Fabrication of Reaction-Bonded Si_3N_4 Matrix Composites Reinforced with Rod-Shaped SiC Particulates by Direct Nitridation

Jing-Feng Li, Shunsuke Satomi, and Ryuzo Watanabe

Graduate School of Engineering, Tohoku University, Aoba, Aramaki-aza-Aoba, Sendai 980-77 Japan
Fax: 81-22-217-7374, e-mail: jf-li@material.tohoku.ac.jp

Abstract: A two-step synthesis process has been proposed to fabricate Si_3N_4-SiC composites, in which the matrix is reaction-bonded Si_3N_4 and the reinforcement is rod-shaped SiC. The process involves two steps: first to consolidate a mixed Si/SiC_{rod} compact to a sufficiently high relative density, then to nitride Si matrix to Si_3N_4 with concurrent densification resulting from the nitridation reaction. In the present study, the Si/SiC_{rod} powder compacts were hot isostatically pressed, then nitrided by heating from 1350 to 1450 ℃ in N_2 atmosphere at a constant rate. It was found that a higher nitridation rate was obtained due to the SiC addition, even though nitridation reaction became more difficult to take place with increasing Si matrix density. The SiC_{rod} addition acted as diluter to lower the rapid temperature rise due to a SHS-like reaction between Si and N_2. As a result, the melting of Si powder, often observed in such processes, was effectively suppressed. Thus, a reaction-bonded $Si_3N_4/50\%SiC_{rod}$ composite with a relative density of 86%, being denser than normal reaction-bonded Si_3N_4 ceramics, was fabricated by the direct nitridation of the Si matrix by heating from 1350 to 1450 ℃.

Key words: Reaction-bonded silicon nitride, ceramic composite, reaction synthesis, direct nitridation

1. Introduction

Recently, considerable efforts have been made to develop silicon nitride 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_3N_4 ceramics: (1) liquid phase sintering of submicron-sized Si_3N_4 powders with oxide sintering aids of several percentages; and (2) reaction bonding process by the direct nitridation of Si powder compacts with either nitrogen or ammonia. At present, it seems that the first process is predominantly used for the fabrication of high-strength Si_3N_4 ceramics. However, the reaction bonding process is unique, in that densification occurs without dimensional changes, providing a near net-shape process that enables the formation of complex shapes[1-3]. That is because the formation of Si_3N_4 by nitridation 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_3N_4 (RBSN) are high porosity (about 20%) and incomplete nitridation[4]. Usually Si powders with diameters of 5 to 15 μm are used as starting materials for producing RBSN, but the green density obtained by normal forming process is near 64%, which results in the low final density of about 78% as can be simply calculated by 22% increase in density due to the nitridation. As a solution to the first problem, it is considered that RBSN with higher density could be formed by increasing the green density of

Si compacts through pre-sintering prior to the nitridation. Theoretically, RBSN with density exceeding 91% can be formed, if a Si compact is denser than 75% on the assumption that the nitridation will be completed.

On the other hand, complete nitridation condition of Si has been extensively studied not only for the formation of RBSN but also for the synthesis of Si_3N_4 powder. The basic nitriding reaction is as follows[1,2]:

$$3Si(s) + 2N_2(g) = Si_3N_4\ (s)$$
$$\Delta H_{298} = -723\ kJ/mol \qquad (1)$$
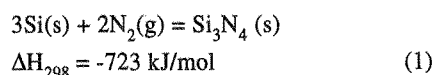
It has been revealed that the large amount of exothermic heat during the nitriding reaction causes the formation of silicon melt-out, consequently incomplete nitridation and a poor nitridation microstructure with large pores and grains[1]. A nitrogen-demand approach has been proposed to control the nitriding exotherm or the temperature of nitriding reaction[1]. One other method for controlling the reaction temperature is to add an inert filler, which does not enter the nitriding reaction, but decreasing the adiabatic temperature[5]. If SiC particulates are incorporated into Si powders, it can be expected that SiC plays double roles in lowering reaction temperature and improving the mechanical properties of RBSN due to composite effects. Figure 1 schematically illustrates the proposed process for fabricating RBSN based composites by the direct nitridation method.
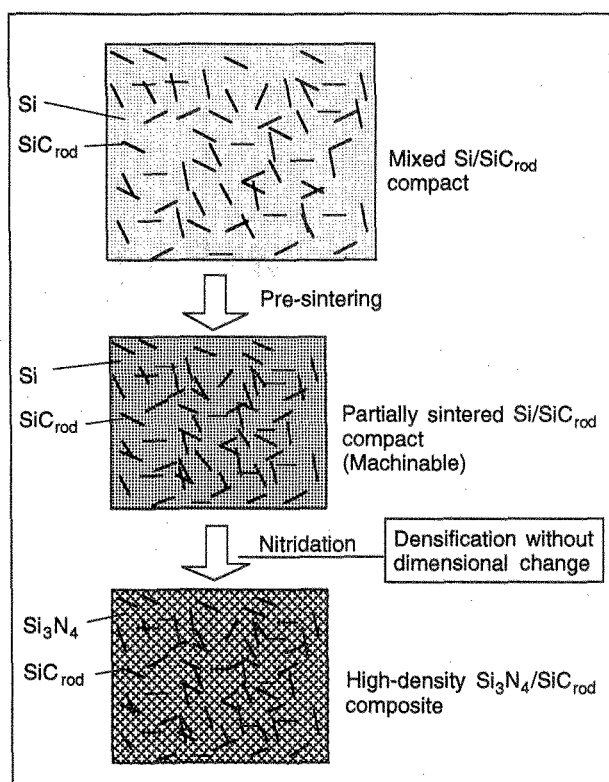
Fig. 1 The proposed process for fabricating RBSN composites with high density.

Therefore, in the present study, rod-shaped SiC particulates (SiC_{rod}) were used as the diluting filler and reinforcement. The green compact of premixed Si and SiC_{rod} was consolidated to a predetermined density, and the nitridation reactions were investigated by under different nitriding conditions, such as temperature and gas pressure to establish the process for fabricating SiC-reinforced RBSN with high density.

2. Experimental Procedure

Commercial Si powder (under 200 mesh, 99.9% purity, Mitsuwa Kagaku Yakuhin K. K., Osaka) and rod-shaped SiC powder (diameter 2.5 μm, aspect ratio 6, Tokai Carbon K. K., Tokyo) were used as starting materials. The Si powders were further pulverized by ball-milling in acetone solution for 48 h using a jar and balls made of Si_3N_4 ceramics, whereas the SiC powder was added to the slurry and mixed for 1 h after milling the Si powder for 47 h to prepare the Si/SiC_{rod} powder mixture. About 23.4 and 55 vol% SiC_{rod} were mixed with Si powder to obtaine 20 and 50 % SiC-reinforced RBSN after complete nitridation as shown in Table 1. After milling, the slurry was dried at 80 ℃ and then deagglomerated with a mortar and pestle. Figure 2 shows the SEM micrographs of ball-milled Si powders, rod-shaped SiC and their mixture. The rod-shaped SiC particulates were relatively uniformly dispersed without significant breaking or pulverization. Cylindrical powder compacts of 10 mm in diameter and 5 mm in
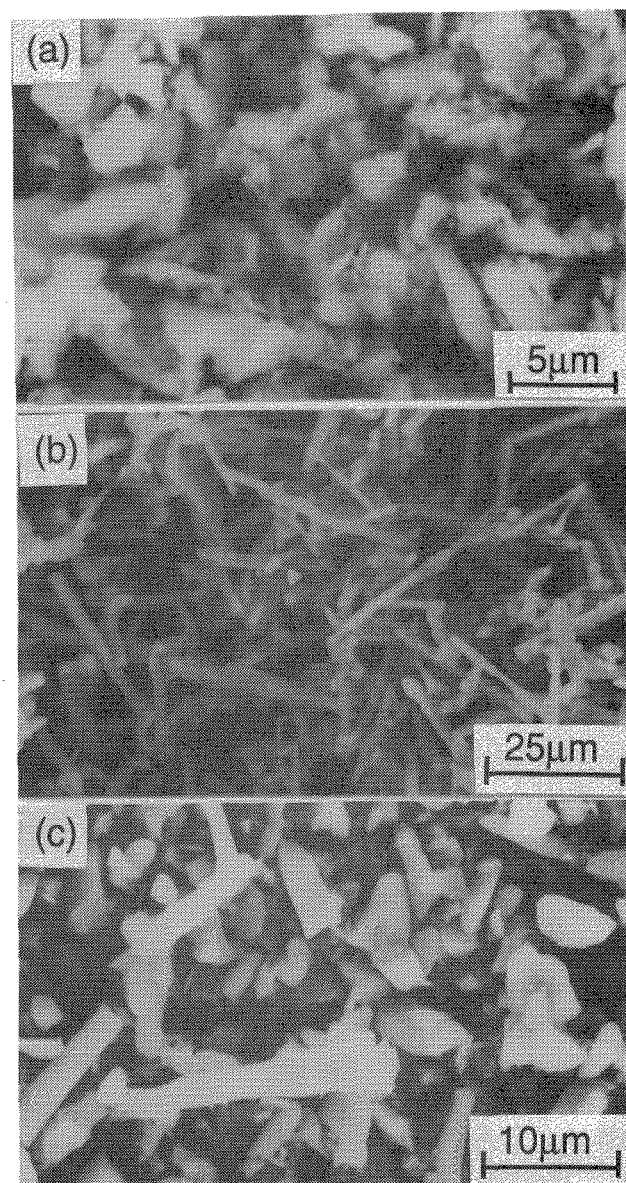

Fig.2 SEM micrographs of the starting powders used the nitridation in the present study. (a) Si powder (after ball-milling for 48 h); (b) Rod-shaped SiC; (c) Mixture of Si/SiC (sample SN5SC).

height were formed by die-pressing at 120 MPa in a carbon steel die and subsequently cold-isostatically pressed at 200 MPa to 56-60% of theoretical density.

In order to increase the density prior to nitridation, the Si and Si/SiC_{rod} green compacts were hot-isostatically pressed (HIP). Although pressureless sintering in an Ar atmosphere was

Table 1 The compositions before and after nitridation.

Sample name	Reactant	Product	Ideal weight gain ratio
SN	Si	Si_3N_4	0.67
SN2SC	Si+23.37vol%SiC	Si_3N_4+20vol%SiC	0.47
SN5SC	Si+54.95vol%SiC	Si_3N_4+50vol%SiC	0.25

attempted, it was found that density could not be raised to 75 %, which is required for obtaining RBSN denser than 95 %. Instead, glass-encapsulated hot-isostatic pressing (HIP) was performed in the present study. The glass-encapsulated specimens were hot-isostatically pressed at 970-1300 °C and 200 MPa for 1 h under Ar gas as a pressure-transmitting medium.

The pre-sintered Si and Si/SiC$_{rod}$ compacts prepared by the above HIP process were placed in a BN crucible and nitrided in an electric furnace with a graphite heater. High purity (99.999%, O_2<0.3 ppm) nitrogen gas was used. Heating rate was 10 °C/min from room temperature to 1350 °C. The weight change before and after the nitridation was measured and related to nitridation rate (α) by the following equation.

$$\alpha = \frac{(m_a-m_b)}{\beta m_b} \times 100\% \qquad (2)$$

where m_a and m_b are specimen weight after and before nitriding reaction, respectively, β is the weight change ratio after complete nitridation depending on the Si content, as shown in Table 1.

The bulk density was determined from the size and weight measured respectively with a micrometer and an electronic balance. For the Si/SiC$_{rod}$ composite compacts, their matrix (Si) relative density (ρ_m), which is needed for comparing the nitridation rate with that of pure Si compacts, is calculated using the following equation on the assumption that the porosity is in the Si matrix:

$$\rho_m = \frac{(1-f)\rho_c}{1-f\rho_c} \qquad (3)$$

where ρ_c is the relative density of the composite, and f is the volume fraction of SiC$_{rod}$.

The nitrided samples were analyzed by X-ray diffractometry (XRD), and the nitridation rate was also estimated from the intergrated intensities of the diffraction peaks of each phase[6]. Scanning electron microscopy (SEM) was used to observe the microstructural change during the nitridation.

3. Results and Discussion

3.1 Densification of Si and Si/SiC$_{rod}$ compacts by HIPing

To determine the HIP-sintering condition suitable for preparing Si and Si/SiC$_{rod}$ compacts with a matrix relative density of about 75%, the relationship between relative densities of Si and Si/SiC$_{rod}$ compacts and HIP-sintering temperature was investigated as shown in Fig.3 (a). A pure Si powder compact densifies very sharply with increasing HIP-sintering temperature; whereas the SiC$_{rod}$ additions retard the densification significantly. The relative density of Si matrix obtained from the data of Fig.3 (a) is replotted against the HIP-sintering temperature, as shown in Fig. 3 (b). Because here Si matrix density of 75% is required, the following nitridation experiments were mainly performed on the Si,

Si/23.4%SiC$_{rod}$ and Si/55%SiC$_{rod}$ compacts prepared by HIP-sintering at 970, 1000 and 1300 °C, respectively.

3.2 Effect of Si matrix density on the nitridation

Figure 4 shows nitridation rate determined from the weight change according to Eq. (2), as a function of Si matrix relative density. The data shown in Fig. 4 represent the highest value obtained under different nitriding conditions for each
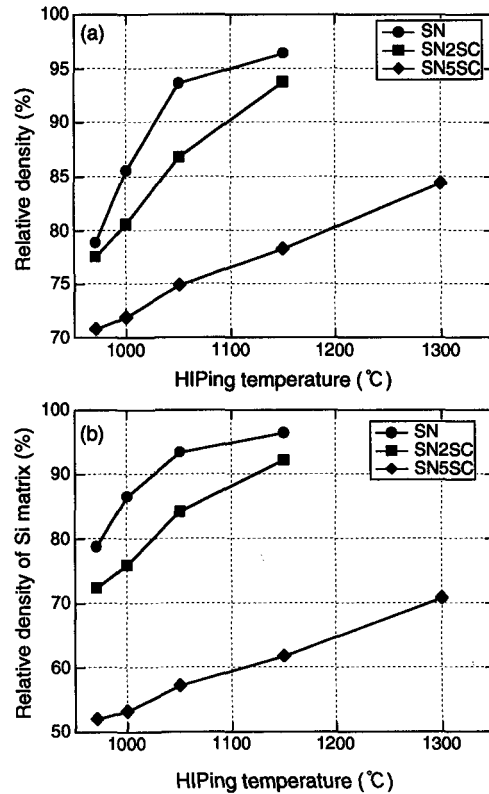

Fig. 3 Variations in relative density of the Si/SiCrod composite (a) and the Si matrix (b) as a function of HIPing temperature.
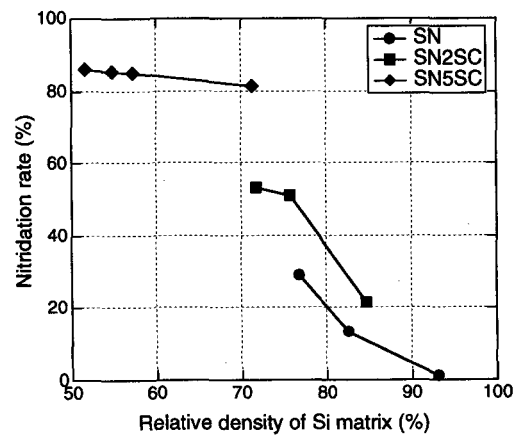

Fig. 4 Nitridation rate estimated from weight gain after the nitriding reaction in the pure Si and Si/SiC$_{rod}$ composites as a function of the Si matrix density.
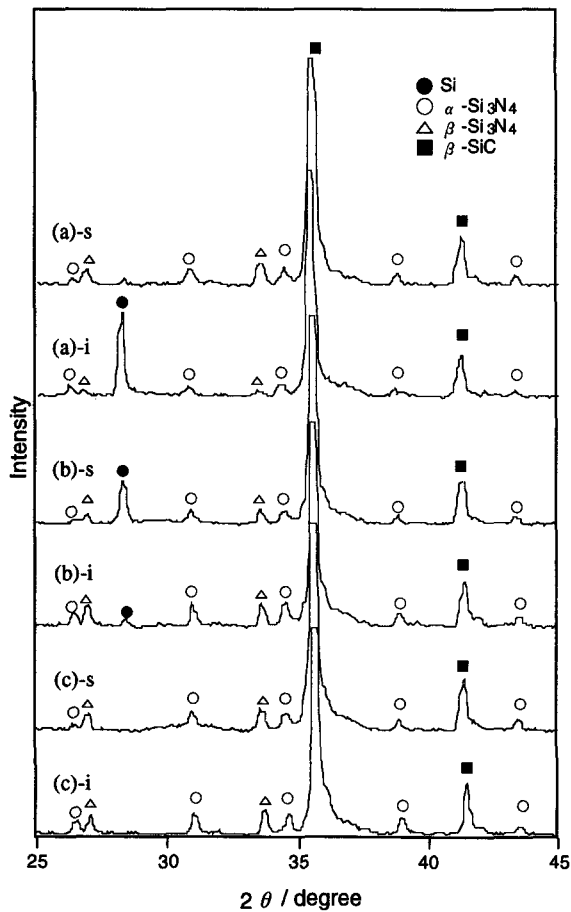
Fig. 5 X-ray diffraction patterns obtained on the surface (s) and inside (i) for the SN5SC sample after nitriding reactions: (a) 1350 to 1420 ℃, within 2 h; (b) 1350 to 1450 ℃, within 2 h; (c) 1350 to 1450 ℃, within 30 h.
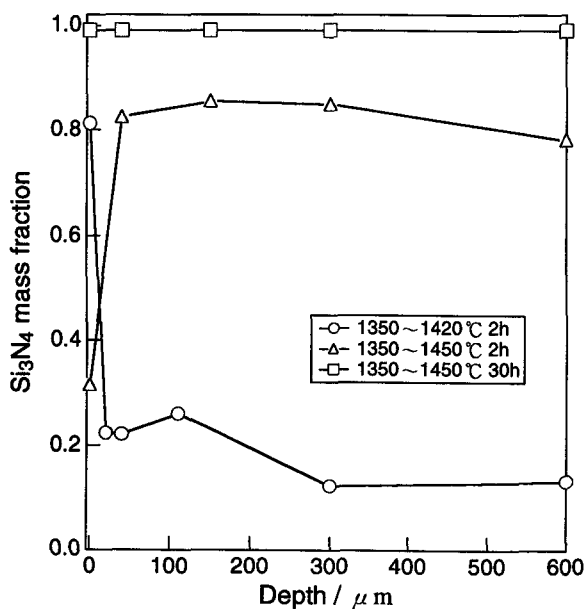

Fig. 6 Variation in Si_3N_4 mass fraction estimated from X-ray diffraction patterns as a function of depth from the specimen surface.

sample. In general, it can be seen that nitridation rate decreases as the Si matrix becomes more dense. It is considered that there are two major factors responsible for decreasing the nitridation rate as a result of densification: (1) increased difficulty for nitrogen gas to move into the interior; (2) area reduction of Si particles exposed to nitrogen gas. Nevertheless, even though the matrix density is almost the same, for example, between 71% and 76%, higher nitridation rate can be obtained in the Si/SiC_{rod} composites, especially in the SN5SC sample containing $55\%SiC_{rod}$. This result has shown the advantage of SiC_{rod} additions into Si powder probably because SiC_{rod} plays an important role in controlling the reaction temperature as described in the introduction. Therefore, the following experiments were concentrated on the nitridation of the $Si/55\%SiC_{rod}$ compact prepared by HIP-sintering at 1300 ℃, with a relative density of 84%, corresponding to Si matrix density of 71%.

3.3 Nitridation to $Si_3N_4/50\%SiC_{rod}$ composite.

It was found that the nitridation reaction was accelerated by increasing nitriding temperature. However, fast nitridation reaction is usually accompanied with the local melting of Si. Nevertheless, in the $Si/55\%SiC_{rod}$ compact, almost no silicon melt-out occurred even if the nitridation was carried out above 1450 ℃, whereas a lot of many melted Si drops appearred on the surface of the Si and $Si/23.4\%SiC_{rod}$ samples after nitriding above 1400 ℃. This result indicated that the overheating due to the exothermal reaction was effectively suppressed by incorporating sufficient amounts of SiC as the diluting filler to Si matrix . Furthermore, as reported by the other investigation[1], a higher nitridation rate was obtained by heating from 1350 to 1450 ℃ at a low constant rate rather than soaking at a fixed temperature (furnace temperature).

Figure 5 shows XRD patterns obtained in the surface and inside of the $Si/55\%SiC_{rod}$ compact nitrided under three conditions, and their composition distributions along the depth direction are shown in Fig. 6. When the nitriding reaction was conducted by heating from 1350 to 1420 ℃ within 2 h, Si_3N_4 was only formed on the surface with a lot of unreacted Si remaining inside. When the peak temperature was raised to 1450 ℃, only a thin surface layer contained unreacted Si, but the whole sample was about 80% Si_3N_4 after the nitriding reaction. The nitridation rates measured from the weight gains according to Eq. (2) also increased from 30 to 73 %, when the peak temperature was increased from 1420 to 1450 ℃. Although the nitridation can be enhanced greatly by increasing the nitriding temperature, a small amount of silicon melt-out was formed when the $Si/55\%SiC_{rod}$ compact was nitrided by heating from 1350 to 1450 ℃. As a result, relatively large amounts of Si phase were detected by XRD on the surface in spite of the high Si_3N_4 fraction inside the compact. However, at a lower heating rate from 1350 to 1450 ℃, i.e., as the heating period was prolonged to 30 h, more higher nitrida-
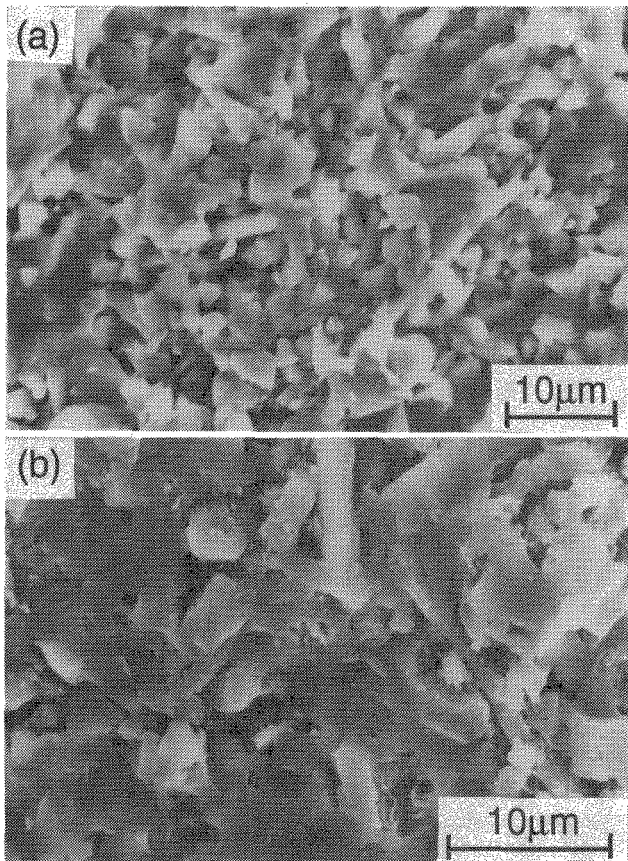
Fig. 6 Comparison of the SN5SC sample (designed to be Si_3N_4/ 50%SiC_{rod} after complete nitridation) before (a) and after (b) nitridation.

ticles or whiskers can be observed in the space between the formed Si_3N_4 grains and SiC_{rod} particulates. The XRD showed that about 50 % α-Si_3N_4 was formed in the Si/55%SiC_{rod} compact. The small particle and whisker are considered to be α-Si_3N_4, because α-Si_3N_4 tends to form on the surface from a gas phase reaction[2]. The nitridation reaction at high temperatures near the melting point of silicon would cause the Si evaporation, and consequently resulting in a concurrent reaction bewteen gaseous Si and N_2.

4. Summary

(1) The synthesis of reaction bonded Si_3N_4 (RBSN) matrix composites with whisker -like SiC reinforcements was attempted in the present study. To obtain RBSN/SiC composite with high density, the SiC-dispersed Si powder compacts were consolidated to a predetermined density by hot-isostatic pressing (HIP), then nitrided by continuous heating from 1350 to 1450 ℃.

(2) Nitridation reaction becomes difficult to occur with increasing Si matrix density. However, it was found that a higher nitridation rate was also obtained due to the SiC addition. The SiC addition plays an important role in lowering the rapid temperature rise in the reactant due to a SHS-like reaction between Si and N_2. As a result, the formation of Si meltout, often observed in the pure Si powder compact, was effectively suppressed in Si/SiC composite powder compact. The nitridation within the Si/SiC compacts can be further increased by heating from 1350 to 1450℃ at a slow constant rate.

(3) The relative density of the obtained Si_3N_4/50%SiC_{rod} composite was about 86%, being higher than conventional reaction-bonded Si_3N_4.

tion rate was obtained without the formation of silicon melt-out. As shown in Fig. 6, the Si matrix was almost totally and uniformly converted to Si_3N_4 by continuously heating from 1350 to 1450℃ within 30 h. However, the nitridation rates obtained under this condition was about 89 % if measured from the weight gains according to Eq. (2), being lower than the value shown in Fig. 6. As described above, the Si/SiC_{rod} compact used for the nitridation had a matrix relative density of 71%. If the Si matrix was completely nitrided, the matrix density will increase to 86.6%. This means that a Si_3N_4/50%SiC_{rod} composite with a relative density of about 93 % can be obtained. In fact, the bulk density of the nitrided SN5SC sample was measured to be 2.73 g/cm^3, approximately being 86% as composite relative density. Therefore, the evaporation of Si and decomposition of the formed Si_3N_4 during the nitriding reaction probably occurred, consequently the weight gain was lower than that expected from an ideal nitridation reaction as shown in Eq. (1).

Figure 7 shows the SEM micrographs of the fractured surfaces of the Si/SiC_{rod} compact before and after nitridation. The nitridation resulted in an obvious change in matrix microstructure with increased density. In the nitrided sample, some small par-

References:
1) J. A. Mangels, *Am. Ceram. Soc. Bull.*, **60** [6] 613-617 (1981).
2) G. Ziegler, J. Heinrich, G. Wötting, *J. Mater. Sci.*, **22**, 3041-3086 (1987).
3) H. M. Jennings, B. J. Dalgleish, P. L. Pratt, *J. Mater. Sci.*, **23**, 2573-2583 (1988).
4) H. Abe, M. Kawai, T. Kanno, K. Suzuki, *"Ceramic Science Series 5: Engineering Ceramics"* (edited by T. Yamaguchi and H. Yanagida), Gihodou, (1988), pp.94.
5) R. A. Cutler, K. M. Rigtrup and A. V. Virkar, *J. Am. Ceram. Soc.*, **75** [1] 36-43 (1992).
6) A. Shinmi, J. Koike, S. Kimura, K. Maruyama, H. Oikawa, *J. Ceram. Soc. Japan*, **104** [7] 662-667 (1996).