Fabrication and characterization of SiC rod-particulate-reinforced reaction-bonded Si$_3$N$_4$ composites

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Abstract

Reaction-bonded Si$_3$N$_4$ composites reinforced by whisker-like SiC rod particulates have been fabricated by nitriding SiC$_{rod}$-containing Si powder compacts, which were presintered to a controlled density by spark plasma sintering (SPS). The effects of processing parameters, including presintered density, SiC$_{rod}$ content, nitriding temperature, atmosphere pressure and heating rate on the nitridation reaction were investigated. It was found that the addition of SiC$_{rod}$ to Si powders led to easier control of complete nitridation compared to the case of pure Si powder compacts, probably because the SiC$_{rod}$ not only acted as diluting filler to suppress the rapid rise in temperature resulting from an SHS-like reaction between Si and N$_2$, but also provided paths for diffusion of reactant gases. The density of the reaction-bonded Si$_3$N$_4$–50 vol% SiC$_{rod}$ composites was increased up to near 90% which is quite a lot higher than that of conventional reaction-bonded Si$_3$N$_4$ ceramics, by using SPS to improve the density prior to nitridation. The relative density increased from ∼70 to 90% after the nitridation without appreciable dimensional change, being characteristic of reaction-sintering. As the reinforcement in the reaction products, the SiC$_{rod}$ improved Young's modulus and bending strength both at ambient and elevated temperatures, as well as thermal and electric conductivity. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; Mechanical properties; Reaction bonding; SiC particulates; Si$_3$N$_4$; Spark plasma sintering; Thermal properties

1. Introduction

Considerable efforts have been made during the past two decades to develop silicon nitride (Si$_3$N$_4$) and its related ceramics for high-temperature structural applications by utilizing its feasibility of microstructural tailoring for improving mechanical properties. Two major processes can be used for fabricating Si$_3$N$_4$ ceramics: (1) liquid phase sintering of submicron Si$_3$N$_4$ powders with oxide sintering aids; and (2) the reaction-bonding process by the direct nitridation of Si powder compacts in either nitrogen or ammonia gas. At present, it seems that the first process is predominantly used for the fabrication of high-strength Si$_3$N$_4$ ceramics. However, the reaction-bonding process is unique, in that densification occurs without any sintering additive and macroscopic dimensional changes.[1–3] That is because the niitridation of Si is accompanied by 22% volume expansion that occurs in the void space of the Si powder compact. The problems pertaining to the reaction-bonded Si$_3$N$_4$ (RBSN) are high porosity (about 20%) and incomplete nitridation. Usually the green density of the starting Si powder compact is at the level of 60%, which results in the low final density less than 80% even after complete nitridation. Increasing the green density of Si compacts should be a solution. Theoretically, it is the assumption that complete nitridation RBSN with density exceeding 91% can be formed from a Si powder compact with a density > 75%.

Since the nitriding reaction, $3Si(s) + 2N_2 (g) = Si_3N_4 (s)$, is highly exothermic, the nitridation of a Si powder compact may proceed at a manner of SHS (self-propagating high-temperature synthesis),[4–6] resulting in incomplete nitridation and a poor microstructure with large pores and grains. Complete nitriding conditions of Si have been extensively studied not only for the formation of RBSN but also for the synthesis of Si$_3$N$_4$ powder. In our previous study,[7] we found that the addition of inert fillers into the reactant compacts was effective to control the nitriding process. In the present study, whisker-like SiC particulates were used as the diluting fillers, which were also expected to improve the mechanical properties of the resultant products. Fig. 1 illustrates the proposed process for fabricating RBSN composites. The green compacts of premixed Si and

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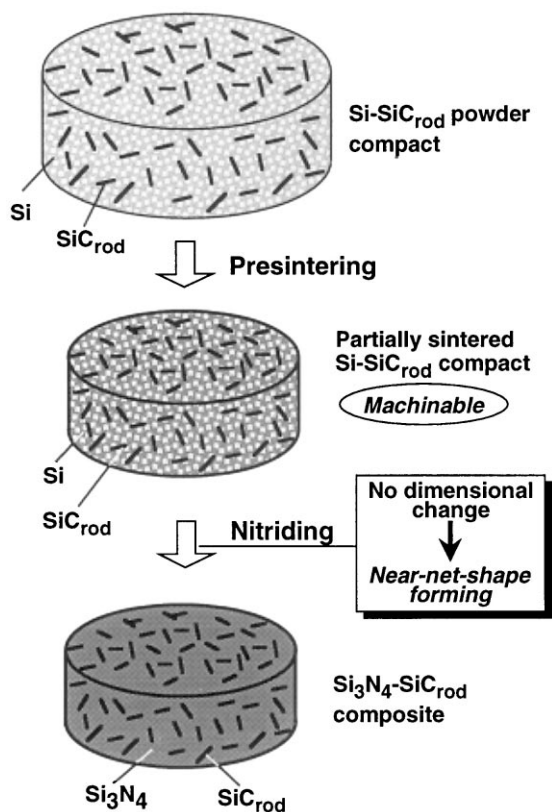*E-mail address:* jf-li@material.tohoku.ac.jp (J.-F. Li).

Fig. 1. Schematic illustration of the proposed process for fabricating reaction-bonded Si_3N_4 matrix composites with SiC reinforcement.

Fig. 2. SEM micrographs of the starting materials. (A) Si powder milled for 48 h, (B) as-received SiC rod-shaped powder.

whisker-like or rod-shaped SiC particulate (SiC_{rod}) were presintered to a predetermined density, then nitrided under an optimal condition to SiC-reinforced RBSN with high density.

2. Experimental

2.1. Starting powder

Commercial Si powder (under 200 mesh, 99.9% purity, Mitsuwa Kagaku Yakuhin Co. Ltd., Japan) and rod-shaped SiC powder (SiC_{rod}, diameter 2.5 μm, aspect ratio 6, Tokai Carbon K. K., Japan) were used as the starting materials. The Si powder was pulverized by ball-milling in acetone solution for 48 h using a jar and balls made of Si_3N_4 ceramics, and then the SiC_{rod}, powder was added to the slurry and mixed for the final 1 h to prepare the Si–SiC_{rod} powder mixture. Fig. 2 shows the SEM micrographs of the ball-milled Si and as-received SiC_{rod} powders. As shown in Fig. 2(A), the milled Si powder had a wide particle size distribution in the range from 10 μm to submicron in diameter. The SiC_{rod} contents for the powder mixtures designed for various Si_3N_4 to SiC ratios after complete nitridation were shown in Table 1. After milling, the slurry was dried at 80°C in air. Relatively uniform mixing was
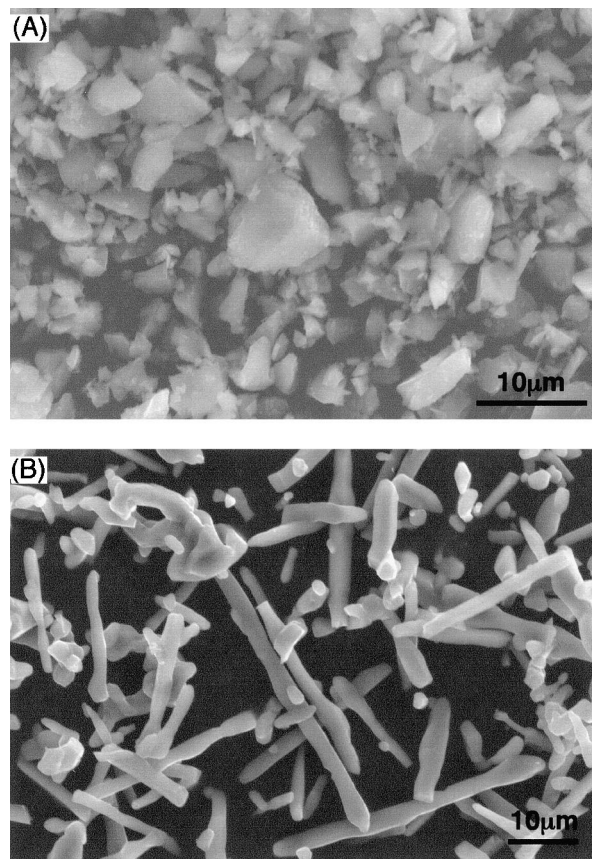
Table 1
Sample name, composition and weight gain after complete nitridation

Sample name	Reactant	Product	Weight gain after complete nitridation, (%)
SN	Si	Si_3N_4	66.5
SN2SC	Si + 23.37vol%SiC	Si_3N_4 + 20vol%SiC	46.8
SN3SC	Si + 34.36vol%SiC	Si_3N_4 + 30vol%SiC	38.7
SN4SC	Si + 44.8lvol%SiC	Si_3N_4 + 40vol%SiC	31.4
SN5SC	Si + 54.95vol%SiC	Si_3N_4 + 50vol%SiC	24.8

achieved without marked breaking or pulverization of the SiC rods.

2.2. Presintering and nitriding

As shown in Fig. 1, the Si and Si–SiC_{rod} compacts to be used as the preforms for subsequent nitridation must be presintered to the proper high density. Although pressureless sintering in an Ar atmosphere was attempted, it was found that the density remained below 60% even for the pure Si powder compact due to the poor sinterablity of Si. Instead, the presintering was conducted by using spark plasma sintering (SPS).[8,9] The powder was filled into a carbon-foil lined graphite die of

the SPS apparatus and pressed at 20–100 MPa. The temperature was increased at rates as high as 110–170°C min^{-1} by applying a high dc current to the die and specimen. After presintering, the surface layer was well removed using SiC paper.

The presintered Si and Si–SiC$_{rod}$ compacts were placed in a BN crucible and nitrided with high purity (99.999%, O$_2$ < 0.3 ppm) nitrogen gas in an electric furnace with a graphite heater. The furnace temperature was increased to 1350°C at a fast rate of l0°C min^{-1}, then to a peak nitriding temperature (1450°C) within 30 h in most cases. After nitriding, the samples were cooled at a rate of 10°C min^{-1}. The change in weight before and after nitridation was measured and used as a measure of nitridation rate.

2.3. Characterization

The nitrided specimens were analyzed by X-ray diffractometry (XRD) with Cu-K_α radiation. Scanning electron microscopy (SEM) was used to investigate the microstructural change after nitriding.

Fracture strength was measured from room temperature to 1400°C in a 4-point bending test with lower and upper spans of 20 and 10 mm, respectively. The bending test was performed at a crosshead speed of 0.5 mm min^{-1} by using specimens of nominal dimensions 24×2.0× 1.5 mm. The elevated temperature strength was measured in an argon atmosphere using a SiC jig built in the chamber of an electric furnace. The deflection at the center of the bending specimen could be directly monitored, and was used to calculate Young' modulus. The prospective tensile surfaces were ground and polished to achieve a mirror-like surface finish prior to mechanical testing. Fracture toughness was measured by the Vickers indentation microfracture (IM) technique under a load of 98 N, and the values were calculated using the equation proposed by Niihara et al. for median cracks.[10] Vickers microhardness was measured at a load of 9.8 N. Electrical conductivity was measured using two-probe method. Thermal diffusivity and heat capacity were measured by the laser flash method. Thermal conductivity was calculated from the product of thermal diffusivity, density and heat capacity.

3. Results

3.1. Density control of Si and Si–SiC$_{rod}$ by SPS

Theoretically, to obtain reaction products with high density it is necessary to increase the green density of the starting compact. On the other hand, complete nitridation became remarkably difficult with increasing density of Si phase.[7] To control the density before nitridation, the relationship between relative densities of Si and Si–SiC$_{rod}$, compacts and SPS processing temperatures and

pressures was investigated, and the results were shown in Fig. 3. The density increased sharply in the pure Si powder compact with increasing temperature, whereas the density changed slightly in the composite compact with the highest volume fraction of SiC$_{rod}$ even at high temperatures near the melting point of Si when the pressure was 20 MPa. This result indicated that the sintering of Si matrix in the composites was significantly retarded by the presence of the whisker-like SiC rod. However, the density of the Si–SiC$_{rod}$ could be improved effectively by increasing the pressure. The presintered density for the composites must be set higher to obtain the same density after nitridation, since the density increment during nitridation becomes smaller for the sake of the decreased volume of Si matrix as the SiC$_{rod}$ content is increased. For example, the relative densities are required to 75.0 and 82.3% respectively for the Si and Si–SiC$_{rod}$ compacts to be nitrided to the nearly same density of monolithic Si$_3$N$_4$ and Si$_3$N$_4$–50% SiC$_{rod}$ composites. To meet such requirements, the optimal SPS process parameters were determined for each composition.

3.2. Nitridation

XRD analysis and weight measurement showed that nitridation was found to be strongly dependent on the nitriding temperature, i.e. furnace temperature. The melting point of Si appeared to be a critical temperature, just above which fast nitridation occurred with little residual silicon. Fig. 4 shows the XRD patterns of the Si–SiC$_{rod}$ compacts nitrided at three temperatures around the melting point of Si. As seen in Fig. 4, almost no traces of Si remained after nitriding at l450°C, whereas the specimen nitrided at 1400°C contained a lot of unreacted Si phases. Lei[11] has given the reasons for the
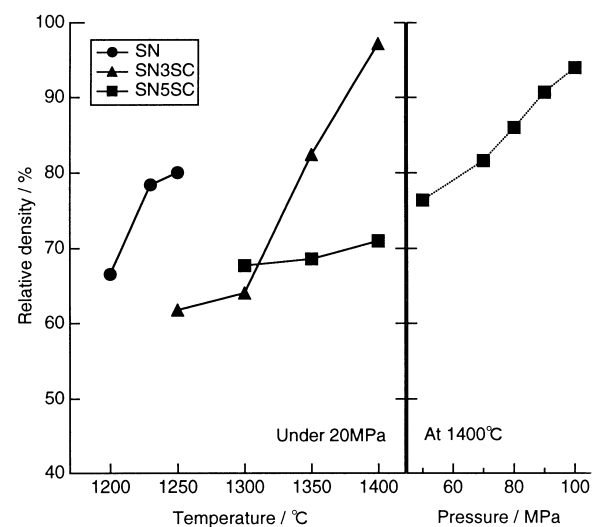

Fig. 3. Change in relative density of the Si–SiC$_{rod}$ compacts presintered by SPS, (left) at different temperature under 20 MPa, (right) under different pressures at 1400°C.

enhanced nitridation at temperatures just above the melting point of Si.

For the same nitriding temperature, the quality of the reaction products was affected by heating rate and sequence. Because no significant nitridation occurred below l350°C, as indicated by the result of Fig. 4, the heating rate below 1350°C had less effect on the nitridation; the heating rate used actually was 10°C min^{-1}. Increasing the temperature from 1350 to 1450°C at the same 10°C min^{-1} speed, usually resulted in the formation of large melted Si drops outside the nitrided specimen. It was found that increasing the furnace temperature slowly from 1350 to 1450°C effectively solved such a problem. In the following experiments, the nitriding was conducted by increasing the furnace temperature from 1350 to 1450°C within 30 h. However, even under such a "mild" nitriding condition, the melted Si drops tended to appear on the surface of the specimens of low content of SiC$_{rod}$. For example, Fig. 5 shows the appearance of the nitrided specimens without SiC$_{rod}$ and with the highest content of SiC$_{rod}$ (specimen SN5SC). The melting-out of Si was much more severe in the former than the latter. All the following nitriding experiments were conducted by increasing the furnace temperature from 1350 to 1450°C within 30 h.

To determine the optimal nitriding condition, experiments were conducted under three different pressures (0.1, 1 and 10 MPa) of N$_2$. It was found that the nitridation was somewhat less complete at 0.1 MPa, but no apparent difference was observed at two other higher pressures. Nevertheless, the resulting reaction product at 10 MPa was composed of more α-Si$_3$N$_4$, particularly with many α-Si$_3$N$_4$ whiskers being on the surface as compared with that nitrided at 1 MPa. Being characteristic of reaction-sintering, the dimensional change

accompanied by the nitridation was found to be less than 0.7%. As shown in Table 2, the densities were increased by a factor of ~1.1 after nitriding. A further higher density than 2.85 g cm^{-3} could be reached by accordingly increasing the density of Si–SiC$_{rod}$ compacts, but in this case complete nitridation became much more difficult.

3.3. Property and microstructure

Fig. 6 shows the change in room-temperature bending strength as a function of SiC$_{rod}$ volume fraction. To eliminate the influence of density on strength, the strength data for each composition with almost the same density near 2.6 g cm^{-3} were compared in Fig. 6. Of course, higher strength was actually obtained in the composition of 50 vol% SiC$_{rod}$ by increasing the density, as will be shown later. The addition of SiC$_{rod}$ had

Fig. 5. Appearances of the nitrided specimens. (A) pure Si, (B) the composition designed to Si$_3$N$_4$-50vol%SiC after complete nitridation. The nitriding N$_2$ gas pressure was 1 MPa, and the furnace temperature was increased slowly from 1350 to 1450°C within 30 h.
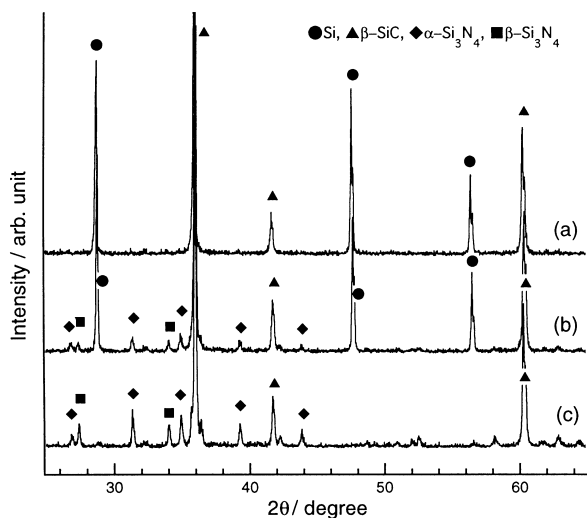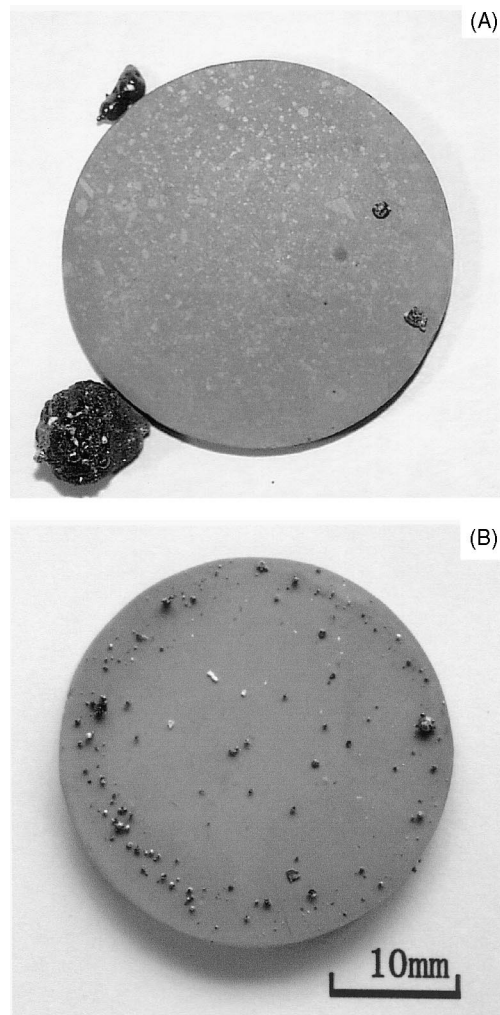
Fig. 4. XRD patterns of sample SN5SC nitrided at different temperatures for 2 h at a N$_2$ gas pressure of 1 MPa. (a) 1350°C, (b) 1400°C, (c) 1450°C.

Table 2
Density and dimensional change in the SN5SC specimens during the nitridation

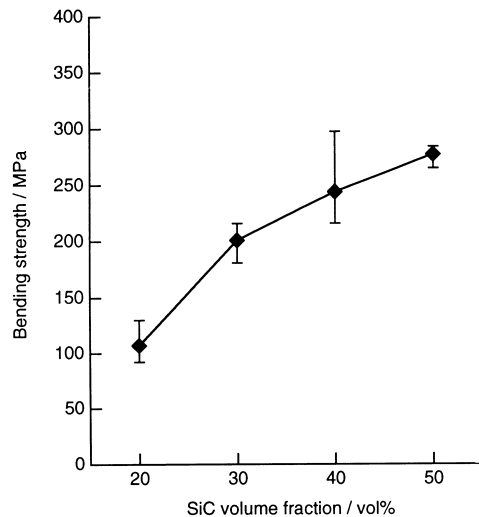| Nitriding condition		Density before nitridation (g cm^{-3})	Density after nitridation (g cm^{-3})	Average dimensional change[a] (%)
Peak temperature (°C)	Nitriding pressure (MPa)			
1450	1	2.36	2.61	+ 0.48
1450	1	2.54	2.81	+ 0.06
1450	10	2.38	2.60	+ 0.64
1450	10	2.50	2.80	+ 0.23
1600	10	2.57	2.85	+ 0.31

[a] " + " Means expansion.

Fig. 6. Change in 4-point bending strength as a function of SiC volume fraction. The densities were near 2.6 g cm^{-3} (relative density is about 78%) for all the compositions (nitrided at 1 MPa).

dual roles in improving the strength. First, the strength was increased mainly due to the well-known whisker-reinforcement effect.[12,13] Additionally, the SiC_{rod} addition enabled the formation of more uniformly nitrided microstructures that consequently achieved higher strength. The microstructural difference is displayed in Fig. 7.

For the same composition, say Si_3N_4–50% SiC_{rod}, the strength was strongly dependent on the density, as shown in Fig. 8. The highest bending strength obtained in the present study reached 408 MPa, in the Si_3N_4–50% Si_{rod} specimen nitrided at 10 MPa of N_2, with a density of 2.80 g cm^{-3}. Even for the same density, the specimens that were nitrided at 10 MPa showed higher strength than that at 1 MPa. Heinrich[14] has investigated the mechanical properties of conventional monolithic RBSN ceramics nitrided at different N_2 pressures and found that the bending strength was increased by more than 50% when the nitriding pressure was increased from 0.1 to 50 MPa. The strength improvement has been concluded to be due to the effect of microstructural
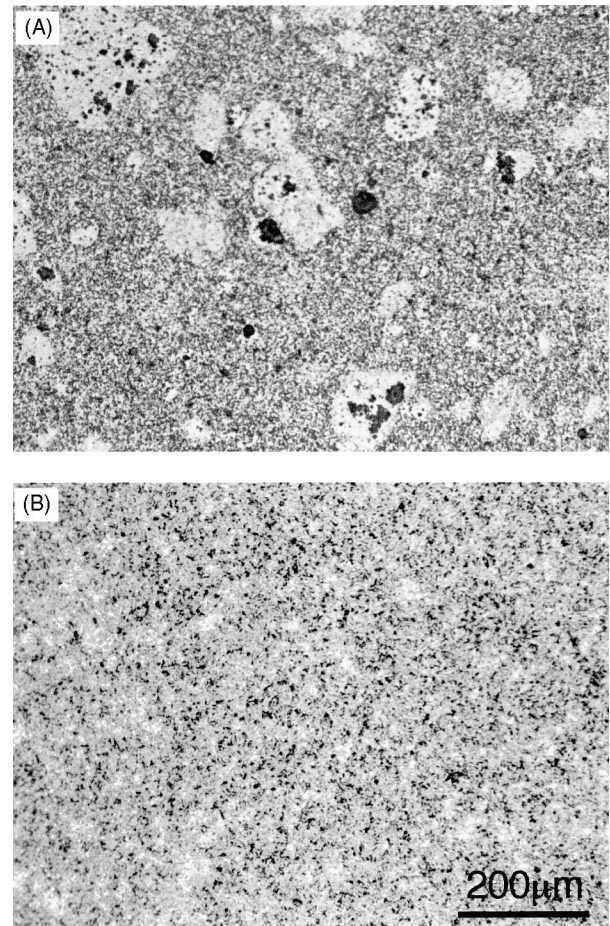

Fig. 7. Optical micrographs of the polished surfaces of nitrided samples. (A) pure Si, (B) the composition designed to Si_3N_4–50vol%SiC after complete nitridation. Both were nitrided at 1 MPa.

refinement achieved at high N_2 pressure.[14] The strength of the specimen with a density of 2.85 g cm^{-3} was not higher than that with a density 2.80 g cm^{-3}, probably because a certain amount of residual Si phases remained in the specimen when the density of the corresponding preform was too high for complete nitridation.

Fig. 9 shows the SEM micrographs of the polished and fractured surfaces of the specimens (SN5SC) with the highest strength. The SiC rod particulates keeping
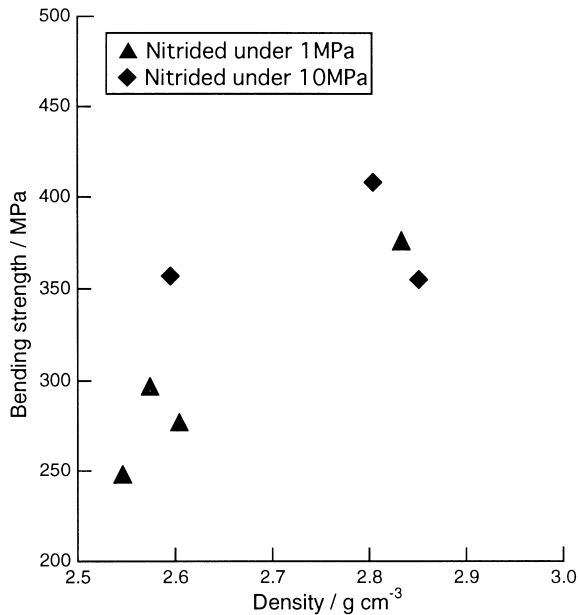
Fig. 8. Relationship between bending strength and density in the Si$_3$N$_4$-50vol%SiC composites.

Fig. 9. Microstructure of the synthesized Si$_3$N$_4$-50vol% SiC, composite (nitrided at 10 MPa). (A) polished surface, (B) fractured surface.

their as-received forms were often observed on the polished and fractured surfaces, and pores were usually in the surrounding of the SiC particulates. The porosity was estimated to be near 10%, in good agreement with the above density (2.80 g cm^{-3}). Most of the Si$_3$N$_4$ grains are well bonded so that transgranular fracture was the main mode in the Si$_3$N$_4$ matrix. Apart from such Si$_3$N$_4$ grains with diameters of 2–3 μm, some small particles, which are likely to be α-Si$_3$N$_4$ resulting from the reaction between gaseous Si and N$_2$,[3] were observed on the surfaces of the large Si$_3$N$_4$ grains and SiC$_{rod}$ particulates. Actually, the XRD analysis showed that the volume fraction of α-Si$_3$N$_4$ formed in the Si-55% SiC$_{rod}$ compact was ∼50%. The nitrided microstructure is fairly dense, with pores which are smaller and uniformly distributed.

Fig. 10 shows the temperature dependence of Young's modulus and bending strength of the strongest SN5SC specimen. It is known that reaction-bonded Si$_3$N$_4$ ceramics usually exhibit little strength degradation at elevated temperatures because of the non-existence of oxide additives, as compared with normally sintered Si$_3$N$_4$ ceramics with oxide grain boundary phases. The present composites also had a good refractory characteristic. No significant decreases in the Young's modulus and bending strength were observed at temperatures below 1100 and 1300°C, respectively. The bending strength decreased apparently, above 1300°C, possibly due to creep deformation of the reaction-bonded Si$_3$N$_4$ matrix and the interfaces between the matrix and SiC rods. Because Young's modulus was fairly high and the stress–strain curves were almost liner before rupture, even at 1400°C, suggesting that the present Si$_3$N$_4$–SiC$_{rod}$ composites were almost free of unreacted Si phases.
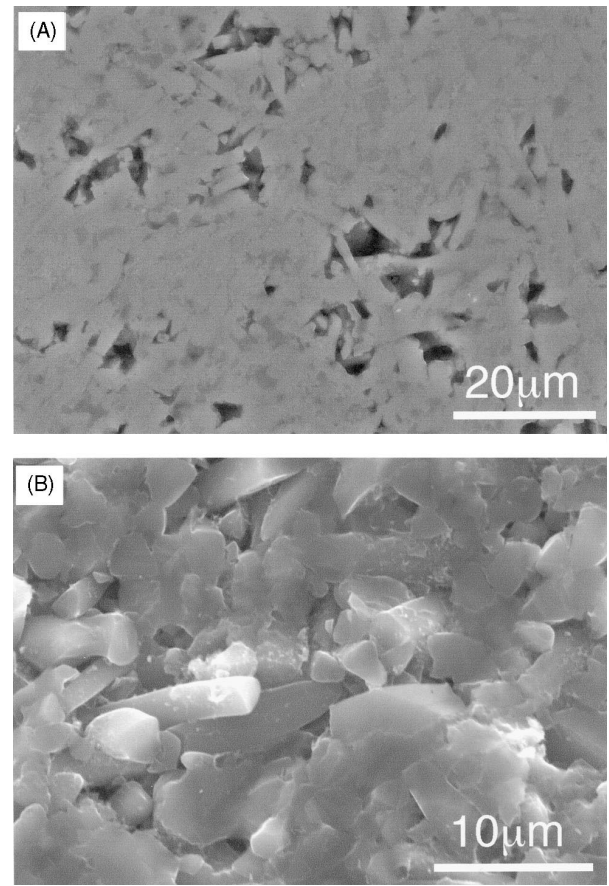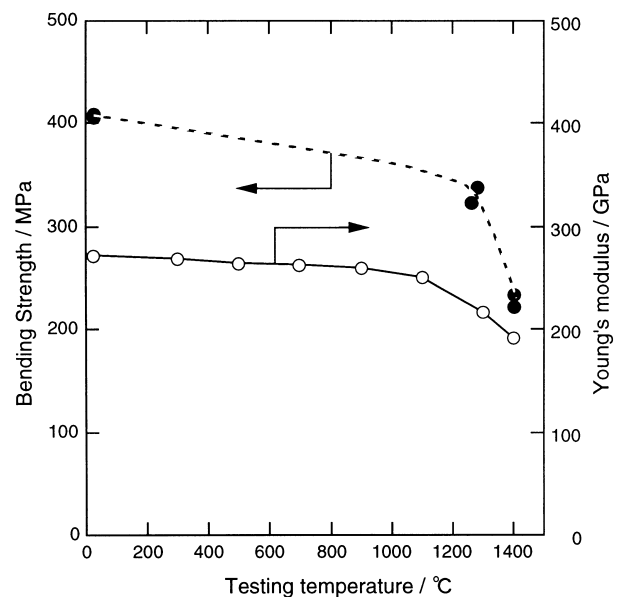

Fig. 10. Temperature dependences of bending strength and Young's modulus of the Si$_3$N$_4$-50vol% SiC$_{rod}$ composites (nitrided at 10 MPa).

Table 3
Properties of the obtained Si_3N_4–50%SiC_{rod} composites

Nitriding condition		Vickers hardness (GPa)	Fracture toughness (MPa m$^{0.5}$)	Thermal conductivity (W m^{-1} K^{-1})	Electric conductivity (S cm^{-1})
Peak temperature (°C)	Nitriding pressure (MPa)				
1450	1	7.0	4.3	67.74	82.2
1450	1	11.8	4.3	–	–
1450	10	9.4	4.4	63.13	147
1450	10	13.5	4.3	99.19	133
1600	10	9.9	3.9	–	–

Table 3 summarizes other important properties, such as Vickers hardness, fracture toughness, thermal conductivity and electric conductivity. Compared with conventional monolithic RBSN ceramics,[1–3] the present composites possess not only higher fracture strength as shown above, but also higher fracture toughness due to the SiC_{rod} reinforcement. Remarkably high thermal conductivity was obtained in the present composites, which may lead to excellent thermal shock resistance. Good electric conductivity is due to the connectivity of SiC_{rod} reinforcement.

4. Discussion

As mentioned above, the problem encountered in the reaction-bonded Si_3N_4 ceramics is that the large amount of exothermic heat released during nitriding results in the rise in local temperature inside the reactant compact and consequently causes the melting of Si on a macroscopic scale. The formation of liquid Si inhibits diffusion of nitrogen from outside the reactant compact due to collapse of the pore openings. SiC_{rod} first acted as diluting fillers to suppress the rapid rise in temperature in the reactant compacts due to an SHS-like reaction between Si and N_2. This is because the SiC rods separated the reaction areas and partially absorbed the heat that was released by the nitridation of the neighboring Si particles. As a result, nitridation reaction in a burst form was suppressed with increasing SiC_{rod} content. The addition of diluting fillers is often used to control reaction temperature for the reaction synthesis of ceramic powders.[15] If the nitriding reaction begins below the melting point of Si (1414°C) and proceeds at an adiabatic state, the thermodynamic calculation based on the following reaction showed that the adiabatic temperature (T_{ad}) can be reduced by 760°C in the composite reactant consisting of Si-54.95vol% SiC_{rod} (the starting composition of the SN5SC sample)

$$3Si + 2N_2 + xSiC = (Si_3N_4)_{1-x}(SiC)_x$$
$$\Delta H_{298} = -723 kJ/mol$$
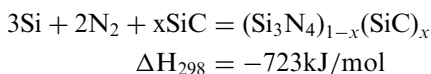
That is why the Si meltout almost disappeared in the SN5SC composition. Additionally, the network of whisker-like SiC rod particulates created many channels for the path of nitrogen to diffuse from outside the reactant compacts, leading to complete nitridation.

5. Conclusions

1. Reaction-bonded Si_3N_4 matrix composites reinforced with SiC rod-particulates have been fabricated by nitriding Si powder compacts containing the SiC rod-particulates. High-density composites can be obtained by increasing the density before nitridation by means of spark plasma sintering (SPS).
2. The addition of SiC_{rod} to Si powders leads to easier control of complete nitridation compared with the case of pure Si compacts, probably because the addition of the inert SiC particulates not only suppresses the rapid rise in temperature by diluting the exothermic reaction between Si and N_2, but also provides paths for the diffusion of reactant gases.
3. Keeping the characteristics of the reaction bonding process, the density increases from −70% for the presintered Si–SiC_{rod} compacts to 90% for the reaction products without appreciable dimensional change.
4. Because of the reinforcement effects of SiC_{rod}, the obtained composites show higher Young's modulus and bending strength both at ambient and elevated temperatures, as compared with monolithic reaction-bonded Si_3N_4. Thermal and electhc conductivity are also high because of the connectivity of SiC_{rod} particulates.

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