-Si_3N_4 powder mixture containing 1 mol% Y_2O_3 and 1 mol% Nd_2O_3 was ball-milled in ethanol for 48 h. One mass% β-Si_3N_4 seed crystals were then added and additional ball-milling was performed for 46 h. Another powder mixture without β-Si_3N_4 seed crystals was prepared in a similar way with a ball-milling time of 94 h. The powder mixtures with and without β-Si_3N_4 seed crystals were die-pressed under 20 MPa and isostatically pressed under 200 MPa. The specimens were sintered for 4 h at 2273 K in 300 MPa N_2 gas. Then, additional firing was conducted at 2473 K for 4 h in 300 MPa N_2 gas. This firing process was repeated four times, with a maximum

firing time of 16 h. The microstructures of the sintered materials were observed using scanning electron microscopy (SEM), and the sizes of elongated grains were evaluated by the line interception method. The bulk densities of the sintered specimens were determined by the Archimedes method.

Evaluation of thermal conductivity

Thermal diffusivity and specific heat at room temperature were measured by the laser flash method using a ruby laser and InSb for the infrared detector. Disk specimens were ground to the dimensions of 10 mm in diameter and 2 mm in thickness. Thermal conductivity (κ) was calculated according to the equation:

$$\kappa = \alpha C_p \rho \tag{1}$$

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

Results

The bulk densities of the specimens were almost equal to the theoretical density of Si_3N_4, indicating that complete densification occurred. Figure 1 shows scanning electron micrographs of the materials: sintered for 12 h with β-Si_3N_4 seed crystals (SC12, Figs a and b), sintered for 16 h with β-Si_3N_4 seed crystals (SC16, Figs c and d), and sintered for 12 h without β-Si_3N_4 seed crystals (NC12, Figs e and f). All the samples had a duplex microstructure composed of elongated grains in a matrix of relatively small-grained silicon nitride. Note that the area ratios of the grains are almost 90% in all the samples presented in Fig. 1. Furthermore, the aspect ratio of the elongated grains in SC12 (~3.0) was greater than that of NC12 (~2.2). This suggests that the growth of rod-like β-Si_3N_4 grains is initiated from the β-Si_3N_4 seed crystals. Grain growth was promoted with a longer firing time (SC12 and SC16) at 2473 K. The average length of elongated β-Si_3N_4 grains was 48 μm and the average diameter was 16 μm for SC12, while the average grain sizes of SC16 were 58 μm in length and 22 μm in diameter.

Figure 2 shows the thermal conductivities calculated with Eq. (1) for SC12, SC16 and NC16 and plotted *vs.* the firing time at 2473 K. The highest isotropic thermal conductivity of 149 W m^{-1} K^{-1} was obtained for SC12. This value is higher than that previously reported (120 W m^{-1} K^{-1}) [10] due to the promotion of further grain growth, although a much higher value (162 W m^{-1} K^{-1}) has been reported for a material that had a one-dimensionally controlled microstructure and exhibited anisotropy [11]. A prolonged firing time of 16 h resulted in a reduction in thermal conductivity to approximately 120 W m^{-1} K^{-1}, indicating the existence of an optimal firing time. The reasons for this reduction in thermal conductivity are discussed in the following section.

Discussion

Silicon nitride is usually densified in a liquid-phase sintering process using sintering aids such as MgO, Y_2O_3, $Y_2O_3+Al_2O_3$ and $Y_2O_3+Nd_2O_3$ because of its low self-diffusion coefficient. Controlling the additives that remain as the amorphous phase in grain boundaries is considered to be important for improving thermal conductivity in these classes of silicon nitride ceramics. Figure 3 shows the thermal conductivity of silicon nitride ceramics as a function of the average short diameter of elongated grains. According to the theory of Goldsmidt and Penn [14], the thermal conductivity of sintered materials is governed by phonon scattering at grain boundaries and is proportional to the square root of the grain size ($\kappa \propto D^{1/2}$, κ: thermal conductivity, D: grain diameter) up to its intrinsic value, which is assumed to be in the range of 180–320 W m^{-1} K^{-1} [15]. As shown in Fig. 3, the relationship between thermal conductivity (κ) and the average short diameter of elongated grains (D) agrees well with this theory in a small diameter range of less than 5 μm. This is consistent with the reduction in the number of grain boundaries crossing the heat flux as the grain size increases.
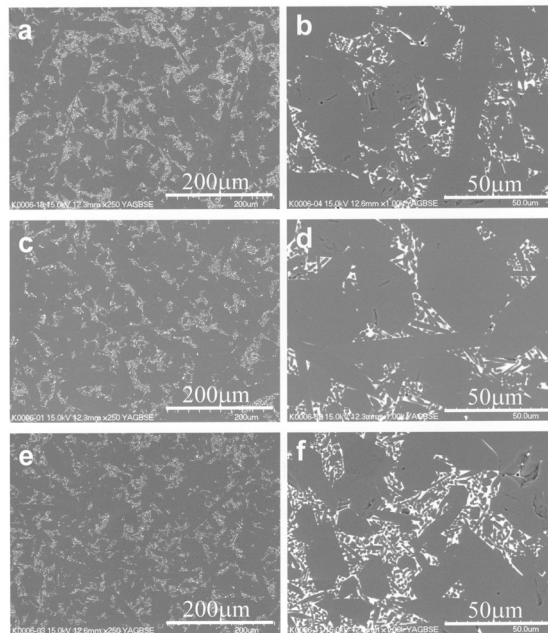

Fig. 1 Scanning electron micrographs of silicon nitride materials sintered at 2473 K. a – sintered for 12 h with β-Si_3N_4 seed crystals (SC12), c – sintered for 16 h with β-Si_3N_4 seed crystals (SC16), and e – sintered for 12 h without β-Si_3N_4 seed crystals (NC12); b, d and f – are close-up photos of a, c and e, respectively

The NC12 and SC12 samples showed little difference in their microstructures, although there was a large difference in their thermal conductivities. This can be ex-
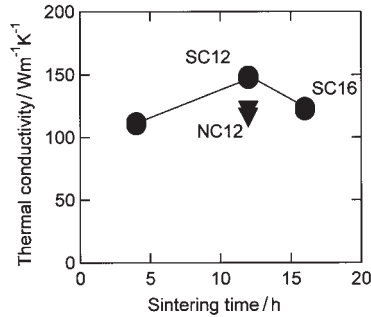
Fig. 2 Thermal conductivity of silicon nitride sintered at 2473 K as a function of sintering time

plained by the reduction of defect concentrations, which work as point defects to scatter phonons, and by the use of high-quality seed crystals as nuclei for grain growth that presumably resulted in the generation of elongated silicon nitride grains with a low defect concentration. We have previously reported on the relation between the defect concentration of elongated grains and thermal conductivities of sintered materials [11, 16]. Some defects and second phases are present inside the elongated grains of a sintered body with low thermal conductivity developed from the addition of low-quality seed crystals. On the other hand, there are almost no defects and second phases in a sample with high thermal conductivity developed from the addition of high-quality seed crystals. These results indicate that the presence of defects and second phases inside the elongated grains strongly affects the thermal conductivity of sintered β-Si$_3$N$_4$ materials.

Furthermore, grain growth leads to deviations from the theory proposed by Goldsmid and Penn as shown in Fig. 3. From the SEM results (Fig. 1 c and d), the crystal growth of the elongated grains in the sample with 16 h of additional firing seems almost spatially completed. At the final stage of liquid-phase sintering, grain
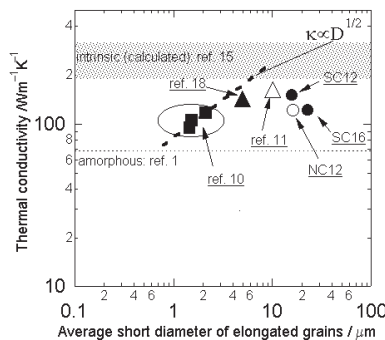

Fig. 3 Thermal conductivity of silicon nitride as a function of the average diameter of the short axis in elongated silicon nitride grains. Additional data points are also plotted in the figure

growth is generally accelerated due to the decrease of the diffusion length in the liquid [17]. This may induce defects, such as stacking faults and dislocations in elongated grains because of the interaction between the grains. Therefore, the reduction of thermal conductivity due to defects becomes dominant in the stage of elongated grain growth, in spite of a decrease in the number of grain boundaries. A similar explanation can be applied to the high thermal conductivity observed for the one-dimensional controlled samples. In this case, controlling the crystal growth direction by one-dimensional seeding works to prevent interaction between the elongated grains during grain growth, and that seems to result in high thermal conductivity.

Improvement of thermal conductivity can be achieved in the following ways. The grain boundary phase is designed by choosing a suitable additive composition to avoid the formation of low thermal conductive phases. Furthermore, the shape and orientation of elongated grains are controlled to one-dimensional and two-dimensional microstructures so as to reduce the number of grain boundaries. Reduction of the defects in the elongated grains is also effective in improving thermal conductivity, and the use of synthesized high-quality β-Si_3N_4 whisker-like crystals can reduce the defect concentration.

Conclusions

An advanced silicon nitride material was produced from β-Si_3N_4 powder doped with Y_2O_3–Nd_2O_3 and sintered at 2273 K, and the effects of the addition of seed crystals and additional firing time at 2473 K on thermal conductivity were examined. The addition of the β-Si_3N_4 seed crystals was found to be effective in improving thermal conductivity due to their low defect and impurity concentrations. A microstructure with elongated silicon nitride grains and a longer firing time both led to higher thermal conductivity. However, an extremely long firing time of 16 h at 2473 K resulted in reduced thermal conductivity, which is attributed to the effect of new defects generated inside the grains. As a result, the highest thermal conductivity of 149 W m^{-1} K^{-1} was attained for the silicon nitride material with elongated grains, and this material was produced with a high firing temperature of 2473 K and a long firing time of 12 h.

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