JOURNAL OF MATERIALS SCIENCE **34** (1999) 3043–3046

High temperature oxidation behavior of CaB_6 sintered body

J. MATSUSHITA*, S. KOMARNENI
Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA
E-mail: sxk1@alpha.mrl.psu.edu

The oxidation at high temperatures of hot-pressed calcium hexaboride (CaB_6) sintered body was investigated in order to determine the suitability of this material for application at high-temperature. The oxidation of samples started at 1273 K, and the weight gain increased with increasing oxidation temperature. © *1999 Kluwer Academic Publishers*

1. Introduction

Calcium hexaboride (CaB_6), a metal boride belonging to the 2 (2A) group, has been attracting a great deal of attention as a material for structures exposed to high temperatures, for surface protection, and for wear-resistant parts used in a corrosive environment, because of its favorable properties such as high melting point (2373 K), high hardness (Hv = 27 GPa), chemical stability and high electrical conductivity (10^3–10^1 S) [1, 2]. Recently, studies have been carried out to determine the feasibility of using CaB_6 as a potential material for improvement of the abrasion resistance of bricks for converter. Hanagiri *et al.* have reported that the addition of CaB_6 together with metal to MgO-C bricks for converter increased the high temperature strength without decreasing the spalling resistance [3, 4]. Unfortunately, although the CaB_6 is known to be resistant up to high temperatures in air, it is rarely used at high temperatures. To date, there have only been few reports regarding the oxidation of CaB_6. In this study, the oxidation of the CaB_6 sintered body from room temperature to 1373 K is investigated in order to determine its suitability for high-temperature application.

2. Experimental

CaB_6 powder made by Advanced Refractory Technologies, Inc., USA (Grade S, No.C-300182, one batch for all tests) was used as a starting material (catalogued values: purity = 99%, median particle size = 8 μm). The powder was packed in a carbon vessel in a resistance furnace provided with carbon heating elements and sintered by hot-pressing in vacuum at 1923 K for 1 h under 40 MPa pressure. The heating rate was 15 K/min.

The density of the sintered body was measured by the Archimedes' method. The relative density of sintered body was approximately 100%. All the samples for oxidation studies were fabricated by sintering at 1923 K. The sintered body was cut into 2 × 2 × 20 mm size and the surfaces were polished with a diamond disk prior to oxidation studies.

Isothermal oxidation in air was carried out in an electric furnace maintained at the desired temperature (±1 K). The sample to be evaluated, was weighed carefully and placed in an α-alumina boat. This highly pure α-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 a prescribed period, the sample, together with its boat, was removed from furnace, allowed to cool and reweighed carefully. Mass data were obtained with an accuracy of ±0.1 mg using an electric balance.

A few typical samples of partly oxidized samples were subjected to X-ray diffraction (XRD) analysis for phase evolution using an X-ray diffractometer (CuK_α/Ni filter, 40 kV, 30 mA) from Philips Ltd. The powder 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.

Morphological changes of microstructures and the specimen surfaces were examined by scanning electron microscope (SEM) from Elionics Co., Ltd., Japan.

3. Results and discussion

Oxidation of CaB_6 is expected to yield the following oxides:

$$CaB_6 + 5O_2 \rightarrow CaO + 3B_2O_3 \tag{1}$$

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 increasing oxidation time. Thus, the weight gain due to the oxidation of the sample was measured in order to evaluate relative oxidation resistance [5, 6].

The oxidative weight gain of the sample from 473 to 1373 K versus oxidation temperature and time is shown

---

* *Permanent address*: Department of Applied Chemistry, Tokai University, Hiratsuka 259-1292, Japan.

0022–2461

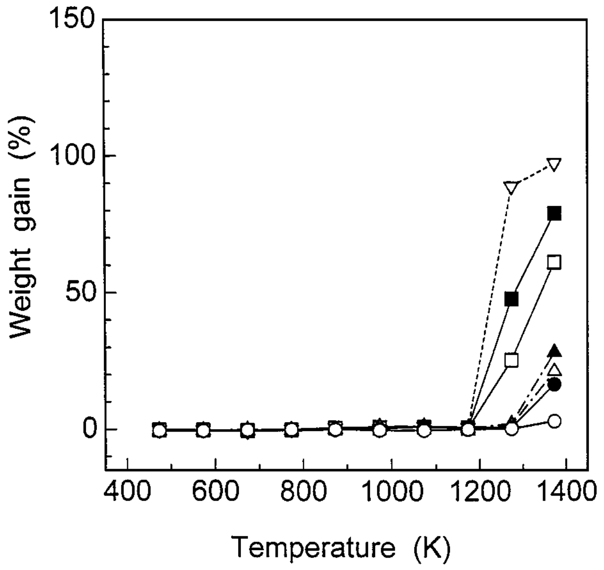

Figure 1 Weight gain with oxidation as a function of temperature and time: ○: 5 min, ●: 0.5 h, △: 1 h, ▲: 2 h, □: 5 h, ■: 10 h and ▽: 25 h.

in Fig. 1. The weight gain of the sample oxidized below a temperature of 1173 K for 1 h was approximately 1%. However, even if the oxidation time was extended, an additional weight change did not occur. Thus, the sample showed a good oxidation resistance at a high temperature of 1173 K. Significant oxidation of samples started at 1273 K, and the weight gain increased with increasing oxidation temperature. The samples oxidized at and above 1273 K also exhibited increasing weight gain with increasing oxidation time. The oxidation proceeded in accordance with the parabolic law during the initial oxidation stage. For samples at and above 1273 K, oxidation including initial stages followed the parabolic rule. This trend implies that the calcium 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 2–4 show the results of the powder X-ray diffraction analysis of samples oxidized at 473 to 1373 K in air. The X-ray diffraction data of the starting powder only showed peaks of CaB_6 (Fig. 2). A similar result was obtained for samples treated in air at 473 K for 25 h; the weight gain was below 1%. The result of X-ray diffraction showed no crystalline phase other than CaB_6 in the sample (Fig. 2). The samples heated from 673 to 973 K for 25 h in air showed the presence of an additional phase, calcium borate CaB_4O_7 (Figs 2 and 3). On the other hand, the samples oxidized from 1073 to 1173 K for 25 h indicated the formation of CaB_6 and calcium borate CaB_2O_4. However, the peaks of CaB_4O_7 could not be identified (Fig. 4). A sample oxidized at and above 1273 K for 25 h did not exhibit any diffraction peaks, i.e., became amorphous. Postulated oxidation products such as CaO and B_2O_3 could not be detected (Fig. 4).

From the above data, we suggest that the low temperature oxidation (673–973 K) of CaB_6 follows the equation:

$$CaB_6 + 5O_2 \rightarrow CaB_4O_7 + B_2O_3 \tag{2}$$

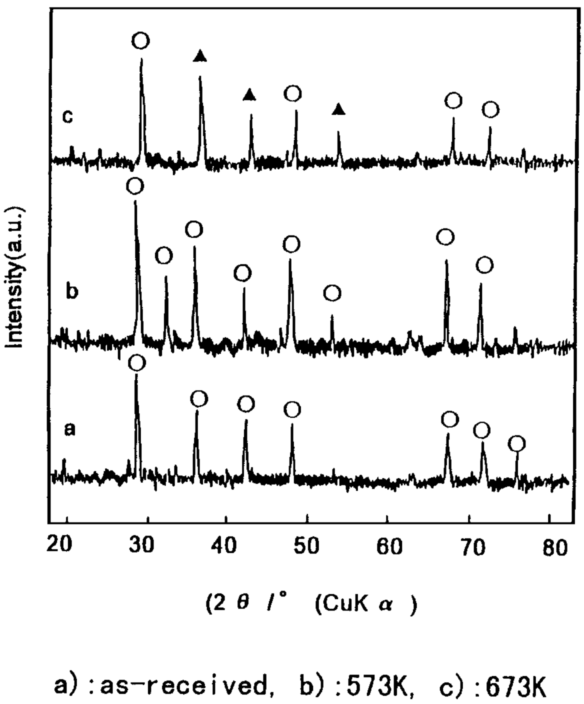

Figure 2 X-ray diffraction patterns of the oxidation surfaces at (a) room temperature (as-prepared), (b) 573 K and (c) 673 K. The oxidation time was 25 h. ○ and ▲; the peaks corresponding to CaB_6 and CaB_4O_7, respectively.

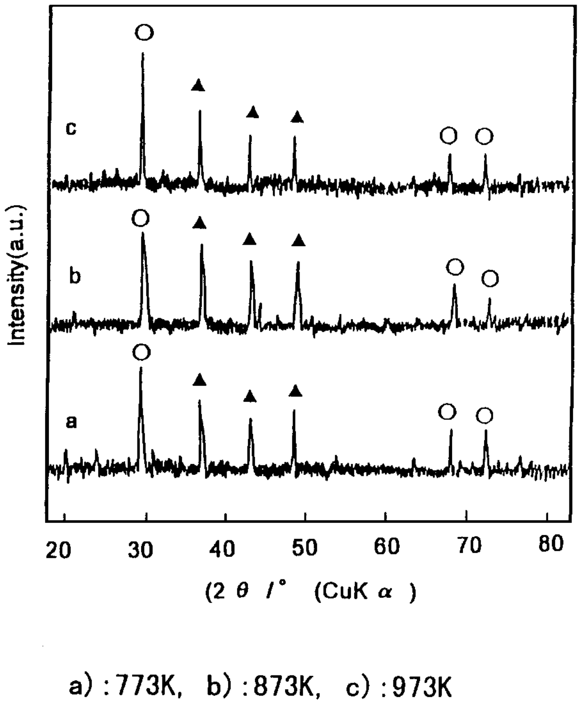

Figure 3 X-ray diffraction patterns of the oxidation surfaces at (a) 773 K, (b) 873 K and (c) 973 K. The oxidation time was 25 h. ○ and ▲: the peaks corresponding to CaB_6 and CaB_4O_7, respectively.

Reaction (4) may be considered as a first step in oxidation. In the temperature range of 973–1073 K, CaB_2O_4 forms as follows:

$$CaB_4O_7 \rightarrow CaB_2O_4 + B_2O_3 \tag{3}$$

Furthermore, as a second step to oxidation (1073–1173 K), the following oxides could be produced:

$$CaB_6 + 5O_2 \rightarrow CaB_2O_4 + 2B_2O_3 \tag{4}$$

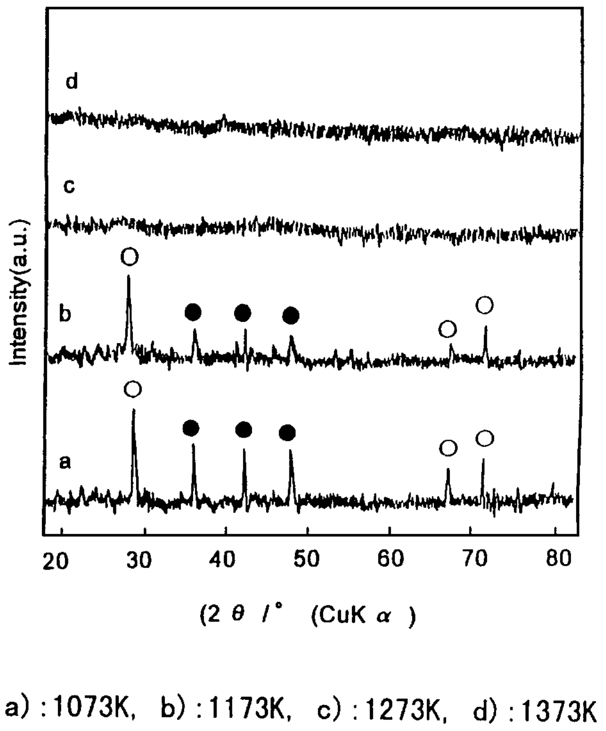

Figure 4 X-ray diffraction patterns of the oxidation surfaces at (a) 1073 K, (b) 1173 K, (c) 1273 K and (d) 1373 K. The oxidation time was 25 h. ○ and ●: the peaks corresponding to CaB_6 and CaB_2O_4, respectively.

SEM photographs of the surface of the sample oxidized at 873 to 1273 K for 25 h is shown in Fig. 5. The surface oxidized at 873 K showed a structure almost identical to the surface of the as-received sample. A coarse grained oxide layer was detected on the surface of the sample oxidized at 873 K (Fig. 5b). Based on the results of the X-ray diffraction analysis, calcium borate was present on the surface of the sample oxidized at 673 to 1173 K. The sample showed very good oxidation resistance at 1173 K because the surface layer of calcium borate formed by oxidation, acts as a barrier against further oxidation. On the other hand, the surface of the sample oxidized at 1273 K, showed a layer on the surface which appears to be vitreous.

4. Summary

To determine the suitability of CaB_6 for high-temperature applications, we investigated its thermal oxidation process. The CaB_6 sintered body was oxidized from 473 to 1373 K for 5 min to 25 h in air. The weight gain of the sample oxidized below 1173 K for 1 h was approximately 1%. However, even if the oxidation time was prolonged additional weight change did not occur. For samples heated at 1273 K, the weight gain increased with increasing oxidation temperature. The samples oxidized from 1273 to 1373 K exhibited increasing weight gain with increasing oxidation time. Based on the results of SEM and X-ray diffraction analysis, calcium borate (CaB_4O_7) was postulated to be present on the surface of the samples oxidized from 673 to 973 K. The samples showed a good oxidation resistance from 1073 to 1173 K, because the surface film of calcium borate (CaB_2O_4) formed by oxidation acted as an oxidation resistant layer.

References

1. NISSO TSUSHINSHA (ed.), "Handbook on High-Melting-Point Composites," Japanese Edition (Nisso Tsushinsha, Ehime, Japan, 1977).
2. R. W. JOHNSON and A. H. DAANE, *J. Chem. Phys.* **38** (1963) 425.
3. S. HANAGIRI, T. HARADA, S. ASO, S. FUJIWARA, H. YASUI, S. TAKANAGA, H. TAKAHASHI and A. WATANABE, *TAIKABUTU* **44** (1992) 490.

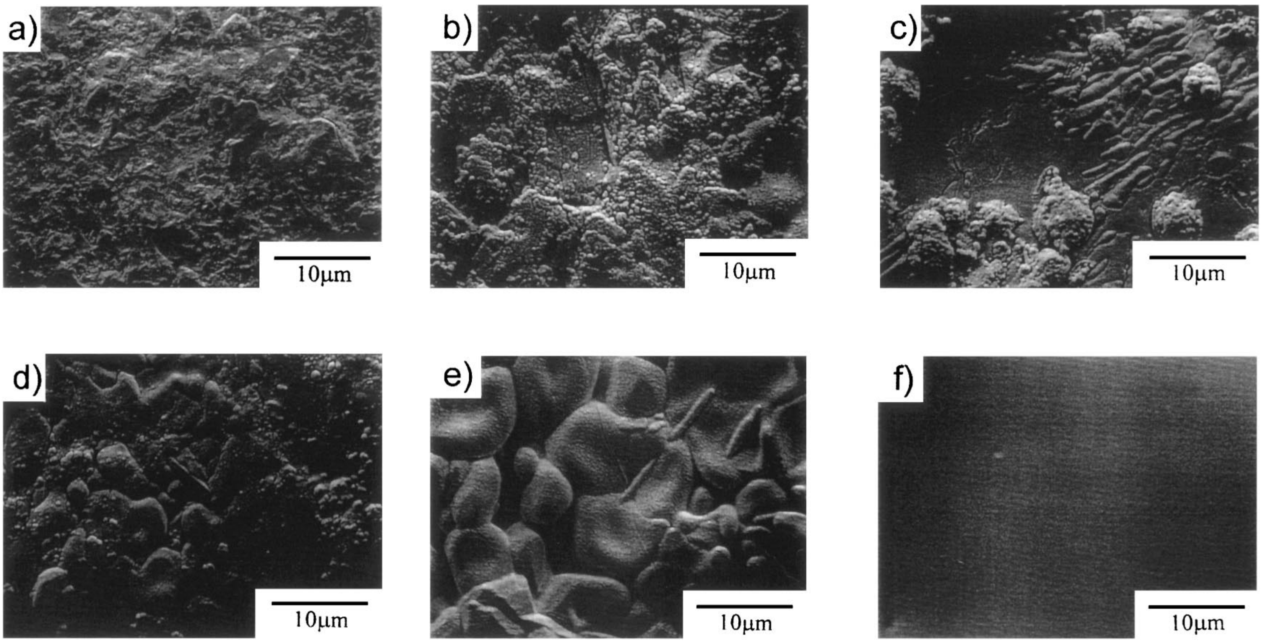

Figure 5 Scanning electron micrographs of the oxidation surfaces at (a) room temperature (as-prepared), (b) 873 K, (c) 973 K, (d) 1073 K, (e) 1173 K and (f) 1273 K. The oxidation time was 25 h.

4. S. HANAGIRI, S. FUJIWARA, H. KASAHARA, I. UMEHARA, H. YASUI, K. NONOBE and H. TAKAHASHI, *TAIKABUTU* **44** (1992) 640.
5. J. MATSUSHITA, S. HAYASHI and H. SAITO, *J. Ceram. Soc. Japan* **98** (1990) 308.
6. J. MATSUSHITA, N. NAGASHIMA and H. SAITO, *ibid.* **98** (1990) 1172.

Received 21 October 1998
and accepted 27 January 1999