

Thermogravimetry, Differential Thermal Analysis, and Mass Spectrometry Study of the Silicon Nitride-Boron Carbide-Carbon Reaction System for the Synthesis of Silicon Carbide-Boron Nitride Composites

Guo-Jun Zhang,*,*,‡ Jian-Feng Yang,*,§,¶ and Tatsuki Ohji*,†

Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Aichi 463-8687, Japan

Japan Science and Technology Corporation (JST) at AIST Chubu, Nagoya, Aichi 463-8687, Japan

Thermogravimetry, differential thermal analysis, mass spectrometry, and X-ray diffractometry were used to study the reaction process of the in situ reaction between Si₃N₄, B₄C, and carbon for the synthesis of silicon carbide-boron nitride composites. Atmospheres with a low partial pressure of nitrogen (for example argon + 5%-10% nitrogen) seemed to inhibit denitrification and also maintain a high reaction rate. However, the reaction rate decreased significantly in a pure nitrogen atmosphere. The experimental mass spectrometry results also revealed that B4C in the Si3N4-B4C-C system inhibited the reaction between Si₃N₄ and carbon and, even, the decomposition of Si_3N_4 . The present results indicate that boron could be a composition stabilizer for ceramic materials in the Si-N-C system used at high temperature.

I. Introduction

RAPHITIC, hexagonal BN-based composites are an important Jcomposite family that shows excellent thermal shock resistance, good thermal conductivity, a low thermal expansion coefficient, and high corrosion resistance under many corrosive circumstances, such as metal melts. In addition, BN composites exhibit self-lubrication, because of the graphitic hexagonal structure of BN, and excellent machinability when the BN fraction reaches ~20 vol%. Accordingly, BN composites have the potential for use in various industrial fields.¹⁻⁶

BN composites usually are fabricated by hot pressing mechanically mixed component powders²⁻⁶ or by mixing reactants that can form the component phases from in situ reactions.^{7–11} In our previous works, 12^{-15} the *in situ* reaction

$$Si_3N_4 + B_4C + 2C = 3SiC + 4BN$$
 (1)

was used to prepare SiC-BN composites with high strength, low elasticity, and good strain tolerance. Compared with the BN composites produced by hot pressing mechanically mixed component powders,12 the obtained in situ SiC-BN composites showed homogeneous microstructures with fine and isotropically distributed BN flakes located at the grain boundaries of the SiC.

According to thermodynamic calculations,¹² B₄C inhibits the reaction between Si₃N₄ and carbon to degas nitrogen, and this reaction has been verified by chemical analysis of the elements in composites obtained by in situ hot pressing.14,15 The present investigation focuses on analyzing the reaction process of Si₃N₄, B_4C , and carbon by thermogravimetry (TG), differential thermal analysis (DTA), mass spectrometry (MS), and X-ray diffractometry (XRD). The effect of various atmospheres on the reaction are discussed in this paper.

II. Experimental Procedure

The raw powders used were Si_3N_4 (E-10 grade, mean particle size 0.5 µm, oxygen content <2%, UBE Industries, Ltd., Yamaguchi, Japan), B₄C (F1 grade, particle size 1 µm, Denki Kagaku Kogyo Co., Ltd., Tokyo, Japan), carbon (No. 2600 grade, particle size 13 nm, Mitsubishi Chemical Corp., Tokyo, Japan), Al₂O₃ (particle size 0.2 µm, Daimei Chemical Co., Nagano, Japan), and Y2O3 (particle size 1.06 µm, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan). In previous work, 12,15 10 wt% Al₂O₃-Y₂O₃ (YA) additives (7:3 weight ratio of Al₂O₃:Y₂O₃) related to the SiC contents in the composites had been added to promote densification and reaction and to improve crystallization of the BN phase. To create a similar reaction condition in the chemical composition, 10 wt% YA additives related to the Si₃N₄ contents in the mixed powders were added in the present work. Three mixed-powder specimens were prepared by ball milling for 24 h in ethanol, using ZrO_2 (Y₂O₃) balls, and subsequently dried. The sample designations are given in Table I.

TG-DTA (Model 2020, MAC Science Co., Ltd., Yokohama, Japan) for the silicon nitride-boron carbide-carbon (SN-BC-C) specimen was conducted from room temperature to 1700°C, at a heating rate of 10°C/min, in flowing, high-purity argon, 95% argon + 5% nitrogen, 90% argon + 10% nitrogen, and nitrogen gas of 150 mL/min, to investigate the influence of various atmospheres on the reaction process. Measurement was performed twice for each condition, and very good repeatability was obtained. MS (TG-MS Analyzer, Shimadzu Corp., Kyoto, Japan) was conducted from room temperature to 1500°C, at a heating rate of 10°C/min, in flowing helium gas of 30 mL/min. The maximum temperature was 1700°C for the TG-DTA and 1500°C for the TG-MS experiments. The phase compositions of the SN-BC-C specimen (mixed powder compact formed by uniaxial pressing, under 60 MPa) pressureless heat-treated at various temperatures from 1200° to 1700°C, for 30 min, under 1 atm of nitrogen or argon, were determined by XRD (Model 2500V, Rigaku Denki Co., Tokyo, Japan), using CuKα radiation.

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Member, American Ceramic Society. [†]Synergy Materials Research Center, National Institute of Advanced Industrial

⁵Synergy Materials Research Center, Future 1997 Science and Technology. ⁴Now with Synergy Ceramics Laboratory, Fine Ceramics Research Association (FCRA), Nagoya, Aichi 463-8687, Japan. ⁸Japan Science and Technology Corporation. ⁴Now with Synergy Materials Research Center, AIST, Nagoya, Aichi 463-8686, Japan

Specimen		Chemical composition (wt%)				
	Actual chemical composition	Si ₃ N ₄	B ₄ C	С	Al ₂ O ₃	Y ₂ O ₃
(1) SN (2) SN–C (3) SN–BC–C	90 wt% Si ₃ N ₄ + 10 wt% YA 1 mol Si ₃ N ₄ + 2 mol C + 10 wt% YA related to Si ₃ N ₄ 1 mol Si ₃ N ₄ + 1 mol B ₄ C + 2 mol C + 10 wt% YA related to Si ₃ N ₄	90 78.66 60.05	0 0 23.66	0 13.47 10.28	7 5.51 4.20	3 2.36 1.80

III. Results

The TG-DTA results obtained from the SN-BC-C specimen in argon, with different partial pressures of nitrogen, are shown in Fig. 1. In all atmospheres, weight loss occurred after ~1150°C. However, the values of weight loss up to 1500°C decreased in the nitrogen-containing atmosphere, because of inhibited decomposition of Si₃N₄. On the other hand, Fig. 1 shows obvious differences in the DTA curves for the different atmospheres. In the atmospheres with a low partial pressure of nitrogen, a sharp exothermic peak occurred at temperatures >1700°C. The exothermic reaction was remarkably inhibited in the pure nitrogen atmosphere, but a small exothermic peak appeared before the large exothermic peak at 1590°C. This small exothermic peak moved to 1548° and 1536°C in atmospheres with 10% and 5% nitrogen, respectively. In the pure nitrogen atmosphere, only a small exothermic peak appeared. The results demonstrated that the rate of the exothermic reaction was very slow in a pure nitrogen atmosphere.

The XRD patterns of the SN–BC–C specimens heat-treated at 1200°–1700°C in nitrogen or argon, and that of the mixed raw powder, are shown in Fig. 2. At 1200°C, although the main reaction apparently had not occurred, all of the peaks for α -Si₃N₄ shifted slightly to larger diffraction angles in both atmospheres. Thus, some compositional change occurred with α -Si₃N₄, even at such low temperature. In addition, because of the addition of YA sintering aids, peaks corresponding to YO_{0.04}C_{0.5} (ICDD[¶] Powder Diffraction File Card No. 38-1113), Al₂OC (ICDD Card No. 36-0148), and Y₃Al₅O₁₂ (ICDD Card No. 09-0310) appeared at 1200°C. As the temperature increased, the peak for YO_{0.04}C_{0.5} disappeared in both the nitrogen and the argon atmospheres. On the other hand, the peak for Al₂OC disappeared in the nitrogen

[¶]International Centre for Diffraction Data, Newtown Square, PA.

atmosphere but became stronger in the argon atmosphere, and the peak for $Y_3Al_5O_{12}$ disappeared in the argon atmosphere but became stronger in the nitrogen atmosphere. Moreover, a peak possibly corresponding to Y_5Si_3C (ICDD Card No. 38-0794) appeared at >1450°C in the argon atmosphere. According to the peak intensities of the products BN and β -SiC and the reactants of Si_3N_4 and B_4C , we conclude that the reaction rate was much faster in the argon atmosphere.

MS was performed in a helium atmosphere on the three specimens listed in Table I, and the results are illustrated in Fig. 3 and Table II. As shown in Fig. 3(a), denitrification of all specimens began after $\sim 1000^{\circ}$ C and became substantial after $\sim 1300^{\circ}$ C. With the addition of carbon to the Si₃N₄, denitrification became more intense after $\sim 1400^{\circ}$ C. This finding suggests that the reaction

$$Si_3N_4 + 3C = 3SiC + 2N_2$$
 (2)

occurred intensely above this temperature, although the beginning temperature of the reaction calculated by thermodynamics was 1488°C.¹⁴ Denitrification in the SN–BC–C specimen decreased significantly (see also Table II) over that in either the SN or the SN–C specimen. This result cannot be explained by the decreased Si₃N₄ content caused in the SN–BC–C specimen by the addition of B₄C, compared with that in the SN or SN–C specimen (see Table I and Table II), but it is coincident with the thermodynamic analysis of the reaction system and the results of chemical composition analysis of the final composites prepared by hot pressing.^{14,15}

The degasification behavior of CO and CO₂ for the SN–C and SN–BC–C specimens was also different, as shown in Figs. 3(b) and (c). These figures show that CO was the main gas species evolved. For all specimens, the degasification of physically absorbed CO₂ occurred in the temperature range from room temperature to \sim 600°C, and the peak temperature was \sim 300°C (Fig. 3(c)). Meanwhile, as shown in Table II, the degasification of CO



Fig. 1. TG-DTA spectra of SN-BC-C specimen in various atmospheres.



Fig. 2. XRD patterns of SN-BC-C specimen pressureless heat-treated at 1200°-1700°C, for 30 min, in argon or nitrogen.

and CO_2 was less intense in the SN–BC–C specimen than in the SN–C specimen. Almost no CO or CO_2 could be detected in the SN specimen, except for physically absorbed CO_2 .

Although Si(g), Si₂N(g), Si₂(g), SiN(g), and SiO(g) also were observed by Rocabois *et al.*¹⁶ in the Si₃N₄ system under MS, and the existence of Al₂O(g) and Y₂O(g) was reasonably possible, the pressure of these substances would have been very low at the detector of the mass spectrometric apparatus at the temperature (\sim 250°C) used in the present work; consequently, no attention was paid to these substances in the current study.

IV. Discussion

 Si_3N_4 does not melt but, rather, sublimes at temperatures <1900°C under 1 atm of nitrogen gas:^{16,17}

$$\operatorname{Si}_{3}\operatorname{N}_{4}(s) \to 3\operatorname{Si}(s) + 2\operatorname{N}_{2}(g)$$
 (3)

High nitrogen pressure decreases the decomposition process. Si_3N_4 has been used to produce SiC whiskers, by reduction with carbon.^{18–20} In a nitrogen atmosphere, the reported reduction rate is lower, and thus, the reduction temperature is higher than in an argon atmosphere. Moreover, the morphology of the *in situ* formed SiC is dependent on the atmosphere.¹⁹

In the present investigation, similar results were obtained; that is, reaction (1) occurred rapidly in the argon atmosphere (Figs. 1 and 2). The reaction process was closely related to the decomposition process of the reactant Si_3N_4 . According to the calculated results of Greskovich and Procchazka,²¹ the equilibrium partial pressures of nitrogen gas resulting from the decomposition of Si_3N_4 at different temperatures are ~0.001 atm at 1400°C, 0.005 atm at 1500°C, 0.02 atm at 1600°C, and 0.1 atm at 1700°C. The current DTA results showed that reaction process (1) markedly decreased in the atmosphere with a nitrogen partial pressure of >0.1 atm (Fig. 1). Consequently, the following reaction sequence is suggested:

$$\operatorname{Si}_{3}\mathrm{N}_{4}(s) \to 3\mathrm{Si}(s) + 4[\mathrm{N}] \text{ or } 2\mathrm{N}_{2}$$

$$\tag{4}$$

$$B_4C + 4[N] \text{ or } 2N_2 \rightarrow 4BN + C \tag{5}$$

$$\operatorname{Si}(s) + \mathrm{C} \to \operatorname{SiC}$$
 (6)

where [N] represents a highly reactive nitrogen atom. The difference for specimen SN–BC–C was that B_4C in the reactants

"absorbed" the [N] or nitrogen gas, according to reaction (5), and decreased the denitrification (reaction (3)). This inference was confirmed by MS, as shown in Fig. 3(a).

As shown in Fig. 3(a) and Table II, although denitrification occurred in all three of the specimens, denitrification in the SN–BC–C specimen was the lowest in the experimental temperature range. This result indicates that the reactant B_4C not only "instantly absorbed" the [N] or nitrogen gas decomposed by Si_3N_4 but also inhibited the reaction between Si_3N_4 and carbon (reaction (2)), as expected from thermodynamic analysis.¹² This result may indicate that boron is a good composition stabilizer for ceramics in the Si-N-C system used at high temperature. However, nitrogen will still escape, because of reaction dynamics, including the diffusion and reaction rates of the atoms. This component of nitrogen escape could be decreased in the sintering process for making such *in situ* composites by either hot pressing or increasing the partial pressure of nitrogen in the sintering atmosphere.

A useful inference obtained from Fig. 1 is that using atmospheres with a controlled low nitrogen partial pressure—for example, argon + 5%-10% nitrogen—while making the composites should be beneficial for inhibiting the denitrification process while maintaining the high reaction rate (high exothermic).

The main reason for the degasification behaviors of CO and CO_2 was considered to be carbothermal reduction of the Al_2O_3 and Y_2O_3 additives, as well as the SiO₂ surface oxidation layer of Si₃N₄. Possible reactions related to the formation of CO and CO₂ are as follows:

$$Al_2O_3 + C \rightarrow Al_2O(g) + CO \text{ and/or } CO_2$$
 (7)

$$Al_2O_3 + C \rightarrow Al_2OC + CO \text{ and/or } CO_2$$
 (8)

$$Y_2O_3 + C \rightarrow Y_2O(g) + CO \text{ and/or } CO_2$$
 (9)

$$Y_2O_3 + C \rightarrow YO_{0.04}C_{0.5} + CO \text{ and/or } CO_2$$
(10)

$$YO_{0.04}C_{0.5} + Si \rightarrow Y_5Si_3C + CO \text{ and/or } CO_2$$
(11)

$$SiO_2 + C \rightarrow SiC(s) + CO \text{ and/or } CO_2$$
 (12)

$$\operatorname{SiO}_2 + \operatorname{C} \rightarrow \operatorname{SiO}(g) + \operatorname{CO} \operatorname{and/or} \operatorname{CO}_2$$
 (13)

Calculations made from the amounts of CO and CO_2 , summarized in Table II, and comparison with the starting compositions of the mixed powders, shown in Table I, indicate that not all of the YA

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Fig. 3. MS results for (a) nitrogen, (b) CO, and (c) CO₂.

additives were carbothermally reduced according to reactions (7)–(11). This finding implies that some reasons must exist for the different degasification behaviors in these specimens. In addition, because of reaction (11), the XRD peaks for silicon, formed by reaction (4), were not detected (Fig. 2). Meanwhile, our results suggest that reactions (8), (10), and (11) are faster in the argon atmosphere than in the nitrogen atmosphere, so that almost no $Y_3Al_5O_{12}$ forms at temperatures >1450°C in the argon atmosphere.

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Table II.Accumulated Weight Loss ofVarious Gases by Degasification during MSMeasurements from Room Temperature to1500°C in Helium

	Weight loss (%)			
Specimen	N ₂	СО	CO ₂	
SN	0.630	0.087	0.104	
SN–C	0.783	4.166	0.325	
SN-BC-C	0.344	2.467	0.191	

In regard to the different degasification behaviors of CO and CO_2 for the specimens, one of the main reasons for the lower degasification of CO and CO_2 in the SN–BC–C specimen is considered to be the kinetic competition of reaction (1) with reactions (7)–(13) (contending for carbon). On the other hand, in the case of the SN–BC–C specimen, another explanation may exist for part of the difference in the degasification behaviors of CO and CO_2 , based on the thermodynamic calculation. For example, another reaction might occur in the presence of B_4C :

 $3\mathrm{SiO}_2 + \mathrm{B}_4\mathrm{C} + 2\mathrm{C} \rightarrow 2\mathrm{B}_2\mathrm{O}_3(l,g) + 3\mathrm{SiC}(s) \tag{14}$

The formed B_2O_3 would either produce a glass phase with the sintering additives Al_2O_3 and Y_2O_3 or partially evaporate as B_2O_3 gas. In either case, the formation of CO or CO₂ would be decreased by the formation of B_2O_3 .

Meanwhile, the results demonstrated in Fig. 2 and Table II indicate that the reaction process under the current condition of pressureless heat treatment is much different from that under the hot-pressing condition reported in our previous work.12,14 Previously, we reported no obvious compositional changes when hot pressing was used to prepare SiC-BN composites in an argon atmosphere. This finding points out that the above carbothermal reduction reactions can be inhibited by hot pressing, through preventing the emittance of the gas products CO and/or CO2. In addition, under the present pressureless heat treatment, the rate for reaction (1) (Fig. 2) was much slower than that under hot pressing, where the reaction was almost complete at 1700°C in an argon atmosphere.¹⁴ Thus, applied stress must be beneficial to reaction (1), by increasing the density of the specimen and the contact surfaces of the reactant particles. This finding implies that the reaction process of reaction (1) is diffusion controlled.

V. Conclusions

The reaction process of the *in situ* reaction between Si_3N_4 , B_4C , and carbon was studied by TG, DTA, MS, and XRD. The reaction process proved to be closely related to the decomposition process of Si_3N_4 . Atmospheres with a low partial pressure of nitrogen gas—for example, argon + 5%–10% nitrogen—could inhibit denitrification and, at the same time, maintain a high reaction rate. The reaction rate decreased significantly in a pure nitrogen atmosphere, according to the weakened exothermic peak on the DTA curve. The obtained experimental results also revealed that B_4C in the reaction system Si_3N_4 – B_4C –C inhibited reaction between Si_3N_4 and carbon and, even, the decomposition of Si_3N_4 , itself. In other words, boron should be a good composition stabilizer for ceramic materials in the Si-N-C system used at high temperature.

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