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Oxidation resistance of hot-pressed SiC–BN composites

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Abstract

The oxidation resistance of SiC–BN composites with different BN content hot-pressed from Si_3N_4, B_4C and C was investigated. The oxidized products of SiC and BN were identified to be SiO_2, C and B_2O_3, N_2. SiO_2 and B_2O_3 could further form a borosilicate glass which covered the surfaces of the samples and withstood oxidation because of its flowability and self-healing. The oxidation resistance of the SiC–BN composites in static air atmosphere deteriorated with the increase of temperature as well as of the BN content.

Keywords: B. Composites; D. SiC; BN; Oxidation

1. Introduction

Silicon carbide (SiC) is a candidate material for high temperature structural applications because of its good mechanical properties, and excellent corrosion and oxidation resistance [1,2]. Boron nitride (BN) is incorporated into SiC ceramics to obtain higher thermal conductivity, lower thermal expansion coefficient at high temperature, and hence more excellent thermal shock resistance [2–5]. As SiC–BN composites are generally designed for high temperature structural applications, their oxidation behavior becomes an important issue.

Although the oxidation behavior of SiC and BN ceramics has been investigated for many years, the oxidation mechanisms of SiC–BN composites have not yet been well clarified. The aim of this paper is to investigate the oxidation resistance of hot-pressed SiC–BN composites versus the BN content at high temperature in static air atmosphere.

2. Experimental procedure

The SiC–BN composites were fabricated by the following reaction [5]:

$$Si_3N_4 + B_4C + 2C = 3SiC + 4BN \tag{1}$$

The volume percent of SiC and BN in the composite obtained according to reaction (1) were 46.29% and 53.71%, respectively. The BN content could be adjusted by adding SiC or BN powders in the composite. Al_2O_3 and Y_2O_3 were added as sintering additives. The total content of Al_2O_3–Y_2O_3 additives by a weight ratio of 7:3 was designed to be 10 wt% in the composites. For a comparative study, a monolithic SiC sample was also hot-pressed by using β-SiC powder and additives. With regard to sample designation, B20, for example, meant that the BN content in the composites was 20 vol.%. Five compositions have been investigated, i.e. B0, B20, B40, B53 and B60. The green bodies were hot-pressed at 25 MPa first at 1700 °C for 60 min and then at 1800 °C for 30 min. At temperatures less than 1200 °C, a vacuum of $\sim 10^{-1}$ Pa was kept in the furnace, then nitrogen gas was filled into the chamber up to a pressure of 1.0×10^5 Pa. Main phases of sintered ceramics consisted of β-SiC, h-BN and some YAG (yttrium–aluminum garnet, $3Y_2O_3 \cdot 5Al_2O_3$) formed from the sintering additives [5]. The theoretical densities are shown in Table 1.

The oxidation tests were performed in a static air furnace. The specimens were first dried, and then weighed with a precision of 0.0001 g before and after the oxidation test. For the oxidation tests, samples of 3 mm × 4 mm × 10 mm in size were first placed in a mullite boat, and then the boat was moved into the furnace for a predetermined time after the furnace was heated to the designed temperature. X-ray diffraction (XRD) analysis was carried out at room temperature using Cu Kα

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Table 1
Densities of SiC–BN composite ceramics with different BN content

Density	B0	B20	B40	B53	B60
Theoretical (g/cm^3)	3.317	3.135	2.951	2.824	2.640
Relative (%)	75.1	71.2	68.7	67.7	68.2

radiation. In order to clarify the formation mechanisms of the surface oxidized layers from BN and SiC in the composite, the oxidation behavior of BN, SiC and B_2O_3 powders were examined by a thermogravimetric analyzer (TGA) in air with a heating rate of 10 °C/min. Scanning electron microscopy (SEM) observations were carried out to examine the microstructure of the oxidized layers.

3. Results

Fig. 1 illustrates the weight changes of SiC–BN composites oxidized at 1000 °C. At this temperature, the samples weights nearly keep unchanged from 5 to 20 h. It indicates that the oxidizing products of SiC and BN form an effective protective film to resist further oxidation. However, oxidation becomes much severe with the increase of the BN content in the composites, so the weight gain increased at the same time.

Fig. 2 illustrates the weight changes of SiC–BN composite ceramics oxidized at 1200 °C. For the samples with the BN content of 0, 20 and 40 vol.%, weight gains at 1200 °C are smaller than those obtained at 1000 °C. However, for the composites with the BN content of 53 and 60 vol.%, weight loss happens, and worsens with the increase of oxidizing time.

XRD patterns of the surface of the composites oxidized at 1200 °C for 20 h are shown in Fig. 3. The oxide products include SiO_2, B_2O_3 and C. The amount of SiO_2 in the oxide layers increases despite the decrease of the SiC content. C appears at the oxidized surfaces of the B20 and B40 samples, peaks intensity decreasing with the decrease of the SiC content. The peaks corresponding to B_2O_3 are very weak in the oxidized layers for all the samples.

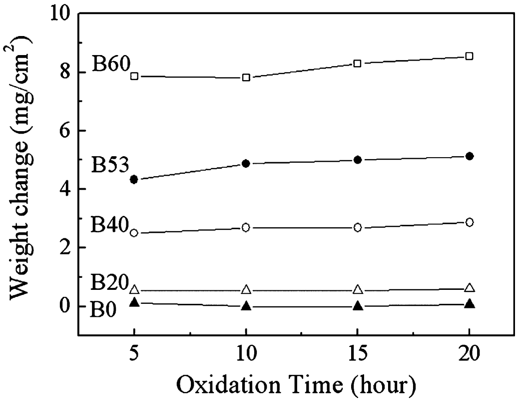

Fig. 1. Weight change vs. oxidation time of the SiC–BN composites at 1000 °C.

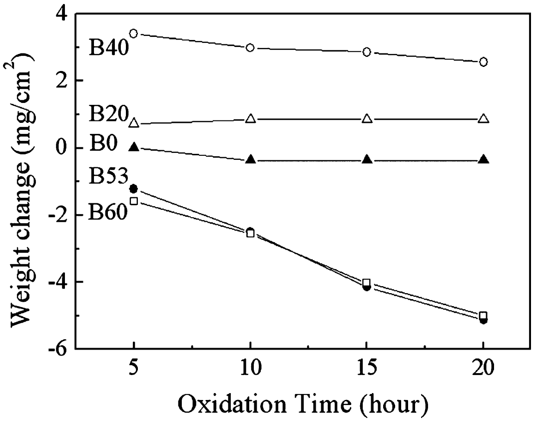

Fig. 2. Weight change vs. oxidation time of the SiC–BN composites at 1200 °C.

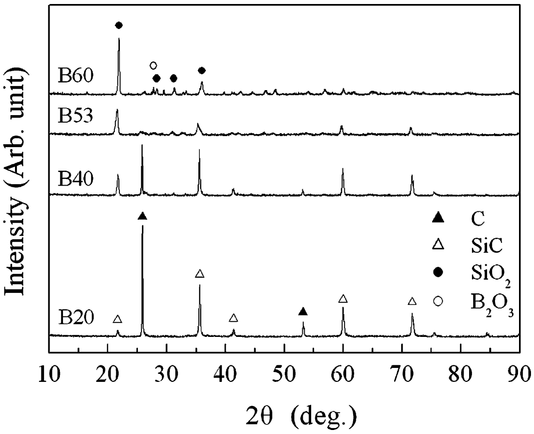

Fig. 3. X-ray diffraction spectra of the surfaces of the SiC–BN composites oxidized at 1200 °C for 20 h.

Surface and profile morphology of SiC–BN composites oxidized at 1200 °C for 20 h are shown in Figs. 4 and 5. The oxidized film of B20 is only a few microns thick and very dense. The oxidized film for the B40 sample is a few microns thick with many pores on the surface. The oxidized surface films become thick and corrugated for the B53 and B60 samples.

4. Discussion

When the SiC–BN composites are exposed to high temperature in air, SiC and BN are oxidized to form SiO_2/SiO [6] and B_2O_3 [7], respectively. The oxidation behavior of SiC can be divided into two categories: passive and active. Passive oxidation forms a coherent and dense SiO_2 layer on the surface, which drastically reduces oxidation rate. Active oxidation forms gaseous SiO, which dissipates away and the oxidation becomes severe [6]. Active oxidation occurs at high temperatures, but the temperature at which the oxidation changes from passive to active, decreases with the decrease of oxygen partial pressure. From a previous study [8], the transition temperature is about 1350 and 1550 °C at partial oxygen pressure of 2.5 and 123 Pa, respectively. For most elevated-temperature application in air, SiC are oxidized to form SiO_2, so the oxidation of SiC in this experiment should be

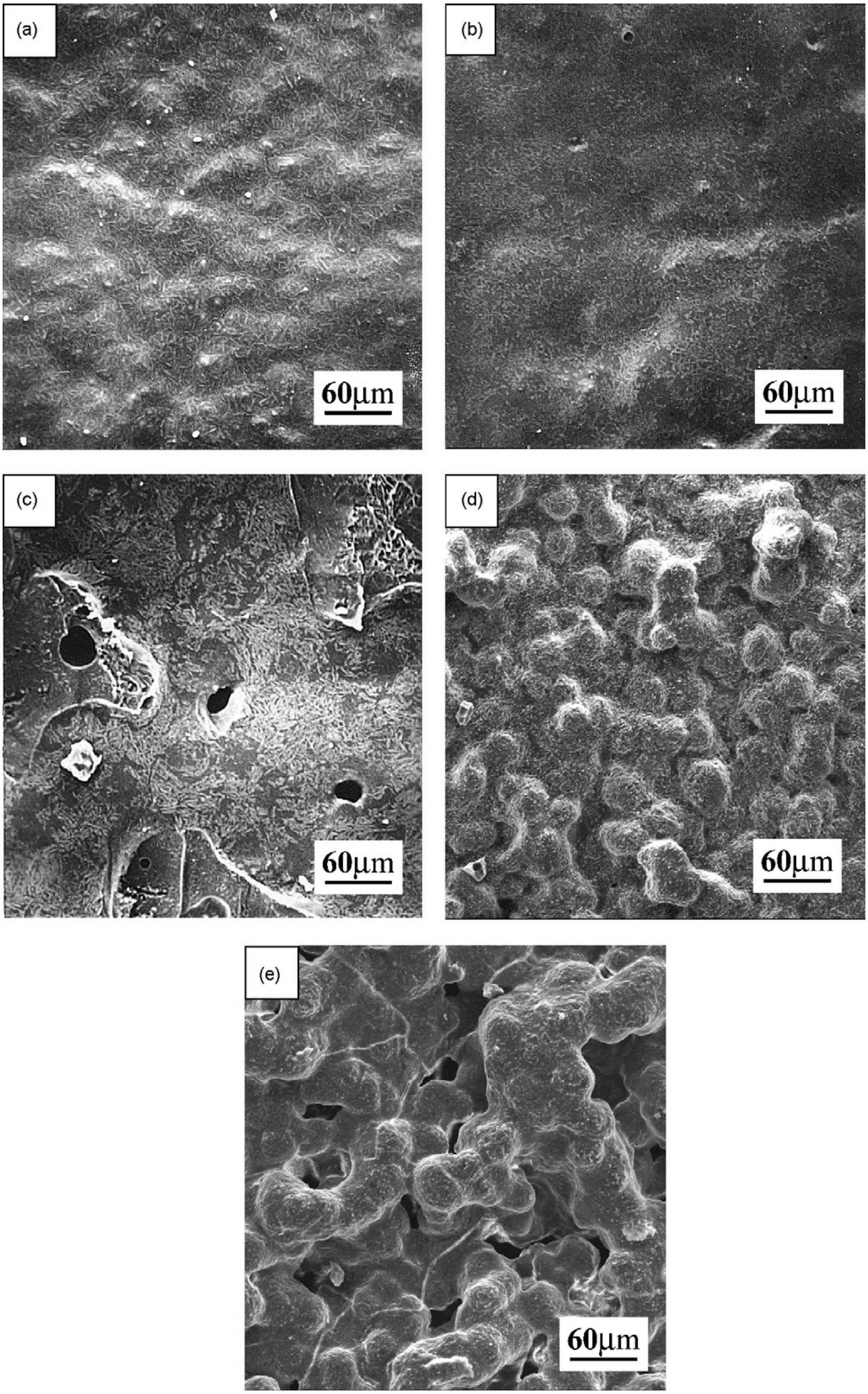

Fig. 4. SEM surface morphology of the oxidized layers of different SiC–BN composites oxidized at 1200 °C for 20 h: (a) B0; (b) B20; (c) B40; (d) B53; (e) B60.

controlled in the region of passive oxidation. In order to improve this, we must consider the possible oxidation reaction of SiC at the oxidizing temperatures of 1000–1200 °C [9]:

$$\mathrm{SiC(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{SiO_2(s,l)} + \mathrm{C(s)} \tag{2}$$

$$(2/3)\mathrm{SiC(s)} + \mathrm{O_2(g)} \rightarrow (2/3)\mathrm{SiO_2(s,l)} + (2/3)\mathrm{CO(g)} \tag{3}$$

$$(1/2)\mathrm{SiC(s)} + \mathrm{O_2(g)} \rightarrow (1/2)\mathrm{SiO_2(s,l)} + (1/2)\mathrm{CO_2(g)} \tag{4}$$

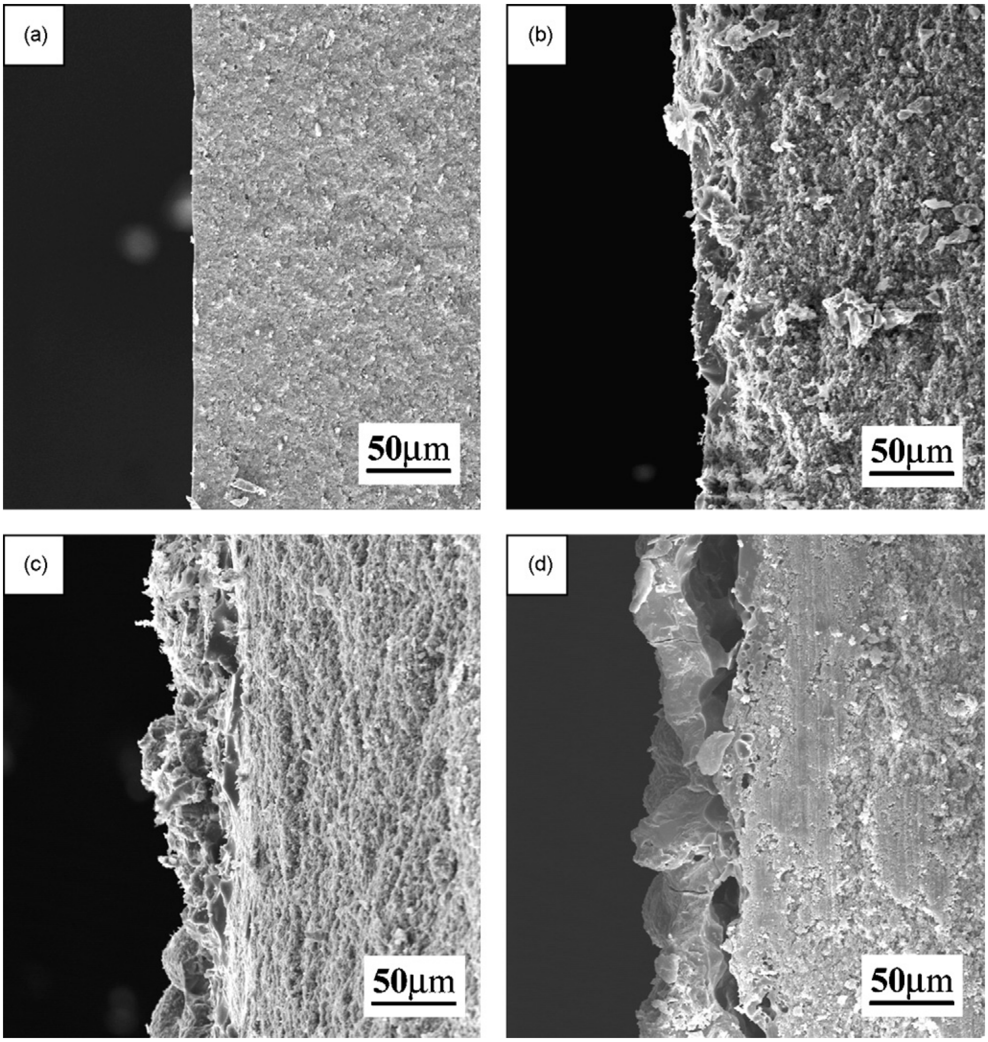

Fig. 5. SEM cross-section images of the oxidized layers of different SiC–BN composites oxidized at 1200 °C for 20 h: (a) B20; (b) B40; (c)B53; (d)B60.

$$\mathrm{SiC(s) + O_2(g) \rightarrow Si(s,l) + CO_2(g)} \tag{5}$$

$$\mathrm{(2/3)SiC(s) + O_2(g) \rightarrow (2/3)SiO(g) + (2/3)CO_2(g)} \tag{6}$$

$$\mathrm{SiC(s) + O_2(g) \rightarrow SiO(g) + CO(g)} \tag{7}$$

$$\mathrm{2SiC(s) + O_2(g) \rightarrow 2Si(s,l) + 2CO(g)} \tag{8}$$

$$\mathrm{2SiC(s) + O_2(g) \rightarrow 2SiO(g) + 2C(s)} \tag{9}$$

The temperature dependence of standard free energies for these reactions is shown in Fig. 6. From room temperature to 1873 °C, reaction (2) has the lowest free energy and dominates for all reactions. The appearance of C in oxidized B20 and B40 samples indicates the analysis of standard free energies for oxidation of SiC to be correct.

BN oxidizes to a liquid oxide (B_2O_3) above ~450 °C as [7]:

$$\mathrm{4BN(s) + 3O_2(g) = 2B_2O_3(l) + 2N_2(g)} \tag{10}$$

Therefore, it is concluded that the oxidations reactions of Eqs. (2) and (10) predominate in the SiC–BN composites. The formation of SiO_2 and B_2O_3 will theoretically lead to a small weight gain.

Fig. 7 shows the TGA curves of BN, SiC and B_2O_3 powders in air atmosphere. The weight of B_2O_3 decreases gradually from room temperature to 1100 °C, and severely decreases above 1100 °C. However, BN powder exhibits a slight weight loss from 200 to 900 °C and a rapid weight gain above 1000 °C. The weight loss of BN below 900 °C may be due to the

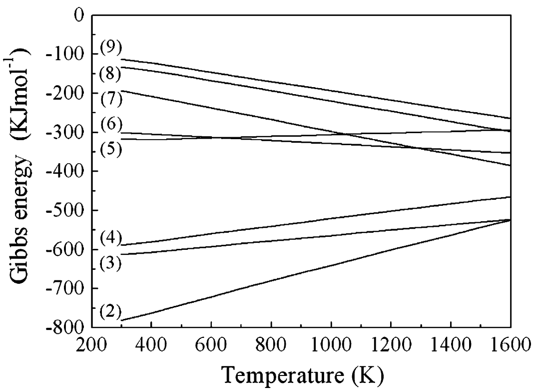

Fig. 6. Temperature dependence of standard free energies for oxidation reactions of Eqs. (2)–(9) in SiC ceramics.

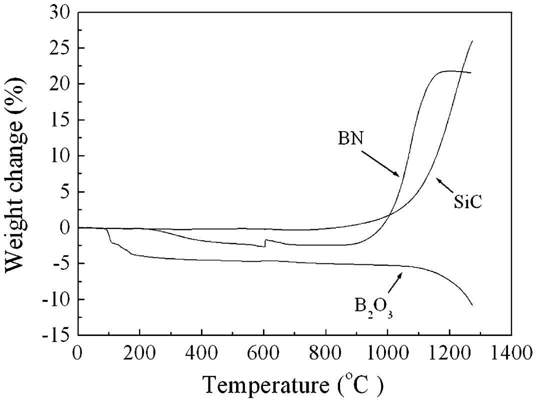

Fig. 7. TGA curves for BN, SiC and B_2O_3 during heating in air atmosphere.

vaporization of B_2O_3, which formed on the original surface of BN before the TGA test. The weight gain of BN powder above 1000 °C in air atmosphere is attributed to rapid oxidation of BN to B_2O_3. It should be noted that the weight curve of BN exhibits a declining behavior due to the vaporization of B_2O_3 above 1100 °C. Weight gain of SiC powder due to the formation of SiO_2 starts at about 1000 °C and becomes significant above 1100 °C. However, weight loss is not observed in this investigation.

SiO_2 and B_2O_3 can react to form a stable borosilicate glass above 372 °C [7]. The borosilicates can form a protective layer which reduces oxidation rate. The higher the SiO_2 content in borosilicate glass, the higher are viscosity and melting point of borosilicate glass which can flow more easily than SiO_2 to cover and protect the surface of samples. However, oxygen diffusivity in borosilicate glass is much larger than in monolithic SiO_2. In addition, B_2O_3 is very sensitive to even small amounts of water vapor in the oxidizing gas stream at high temperature. Liquid B_2O_3 can react with water to form stable HBO_2(g) which can largely vaporize at high temperatures. Higher weight loses happen at higher BN content and temperature, which may lead the amount of mass loss being larger than that of mass gain. So, it can be seen that the weight gains of B0, B20 and B40 oxidized at 1200 °C are smaller than when oxidized at 1000 °C, and weight losses may be observed for B53 and B60 oxidized at 1200 °C. The oxygen diffusivity is more rapid in a B_2O_3-rich borosilicate glass, hence oxidation is enhanced. So the amount of SiO_2 in the oxidized layer increased despite of the decrease of the SiC content, and the content of C simultaneously decreased because of easy access with oxygen (as shown in Fig. 3). A lot of pores will form in the oxidized layer due to continuous volatilization of B_2O_3 and escape of CO_2 formed by the oxidation of C. As a result, the oxide film becomes thick and corrugated with the increase of BN content.

An homogeneous microstructure can be obtained for composites fabricated by reactive hot pressing. Interconnected or open pores are not observed from the SEM micrographs of SiC–BN composites in spite of the low relative densities of samples (see Table 1), so the pores in SiC–BN composites have little influence on the oxidation rate.

5. Conclusions

The oxidation resistance of hot-pressed SiC–BN composites was found to depend on the oxidation temperature and the SiC/BN ratio. SiO_2, C and B_2O_3, N_2 were the oxidized products of SiC and BN, respectively. Some of the oxidized products, SiO_2 and B_2O_3, form a borosilicate film on the surface of the composite. SiO_2-rich borosilicate films more effectively protect the composites from oxidization than B_2O_3-rich borosilicate films. The SiO_2-rich oxidized film was thin and dense, while the B_2O_3-rich film was thick and corrugated.

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