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# High temperature oxidation of silicon hexaboride ceramics

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#### Abstract

Isothermal oxidation of silicon hexaboride  $(SiB_6)$  ceramic powder at high temperature was investigated. The SiB<sub>6</sub> powder samples were heated from room temperature to 1273K for 25 hours in air, and weight changes were measured to estimate the oxidation resistance and nature of the oxide layers on the SiB<sub>6</sub> ceramics. The samples oxidized in the temperature range of 673 to 1273 K for 25 hours exhibited increasing weight gain with increasing oxidation temperature. The oxidation proceeded in accordance with the parabolic law during the initial oxidation stage. The weight gain increased with increasing oxidation temperature. Based on the results of X-ray diffraction analysis, silicon oxide (SiO<sub>2</sub>) and boron oxide (B<sub>2</sub>O<sub>3</sub>) were present on the surface of samples oxidized in the temperature range of 873 to 1273 K. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Several silicon boride phases have been registered in the X-ray cards of the International Center for Diffraction Data. Among them, silicon tetraboride,  $SiB_4$  and silicon hexaboride,  $SiB_6$  have been shown to be potentially useful materials because of their excellent chemical

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Impurity (wt%)			
Al	0.1	Fe	0.1
Ca	0.05	Mg	0.15
Co	0.01	Mn	0.02
Cr	0.001	Ni	0.01
Cu	0.02	Sr	0.01

Table 1 Impurity of as-received  $SiB_6$  powder as starting material

resistance properties.  $SiB_6$  is is more stable at high temperature than  $SiB_4$  in the B-Si binary alloy phase diagram [1].

 $SiB_6$  has been attracting a great deal of attention as a material for thermoelectric applications at high temperatures, because of its favorable properties such as high melting point, chemical stability and high electrical conductivity, low thermal conductivity, and high Seebeck coefficient at high temperature. Chen et al. reported that the Si-B composite had good thermoelectric property at high temperature [2].

Unfortunately, although the monolithic  $SiB_6$  is known to be chemically stable and resistant to high temperatures in air, it is rarely used at high temperatures. To date, there have only been a few reports regarding the oxidation properties of  $SiB_6$ . In this study, the oxidation of  $SiB_6$  powder samples is investigated from room temperature to high temperatures in order to determine its suitability for advanced high-temperature applications.

#### 2. Experimental procedure

 $SiB_6$  powder used in this study is a commercially available powder. The starting material was made by Cerac Corp., U.S.A. and one as-received batch was used for all tests. The purity and median particle size of the sample are 98% and 3  $\mu$ m, respectively. The impurities of the sample by chemical analysis are shown in Table 1.

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) for SiB<sub>6</sub> starting powder was conducted with a thermal analyzer (Model: TG8120, Rigaku Co., Ltd., Japan) using a  $\alpha$ -alumina pan and high-purity  $\alpha$ -alumina standard powder in flowing air (0.5 *l*/min) heated at 10 K/min.

Isothermal oxidation in air was carried out in an electric furnace maintained at the desired temperature. The sample to be evaluated usually consisting of about 500 mg of the powder, was weighed carefully and placed in a high-purity  $\alpha$ -alumina boat. This high-purity  $\alpha$ -alumina boat containing several samples was directly introduced in the hot zone of the furnace at a predetermined operating temperature onto a low-density stabilized zirconia setter. After the prescribed period, the sample, together with its boat, was removed from furnace, allowed to cool and reweighed carefully. Mass data were obtained using an accurate electric balance. The value of weight gain of the sample includes the cooling period in addition to the total oxidation time at treatment temperature.

A few typical samples of partly oxidized samples were subjected to X-ray diffraction



Fig. 1. Results of differential thermal analysis (DTA) and thermogravimetric analysis (TG) for SiB<sub>6</sub> powder.

(XRD) analysis for phase evolution using an X-ray diffractometer (Cu K<sub> $\alpha$ </sub>/Ni filter, 40 kV, 30 mA) from Philips Ltd., Netherlands (Model: APD-1700). The powder X-ray diffraction peaks were identified using the computer program, which incorporates all of the data of the X-ray cards of the International Center for Diffraction Data (ICDD).

Morphological changes of microstructures and the specimen surfaces were examined by scanning electron microscopy (SEM) using a microscope from Elionics Co., Ltd., Japan (Model: ESA-2000).

#### 3. Results and discussion

In general, the evaluation of oxidation resistance of silicon components of silicon carbide (SiC) or silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is carried out by investigating the weight gain accompanying the following reaction [3–5]:

$$SiC(s) + 3/2O_2(g) = SiO_2(s) + CO(g)$$
 (1)



Fig. 2. Change of weight gain with oxidation as a function of temperature and time.

$$Si_3N_4(s) + 3O_2(g) = 3 SiO_2(s) + 2N_2(g)$$
 (2)

 $SiB_6$ , however, is thought to form the following oxides:

$$SiB_6(s) + \frac{11}{2O_2(g)} = SiO_2(s) + 3B_2O_3(s)$$
 (3)

Even if the weight is apparently decreased by the vaporization of  $B_2O_3$  formed as one of the oxidation products at a high temperature, the weight of the sample should increase with the passage of oxidation time. Thus, the weight gain due to the oxidation of the sample was measured in order to evaluate relative oxidation resistance [6, 7].

The result of the differential thermal analysis (DTA) and thermogravimetric analysis (TG) for SiB6 starting powder are shown in Fig. 1. During the initial heating between room temperature to about 850 K, absorbed water is removed from the surface of the sample corresponding to an initial weight loss of about 0.5%. The weight gain increased with increasing oxidation temperature.

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Fig. 3. X-ray diffraction patterns of the oxidation surfaces at a): room temperature (as-received), b): 873K, c): 1073K and d): 1273K. The oxidation time was 25 hours.

Oxidation weight increased sharply near 850 K, so thermogravimetric analysis (TG) and thermal analysis (DTA) were conducted to confirm oxidation initiation temperature. An exothermic peak seen near 850  $\sim$  1100 K in DTA curve is assumed to be due to SiB<sub>6</sub> oxidation. In the TG curve, weight gain by oxidation was confirmed from 850 K, and about 55% of weight gain occurs due to oxidation up to 1273K. Similar measurement was conducted using mixed 50% SiB<sub>6</sub> and 50%  $\alpha$ -alumina powder and the result was almost the same as monolithic SiB<sub>6</sub>, suggesting that no reaction occurred between SiB<sub>6</sub> and  $\alpha$ -alumina.

The oxidative weight gain of the sample at room temperature to 1273 K versus oxidation time is shown in Fig. 2. The weight gain data of the different samples is the average of three



Fig. 4. Scanning electron microscope (SEM) photographs of the surfaces at a): room temperature (as-received), b): 873K, c): 1073K and d): 1273K. The oxidation time was 25 hours.

measurements. The weight gain of the sample oxidized below a temperature of 673 K for 1 hour was approximately 1 %. However, when the oxidation time was extended, additional weight change did not occur. Significant oxidation of samples started at 873 K, and the weight gain increased with increasing oxidation temperature. The samples oxidized at and above 873 K also exhibited increasing weight gain with increasing oxidation time. The oxidation proceeded in accordance with the parabolic law during the initial oxidation stage. This trend implies that the silicon oxide layer produced by oxidation serves as a protective layer against oxygen, causing the oxidation rates to be determined by the diffusion of oxygen through the oxidation layer.

Figs. 3 shows the results of the powder X-ray diffraction analysis of samples oxidized at 873 to 1273 K for 25 hours in air. The X-ray diffraction data of the starting powder only showed peaks of SiB<sub>6</sub> (Fig. 3 (a)). A similar result was obtained for samples treated in air at 473K for 25 hours; the weight gain was below 1%. The result of X-ray diffraction showed no crystalline phase other than SiB<sub>6</sub> in the sample. The samples heated from 873 to 1273 K for 25 hours in air showed the presence of an additional phase, silicon oxide SiO<sub>2</sub> ( $\alpha$ -cristobalite) and boron oxide B<sub>2</sub>O<sub>3</sub> (Fig. 3 (b) ~ (d)).

From the above data, we suggest that room temperature to high temperature oxidation (1273 K) of  $SiB_6$  follows the equation:

$$SiB_6(s) + \frac{11}{2O_2(g)} = SiO_2(s) + 3B_2O_3(s)$$
 (4)

The calculated ideal weight gain change of  $SiB_6$  from eq. (4) is approximately 189.5 %. The weight gain of the sample oxidized at 1273 K for 25 hours was about 95% (Fig. 2). This value is half the value of theoretical weight gain of  $SiB_6$ .

SEM photographs of the surface of the sample oxidized at 873 to 1273 K for 25 hours are shown in Fig. 4. The surface oxidized at 873 K showed a coarsely grained oxide layer (Fig. 4 (b)). Based on the results of X-ray diffraction analysis, silicon oxide and boron oxide were present on the surface of the sample oxidized at 873 K. On the other hand, the surface of the sample oxidized at 1073 to 1273 K showed a glassy appearance because of phase transition to a crystalline phase, SiO<sub>2</sub> along with  $B_2O_3$  as a liquid phase.  $B_2O_3$  may also react with SiO<sub>2</sub> to become amorphous borosilicate glass, and partial vaporization may occur [8–10]. This borosilicate glass was assumed to be a vitreous substance (Fig. 4 (c), (d)). X-ray diffraction peaks other than SiO<sub>2</sub> and  $B_2O_3$  could not be confirmed as oxidation products, and a 3-component Si-B-O compound (silicon borate) was not detected.

### 4. Conclusion

The SiB<sub>6</sub> powder samples oxidized from 873 to 1273K exhibited increasing weight gain with increasing oxidation temperature and time. Based on the results of X-ray diffraction analysis, silicon oxide (SiO<sub>2</sub>) and boron oxide (B<sub>2</sub>O<sub>3</sub>) were postulated to be present on the surface of the samples oxidized from 873 to 1273 K; oxidation was assumed to advance as follows:

 $SiB_6(s) + \frac{11}{2O_2(g)} = SiO_2(s) + 3B_2O_3(s)$ 

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