Oxidation of Boron Carbide–Silicon Carbide Composite at 1073 to 1773 K

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The oxidation behavior of B₄C–(25–60 mol%) SiC composites prepared by arc-melting was investigated in the temperature range of 1073 to 1773 K using a thermogravimetric technique. Liquid borosilicate, solid SiO₂ and carbon were identified as oxidation products by X-ray diffraction and Raman spectroscopy. Mass gain was observed during oxidation at 1073 K, while mass loss due to the vaporization of boron oxide in liquid borosilicate was observed at temperatures of 1273 K and higher. In situ Raman spectra of the surface of B₄C–SiC composites indicated that the silica concentration in the liquid borosilicate increased with increasing SiC content in the composite. Micro-Raman spectroscopy showed that carbon was enriched in the borosilicate layer close to the oxide/composite interface. The parabolic rate constants for B₄C–(50 mol% SiC) composites at 1073 K were proportional to ambient oxygen partial pressures ranging between 30 and 100 kPa. The diffusion of oxygen molecules through the liquid borosilicate layer could be the rate-controlling process. The increase of SiC content in the B₄C–SiC composites improved the oxidation resistance in both the mass gain and mass loss regions.

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1. Introduction

Boron carbide B₄C has been used for engineering materials such as wear parts and abrasives because of its high hardness and excellent wear resistance. Recently, the boron carbide has been expected to be a high temperature thermoelectric material¹² and a first-wall material for a fusion reactor¹³ due to its high figure of merit and low atomic number. Oxidation resistance of the boron carbide is an important issue for its practical applications at high temperatures. The oxidation behavior has been reported by several research groups.²⁴⁻¹⁰ Liquid B₂O₃ was detected as the oxidation product. The liquid B₂O₃ layer cannot effectively protect boron carbide because of its low viscosity and high vapor pressure at high temperatures.¹¹ It is well known that SiO₂ formed on silicon-based materials by thermal oxidation is an excellent protective layer for oxidation.¹² Telle reported that B₄C–SiC composites synthesized by hot-pressing exhibited better oxidation resistance than single phase B₄C.¹³ Liquid B₂O₃ and borosilicate¹³,¹⁵⁻¹⁸ have been reported as oxidation products of composites in the B₄C–SiC–C system. The oxide layers on the composites were analyzed by X-ray diffraction,¹³,¹⁴,¹⁷ X-ray photoelectron spectroscopy¹³,¹⁵ and IR absorption spectroscopy.¹⁸ However, the relationship between the oxidation rate and oxide layer has not been clearly understood in the B₄C–SiC system.

In the present work, the oxidation behavior of B₄C–SiC composites was investigated by thermogravimetry and Raman spectroscopy, and the oxidation mechanism of the B₄C–SiC composites was discussed.

2. Experimental Procedure

B₄C and SiC powders were mixed at specific compositions, and then pressed into 15 mm diameter disks with 5 mm thickness. The disks were arc-melted in an argon atmosphere with a tungsten electrode. The B₄C–SiC composites after arc-melting were cut into plates (10 mm × 10 mm × 1 mm). The plates were polished with diamond paste to 1 μm. SiC content in the composites ranged between 25 and 60 mol%. The quasi-binary B₄C–SiC system contains a eutectic composition at SiC content of 45–50 mol%,¹⁹ and the solid solubilities of both B₄C in SiC and SiC in B₄C are less than 2 mass%.²⁰

The mass change of the composite due to oxidation was measured continuously using an electrobalance. The specimen temperature was increased to a specific value in the flowing argon gas, and then oxygen gas or oxygen–argon gas mixture was introduced to initiate oxidation. The gases used in the present experiments were dried by passing them through CaCl₂ and P₂O₅. The total gas pressure was 100 kPa. The oxygen partial pressures ranged between 30 and 100 kPa in oxygen–argon atmospheres. The oxidation temperatures varied from 1073 to 1773 K. The longest oxidation time was 86.4 ks. After the oxidation, the specimen was cooled in flowing argon gas.

In situ Raman spectra of the surface of B₄C–SiC composites during the oxidation were measured by a back-scattering method (T64000, Jovin-Yvon).²¹,²² An argon ion laser was used as an incident beam at 514.5 nm. The measurement of scattered light was carried out with a triple monochromator and a multi-channel detector. The measuring time for each in situ Raman spectrum ranged from 100 to 300 s.

The oxide films on the specimens after the oxidation experiments were analyzed at room temperature by micro-Raman spectroscopy (T64000, Jovin-Yvon) and X-ray diffraction (CuKα, Ni-filtered, RAD-C, Rigaku).
3. Results and Discussion

3.1 Mass change during oxidation

Figure 1 shows the mass change due to the oxidation of the B₄C–50 mol%SiC composite in an oxygen atmosphere at different temperatures. Mass gain was observed at 1073 K, while mass loss occurred at temperatures of 1273 K and higher. The mass loss rates decreased with time and with decreasing temperature. Figure 2 demonstrates the XRD patterns of the surface of B₄C–SiC composites after oxidation in an oxygen atmosphere for 86.4 ks. SiO₂ was detected on the B₄C–SiC composites oxidized at 1473 and 1773 K. Liquid B₂O₃ and solid SiO₂ could be formed by the oxidation of B₄C and SiC in the composite, respectively. SiO₂ might be soluble in liquid B₂O₃ up to around 60 mol% at 1073 K and would form liquid borosilicate.²³) Ogawa et al. reported liquid borosilicate would be rapidly formed by the dissolution of SiO₂ in liquid B₂O₃.¹⁸) Other research groups detected the borosilicate on the B₄C–SiC composites¹³) and B₄C–SiC–C composites¹⁵,¹⁷,¹⁸) by X-ray photoelectron spectroscopy and IR absorption spectroscopy. As described later, the liquid borosilicate was investigated by Raman spectroscopy in the present work. The mass loss observed in the oxidation of B₄C–SiC composites at 1273 K and higher might be caused by vaporization of B₂O₃ in the liquid borosilicate. Figure 3 shows the surface of the B₄C–50 mol%SiC composite oxidized at 1773 K for 86.4 ks. Pores were observed on the surface, which were formed by the vaporization of B₂O₃. The silica concentration in the liquid borosilicate increased by the vaporization of B₂O₃, and then a solid SiO₂ phase formed in the liquid borosilicate when the SiO₂ concentration exceeded the solubility value.²³)

Mass losses due to the oxidation of B₄C⁸) and the B₄C–SiC composites in the present work are compared in Fig. 4. The addition of SiC to B₄C was effective to decrease mass loss by oxidation. The silica-rich borosilicate and solid SiO₂ phases in the oxide layer could suppress the formation and the vaporization of B₂O₃.

3.2 Observation of oxide layer by Raman spectroscopy

Figure 5 shows the in situ Raman spectra of the surface of the B₄C–50 mol%SiC composite during oxidation in an oxygen atmosphere at 1073 K. The Raman spectra during heating to 1073 K and cooling to room temperature in an argon atmosphere are included in Fig. 5. The Raman peaks B and S due to liquid borosilicate²³) were detected. The Raman peak B around 800 cm⁻¹ was assigned to a breathing
vibration of boroxy rings.\textsuperscript{24–28}) The boroxy rings are equilibrated with isolated BO\textsubscript{3} units in the liquid borosilicate.\textsuperscript{24} The increase of Raman peak B during the cooling process might be caused by the formation of boroxy rings from isolated BO\textsubscript{3} units. The boroxy rings would be thermodynamically stable at low temperatures. A broad Raman peak S around 450 cm\textsuperscript{-1} could be assigned to a bending or rocking of B–O–B, B–O–Si and Si–O–Si bridging bonds.\textsuperscript{24}) In situ Raman spectra of the surfaces of the B\textsubscript{4}C–60 mol\%SiC and B\textsubscript{4}C–25 mol\%SiC composites during oxidation in an oxygen atmosphere at 1073 K are shown in Fig. 6. Furukawa and White\textsuperscript{24} suggested that the Raman peak S corresponded to silica in liquid borosilicate because the intensity of the Raman peak S increased with increasing silica concentration in the liquid borosilicate. Figure 7 demonstrates the change of the intensity ratio of the Raman peak S to the Raman peak B ($I_\text{S}/I_\text{B}$) with oxidation time at 1073 K. The value of $I_\text{S}/I_\text{B}$ increased with increasing SiC contents in the composites. At constant SiC contents, the value of $I_\text{S}/I_\text{B}$ increased with oxidation time, particularly up to 10 ks. This result suggests that B\textsubscript{4}C in the composites might be preferentially oxidized in the initial period.

In addition to the Raman peaks of the liquid borosilicate, the Raman peaks of carbon were observed at 1360 and 1580 cm\textsuperscript{-1} (see Figs. 5 and 6). Figure 8 shows the micro-Raman spectra in the borosilicate on the B\textsubscript{4}C–50 mol\%SiC composite after oxidation in an oxygen atmosphere at 1073 K for 86.4 ks. The intensity of carbon peaks near the oxide/composite interface was stronger than that of the gas/oxide interface. The carbon was enriched in the borosilicate layer near the oxide/composite interface because of lower oxygen partial pressure at the oxide/composite interface than that at the oxide/gas interface. Shimada \textit{et al.} reported the formation of carbon in the initial stage of oxidation of HFC in the

![Fig. 4](image_url) Mass loss of B\textsubscript{4}C and B\textsubscript{4}C–SiC composites due to oxidation.

![Fig. 5](image_url) In situ Raman spectra of B\textsubscript{4}C–50 mol\%SiC composite during heating, oxidation and cooling.

![Fig. 6](image_url) In situ Raman spectra of B\textsubscript{4}C–60 mol\%SiC and B\textsubscript{4}C–25 mol\%SiC composites during oxidation in an oxygen atmosphere at 1073 K.
They assumed that carbon could be present beneath the HfO$_2$ layer or contained in the HfO$_2$ layer. Recently, the presence of carbon in silica layer after oxidation of silicon carbide at 973 K in ozone-containing atmospheres has been shown. These previous reports and the present result suggest that the oxygen partial pressure at the oxide/composite interface was lower than the equilibrium oxygen partial pressure of eq. (1).

\[
C(s) + \frac{1}{2}O_2(g) = CO(g) \quad (1)
\]

The oxidation reactions of Si and B were represented by eqs. (2) and (3), respectively.

\[
\text{Si(s in SiC)} + O_2(g) = \text{SiO}_2(s) \quad (2)
\]
\[
2\text{B(s in B}_4\text{C)} + 3/2O_2(g) = \text{B}_2\text{O}_3(l) \quad (3)
\]

The equilibrium oxygen partial pressures of eqs. (1), (2) and (3), which were calculated using the thermodynamic data, are shown in Fig. 9. The activities of C, SiO$_2$ and B$_2$O$_3$ were assumed to be unity. The activity values of Si and B decided by eqs. (4) and (5), respectively, were used in the calculation, e.g., $6.7 \times 10^{-4}$ for Si and 0.19 for B at 1073 K.

\[
\text{Si(s in SiC)} + C(s) = \text{SiC(s)} \quad (4)
\]
\[
4\text{B(s in B}_4\text{C)} + C(s) = \text{B}_4\text{C(s)} \quad (5)
\]

The activities of SiC and B$_4$C were assumed to be unity because of low solid solubilities of B$_4$C in SiC and SiC in B$_4$C. The formation of carbon at the oxide/composite interface during the oxidation of B$_4$C–SiC composites seems to be thermodynamically possible under the conditions, CO partial pressure $> 10^{-1}$ Pa, at 1073 K.

It was reported that the intensity ratio between Raman peaks at 1360 cm$^{-1}$ and 1580 cm$^{-1}$ ($I_{1360}/I_{1580}$) was 1.2 for amorphous carbon, and the inverse of the crystallite size was proportional to $I_{1360}/I_{1580}$. The value of $I_{1360}/I_{1580}$ evaluated from the Raman spectra in Fig. 8 was above 1, meaning that the carbon could be amorphous or crystalline with a small crystallite size (~3 nm).

### 3.3 Oxidation mechanism

Figure 10 shows the relationships between mass gain (M) and oxidation time (t) for the B$_4$C–50 mol%SiC composite at 1073 K in oxygen–argon atmospheres. The gradient of each curve changed around 1 ks. A high oxidation rate at $t < 1$ ks may be caused by the preferential oxidation of B$_4$C in the composites because liquid B$_2$O$_3$-rich borosilicate has high oxygen permeability and may not be protective for oxidation above 1050 K. In the present work, the gradient at $t > 1$ ks in Fig. 10 is around 0.5, and the oxidation rate seemed to be described by the parabolic law shown in eq. (6).
\[ M^2 = k_p \cdot t \]  

(q) is the parabolic rate constant. Figure 11 shows the effects of ambient oxygen partial pressure on the parabolic rate constant for the B\textsubscript{4}C–50 mol\%SiC composite at 1073 K. The parabolic rate constant was proportional to the ambient oxygen partial pressure. This dependence implies that the rate-controlling process of the oxidation may be the diffusion of oxygen molecules through the liquid borosilicate layer and the oxidation reaction proceeded at the oxide/composite interface. Other research groups\textsuperscript{13,16–18} also reported that the oxygen diffusion in the oxide layer could be the rate-controlling process of composites in the B\textsubscript{4}C–SiC–C system.

Figure 12 shows the parabolic rate constants obtained in the present work comparing with those of B\textsubscript{4}C, SiC and B\textsubscript{4}C–SiC composites reported in literatures.\textsuperscript{4,14,31} The reported\textsuperscript{14} and present \( k_p \) values of B\textsubscript{4}C–SiC composites had values between those of B\textsubscript{4}C\textsuperscript{4} and SiC.\textsuperscript{31} The borosilicate would provide more effective protection for oxidation than liquid B\textsubscript{2}O\textsubscript{3} because of its high viscosity and low oxygen permeability.\textsuperscript{16}

### 4. Conclusions

The oxidation behavior of B\textsubscript{4}C–(25–60 mol\%)SiC composites were investigated in oxygen–argon atmospheres at 1073 to 1773 K. The following results were obtained:

1. Liquid borosilicate, solid SiO\textsubscript{2} and carbon were detected as the oxidation products by X-ray diffraction and \textit{in situ} Raman spectroscopy. The silica concentration in the liquid borosilicate layer increased with increasing SiC content in the composite. Carbon enriched in the borosilicate layer near the oxide/composite interface.

2. Mass gain due to the formation of liquid borosilicate was observed at 1073 K, while mass loss caused by the vaporization of boron oxide in liquid borosilicate was observed at temperatures of 1273 K and higher. The addition of SiC to B\textsubscript{4}C was effective to improve the oxidation resistance both in mass gain and mass loss regions. This was caused by the increase of silica concentration in the liquid borosilicate layer and formation of solid SiO\textsubscript{2}.

3. The parabolic rate constants for oxidation of the composites were proportional to the ambient oxygen partial pressure at 1073 K, and the rate-controlling process of oxidation could be the diffusion of oxygen molecules through the liquid borosilicate layer.
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