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Oxidation behavior of a silicon boride composite

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The oxidation resistance of a silicon hexaboride (SiB₆) composite at high temperature was investigated in order to determine the possibility of its use as an advanced high temperature structural material. Fortunately, monolithic SiB₆ and its composites were known to be chemically stable up to high temperatures. To date, there have been few reports regarding the properties of SiB₆ ceramics. In this study, the oxidation resistance at high temperature of a dense SiB₆ composite prepared from SiB₆ with the addition of 10 mass% C as starting powders has been studied. The samples were oxidized at room temperature up to 1173 K for 25 h in air. The weight changes were measured to estimate the oxidation resistance. The oxidation of samples oxidized for a short oxidation time of 5 minutes started at 973 K, and the weight gain increased with increasing oxidation temperature. On the other hand, at oxidation times of above 1 h, a maximum weight gain value at 973 K was observed. After that a SiB₆ composite oxidized at 973 to 1073 K for 25 h exhibited increased weight gain with increasing oxidation temperature; the oxidation changed in accordance with the parabolic law during the initial oxidation stage. However, even if the oxidation temperature was increased only a slight additional weight change occurred. The weight gain of the sample oxidized at 1173 K for 25 h was approximately 2.5%. Finally, the SiB₆ composite showed a good oxidation resistance at high temperature, because the surface oxide film formed by oxidation acted as an oxidation-resistant layer.

Key words: Silicon boride, Composite, Oxidation, Oxidation resistance, Oxide layer.

Introduction

Several silicon boride phases have been registered in the X-ray cards of the International Center for Diffraction Data. Among them, silicon hexaboride has been shown to be a potentially useful material because of its excellent chemical stability at high temperature. SiB₆ has been attracting a great deal of attention as a material for engineering applications at high temperature, because of its favorable properties such as high melting point, chemical stability, and high electrical conductivity. Chen et al. reported that a Si-B composite had good thermoelectric properties at high temperature [1]. Furthermore, Matsushita reported that SiB₆ had excellent potential as an engineering ceramic [2]. Additionally, SiB_6 with the addition of carbon to form a composite proved to be a good engineering ceramic [3]. Also, monolithic SiB_6 and SiB_6 with the addition of 10 mass% C showed good densification by hotpressing at 1973 K, when both of the samples had a relative density over 99%. The X-ray diffraction patterns of the sintered body of SiB₆ with the addition of 10 mass% C showed that SiB₆ and C changed to B₄C and SiC. The Vickers hardness at room temper-

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ature of the monolithic SiB_6 and SiB_6 -B₄C-SiC composite were about 19 GPa and 23 GPa, respectively. The Vickers hardness of the hybrid SiB_6 composite was higher than the monolithic SiB_6 sintered body [4]. In the present study, the isothermal oxidation of a SiB_6 composite is investigated from room temperature to high temperatures in order to determine its suitability for advanced high-temperature applications.

Experimental Procedure

For the SiB_6 powder, we used commercial material made by Cerac Corp., USA (average particle size of 2 µm and purity of 98 %, one batch for all tests) and the carbon powder was made by Mitsubishi Chemical Co., Ltd., Japan (average particle size of 0.03 µm and purity of 99.9%, one batch for all tests). These powders were formulated in the following proportion (mass %):SiB₆: C = 90:10, and were wet-mixed in ethyl alcohol for 24 h. The mixture was dried at 327 K in air. The powder was packed in a carbon vessel. Next, it was hot press sintered under vacuum at 1973 K for 1 h under 30 MPa pressure. The heating rate was set at 10 K minute⁻¹, but after sintering, the molded substance was allowed to cool slowly in a vacuum atmosphere. Thus, 5 mm \times 5 $mm \times 10$ mm specimens were made. The surfaces were polished using a 45 µm diamond disc, and subjected to mirror-surface finishing using 1 µm diamond paste. The bulk density of the sintered body was measured by

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the Archimedes' method. The relative density of the sintered body was obtained by calculating the ratio of the bulk density to the theoretical density of SiB_6 (2.42) g/cm^3) and carbon (2.26 g/cm^3). Isothermal oxidation in air was carried out in an electric furnace maintained from room temperature to 1173 K for 25 h. Both ends of the specimen were put on a bed made of a high purity alumina sintered lodes in the hot zone of an electric furnace at operating temperature. After the prescribed period, the sample was removed from the furnace, and allowed to cool. Then, the mass changes were measured to estimate the oxidation resistance using an electromagnetic balance. A few typical oxidized sample were subjected to X-ray diffraction (XRD) study for phase characterization. The diffraction peaks were identified using the computer program of the International Center for Diffraction Data.

Results and Discussion

In general, the evaluation of oxidation resistance of B_4C or SiC is carried out by investigating the weight gain accompanying the following reactions [5, 6]:

$$B_4C(s) + 7/2 O_2(g) \rightarrow 2 B_2O_3(s) + CO(g)$$
 (1)

SiC (s) +
$$3/2$$
 O₂ (g) \rightarrow SiO₂ (s) + CO (g) (2)

Then, SiB_6 is thought to form the following oxides [7]:

$$SiB_6(s) + 11/2 O_2(g) \rightarrow SiO_2(s) + 3 B_2O_3(s)$$
 (3)

Furthermore, the SiB_6 composite used in the experiment contains carbon. X-ray diffraction analysis showed that in the constitutional phase of this sintered body, SiC and B_4C were also present besides SiB_6 . Therefore, from the sample used in this experiment, the following oxides could be produced:

$$SiB_6(s) + 11/2 O_2(g) \rightarrow SiO_2(s) + 3 B_2O_3(s)$$
 (4)

$$B_4C(s) + 7/2 O_2(g) \rightarrow 2 B_2O_3(s) + CO(g)$$
 (5)

SiC (s) +
$$3/2$$
 O₂ (g) \rightarrow SiO₂ (s) + CO (g) (6)

Even if the weight change is apparently by the vaporization of B_2O_3 formed as one of the oxidation products at high temperature, the weight gain of the sample should increase with the passage of oxidation time. Thus, the weight gain via oxidation of the sample was measured in order to evaluate the relative oxidation resistance. The SiB₆ composite used in the oxidation test was a dense, sintered body whose porosity was less than 1%. It was assumed that the influence exerted by pores upon the oxidation characteristics could be neglected.

The samples were oxidized at room temperature to 1173 K for 25 h in air. The weight changes were measured to estimate the oxidation resistance. The oxidative weight gain of the monolithic SiB₆ sintered body and the SiB₆-B₄C-SiC composite at high temper-



Fig. 1. Oxidation resistance of monolithic SiB₆ sintered body.



Fig. 2. Oxidation resistance of SiB₆ composite.

ature versus oxidation time are shown in Fig. 1 and Fig. 2, respectively. The oxidation of composite samples oxidized for a short oxidation time of 5 minutes started at 973 K, and the weight gain increased with increasing oxidation temperature. On the other hand, at an oxidation time of above 1 h, a maximum weight gain value at 973 K was observed. After that the SiB₆ composite samples oxidized at 973 to 1073 K for 25 h exhibited a weight gain with increasing oxidation temperature; the oxidation changed in accordance with the parabolic law during the initial oxidation stage. However, even if the oxidation temperature was increased only a slight additional weight change occurred. The weight gain of the monolithic SiB₆ sintered body and the SiB₆-B₄C-SiC composite oxidized at 1173 K for 25 h was approximately 3.3% and 2.5%, respectively. In addition, Matsushita et al. reported that the Vickers hardness at room temperature of the monolithic SiB₆ and the SiB₆-B₄C-SiC composite were about 19 GPa and 23 GPa, respectively [3]. The Vickers hardness of the hybrid SiB_6 composite was higher than monolithic SiB₆ sintered body. Then, the oxidation resistance at high temperature and Vickers hardness of the hybrid SiB₆ composite was higher than monolithic SiB₆ sintered body. SEM micrographs of the surfaces of the SiB₆-B₄C-SiC composites oxidized from 973 to 1173 K for 25 h are shown in Oxidation behavior of a silicon boride composite



Fig. 3. SEM micrographs of the oxidized surfaces (a): as-received, (b): 973 K, (c): 1073 K, and (d): 1173 K. The oxidation time was 25 h.

Fig. 3. The surface oxidized at 973 K showed a structure almost identical to the composite oxidized for only 1 h. It was found that a coarsely grained oxide layer was formed on the surface of the sample oxidized at 1173 K. Based on the results of the X-ray diffraction analysis, SiO₂ and B₂O₃ were present on the surface of both the monolithic SiB₆ sintered body and the SiB₆-B₄C-SiC composite samples oxidized at 1173 K for 25 h. Therefore, it was concluded that these oxides acted as a protective film for the SiB₆ composite, consequently excellent oxidation resistance could be obtained.

Conclusions

The dense SiB₆-B₄C-SiC composite were oxidized from room temperature to 1173 K for 25 h in air. The weight changes were measured to estimate the oxidation resistance. The oxidation of samples oxidized for a short oxidation time of 5 minutes started at 973 K, and the weight gain increased with increasing oxidation temperature. On the other hand, at an oxidation time of above 1 h, a maximum weight gain value at 973 K was observed. After that the SiB_6 composite oxidized from 973 to 1073 K for 25 h exhibited a weight gain with increasing oxidation temperature; the oxidation changed in accordance with the parabolic law during the initial oxidation stage. However, even if the oxidation temperature was increased only a slight additional weight change occurred. The weight gain of the sample oxidized at 1173 K for 25 h was approximately 2.5%. Then, the oxidation resistance of the hybrid SiB_6 composite at high temperature was superior to that of the monolithic SiB_6 sintered body. Finally, the SiB_6 composite showed a good oxidation resistance at high temperature, because the surface film of oxide formed by oxidation acted as an oxidation-resistant layer.

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