



## High-temperature oxidation behavior of boron carbide

Esra Dokumacı<sup>1</sup>, İlker Ozkan<sup>2\*</sup>, A. Bülent Onay<sup>3</sup>

<sup>1</sup>Dokuz Eylül University, Faculty of Engineering, Metallurgical and Materials Engineering Department, 35100, Izmir, Turkey, ORCID ID [orcid.org/0000-0003-3886-3963](https://orcid.org/0000-0003-3886-3963)

<sup>2</sup>Dokuz Eylül University, Torbalı Vocational School, Industrial Glass and Ceramics Department, Dokuz Eylül University, 35860, Izmir, Turkey, ORCID ID [orcid.org/0000-0002-7506-5795](https://orcid.org/0000-0002-7506-5795)

<sup>3</sup>Dokuz Eylül University, Faculty of Engineering, Metallurgical and Materials Engineering Department, 35100, Izmir, Turkey, ORCID ID [orcid.org/0000-0002-2830-1898](https://orcid.org/0000-0002-2830-1898)

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### ABSTRACT

The aim of this study is to determine the cyclic oxidation behavior of boron carbide ( $B_4C$ ) in the air atmosphere at elevated temperatures. For this purpose, as-received  $B_4C$  powders were characterized by XRD and SEM and then shaped by the cold pressing method for oxidation studies. Tests were performed in the air atmosphere at 800°C and 1000°C for 5, 10, 15 and 20 hours. Oxidation behavior of the samples was evaluated by weight changes. XRD, SEM and EDS analyses were also conducted on the oxidized samples. It was observed that cyclic oxidation behaviors of the samples depended on temperature and time. Based on the analyses results and the microstructure observations, volatilization of  $B_2O_3$  had a significant effect on the oxidation of the samples as the temperature increased.

### 1. Introduction

Boron carbide ( $B_4C$ ) is a well-known ceramic and is a promising material used for a wide range of industrial applications.  $B_4C$  has a high melting point, excellent hardness, good mechanical properties, low specific weight, great resistance to chemical agents at room temperature and high neutron absorption cross-section. These properties make  $B_4C$  a valuable potential material for usage in high technology industries, such as fast-breeders, lightweight armors, blasting nozzles and high-temperature thermoelectric conversion. Also, it is used in nuclear power engineering, electrical engineering, and metalworking [1-7].

The oxidation behavior of  $B_4C$ , which has a wide application area, is of great importance. The oxidation of  $B_4C$  ceramic materials both in powder and bulk form have been reported by many researchers. Lavrenko and Gogotsi investigated the oxidation of hot-pressed  $B_4C$  under isothermal conditions and under increasing temperature conditions up to 1500°C [2]. Kılıçarslan et al. studied the partial oxidation of  $B_4C$  particles of different sizes such as 10, 32 and 93  $\mu m$  [4]. Li and Qiu examined the isothermal oxidation behavior of 1.52  $\mu m$ , 22.5  $\mu m$  and 59.6  $\mu m$  particle sized  $B_4C$  at temperatures ranging from 500 to 800°C under air atmosphere [7]. Steinbrück studied isothermal oxidation of pellet and powder form of  $B_4C$  at temperatures between 800 and 1500°C [8]. Lavrenko et al. investigated the oxidation resistance of compact  $B_4C$  at temperatures up to 1200°C under 740 Torr pressure oxygen

atmosphere [9]. Litz and Mercuri studied the oxidation of  $B_4C$  under air, water vapor, and air-water vapor mixture conditions at elevated temperatures [10].

As mentioned above, there are many studies on examination of the microstructure, mechanical properties, and oxidation properties of the powder and dense-sintered  $B_4C$  samples. In addition to these studies, cyclic oxidation behavior of cold pressed  $B_4C$  should also be investigated. The present study was carried out to be able to fill this gap in the literature. The aim of this paper is to observe the cyclic oxidation behavior of cold pressed  $B_4C$  pellets in the air at elevated temperatures. The result of this study is meaningful for in situ usage and processes for non-sintered and compacted  $B_4C$ .

### 2. Materials and methods

In this study, commercial  $B_4C$  powders obtained from Alfa Aesar were used. According to the information received from this company,  $B_4C$  powder is in 22-59  $\mu m$  size.

$B_4C$  pellets were formed by using a mould with a 20 mm diameter under 150 bar pressure. To improve the plasticity and mechanical strength of the pellets carboxymethylcellulose (CMC) was added as an aqueous solution (4% wt.). For each pellet, only 0.42 g of this solution was used. CMC was added at very small quantities so the effect of it on the total weight change was neglected. It was observed that, after drying at

\*Corresponding author: [ilker.ozkan@deu.edu.tr](mailto:ilker.ozkan@deu.edu.tr)

110°C, pellets became harder and therefore were suitable to use in the oxidation tests. To be able to measure properly, weight changes of the pellets after the oxidation tests, it was necessary to drill a hole through the pellets. Pellet samples were then suspended inside a quartz crucible (Figure 1).

Oxidation tests were conducted in a box furnace at temperatures 800 and 1000°C for a total of 20 h in 4 cycles each lasting 5 h. Weight changes and dimensions of the samples after each oxidation test were measured and the oxidation behavior of the sample was evaluated by weight change-time graphics. An X-ray diffractometer Rigaku D/Max-2200/ PC) with a CuK $\alpha$  tube was used to determine the oxide products formed on the surface of B<sub>4</sub>C pellet samples after oxidation tests. Samples were mounted in a polyester mold and ground with SiC

sandpapers. The cross-sectional morphologies of the oxidized B<sub>4</sub>C pellets were investigated by JEOL-JSM 6060 Scanning Electron Microscope (SEM).

### 3. Results and discussions

XRD analysis of the as-received B<sub>4</sub>C powder can be seen in Figure 2. XRD data matched well to that of the boron carbide phase registered as 035-07983 in the ICDD database and only B<sub>4</sub>C phase was observed.

Figure 3 shows the SEM images of the as-received B<sub>4</sub>C powder sample without any additives and any compaction. The grains appear to have similar sizes. Also, almost all the grains are observed to have sharp edges.

Figure 4 shows the results of the cyclic oxidation tests in the air. These graphs indicate that B<sub>4</sub>C pellet

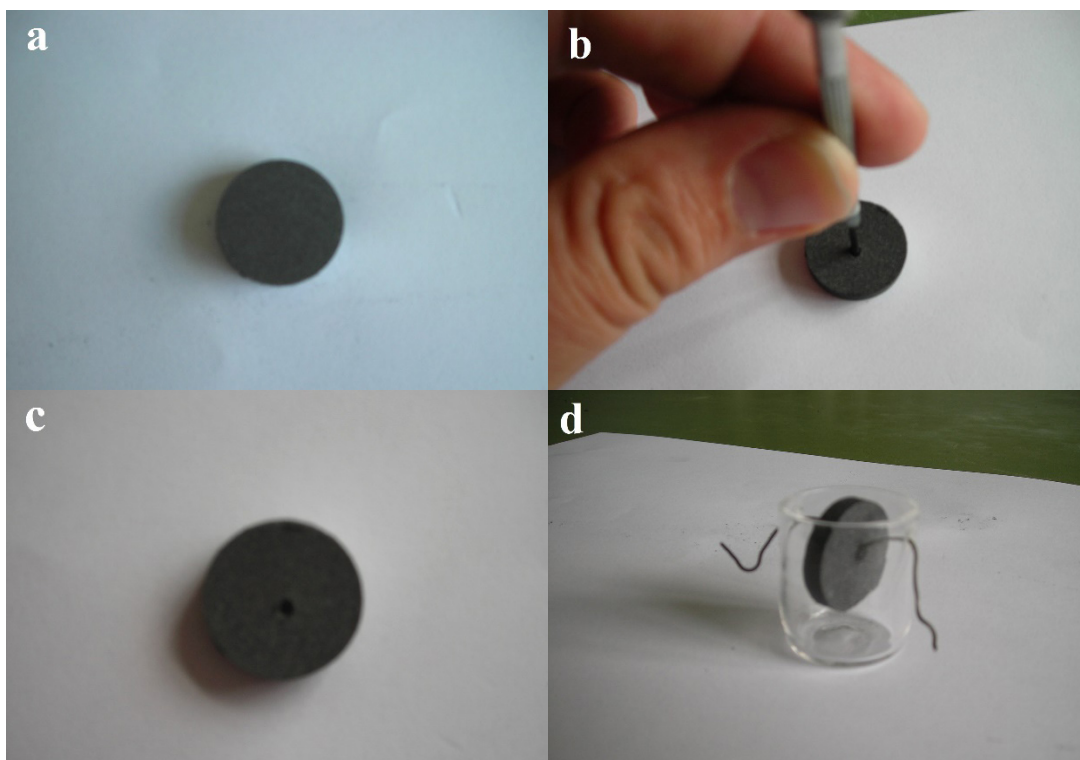


Figure 1. (a)-(d) Drilling a hole on the pellet and preparing it for the oxidation tests.

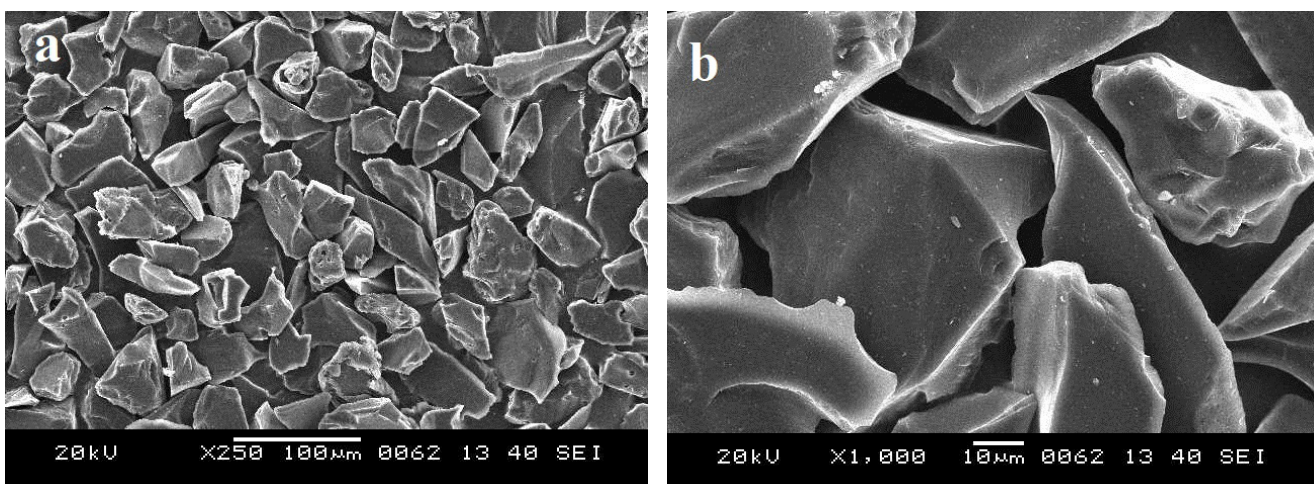


Figure 3. SEM images of as received B<sub>4</sub>C powder.

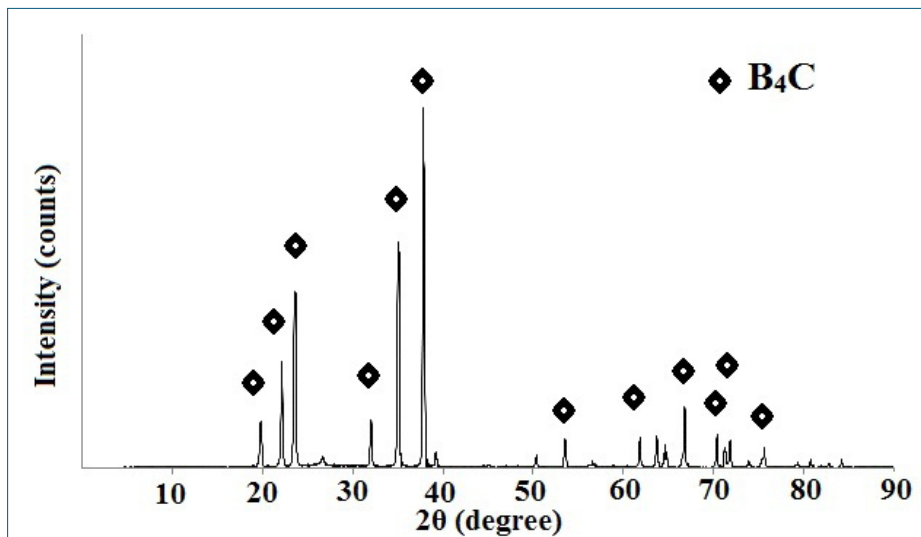
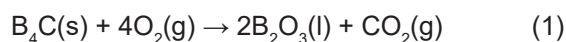


Figure 2. XRD analysis of  $B_4C$  powder.

samples gained weight during oxidation at  $800^\circ\text{C}$  and  $1000^\circ\text{C}$ . In Figure 4, it can also be seen that weight changes of the samples increased with temperature. This suggested that the behavior is of an Arrhenius type. Since the corrosion products are formed by the reaction of the elements in the borides with the oxygen in the environment, the rate of the reaction is controlled by the diffusion of the elements involved. Thus, the diffusion process is expected to be the mechanism that controlled the kinetics of the oxidation of boron compounds.

After 5-hours oxidation tests, a rapid weight gain was observed for both temperatures. These results suggested that during the first five hours an oxide layer formed rapidly over the sample surface. However, after 10-hours oxidation tests, the rate of weight gain decreased due to the oxide layer formation on the surface. Properties of the oxide products have significant effects on the weight changes, so they need to be considered carefully. Oxidation reaction of  $B_4C$  is as follows [4, 7]:



During the first five hours, formation of  $B_4C$  and  $B_2O_3$  phases caused a rapid weight gain. After that, they behaved as a protective layer and the rate of weight gain decreased due to the volatilization of liquid  $B_2O_3$ . It is apparent that formation of  $B_4C$  causes the weight gain and  $B_2O_3$ , whereas volatilization of  $B_2O_3$  causes the weight loss. Although the liquid phase was expected to be volatile at high temperatures, the observed weight gains for these samples suggested that the amount of the solid oxide formed must have been higher than the amount of volatile boron-containing products. According to the literature,  $B_2O_3$  phase is liquid over  $450^\circ\text{C}$  and its boiling temperature is about  $1600^\circ\text{C}$ . Thus, around  $1000^\circ\text{C}$ , the vapor pressure of this phase increases significantly [11, 12]. Other researchers reported that the vapor pressure of boron oxide becomes significant at  $750^\circ\text{C}$  [13]. Carbon in the  $B_4C$  compound could form only gas phase products during the tests. However, weight gains were

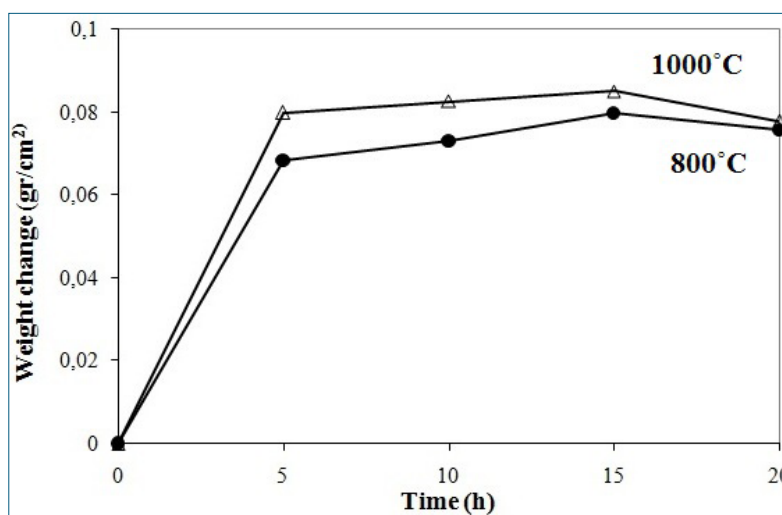


Figure 4. Relative weight changes of the  $B_4C$  pellets oxidized at  $800^\circ\text{C}$  and  $1000^\circ\text{C}$ .

observed for this compound at 800°C and 1000°C. After 20 hours of oxidation, weight losses were observed for B<sub>4</sub>C. These results can be explained by proposing that at low temperatures the initial weight increase was caused by boron oxide formation whereas at higher temperatures, weight loss was caused because of the volatilization of B<sub>2</sub>O<sub>3</sub> phase and formation of the gas phase carbon oxide products.

XRD analyses of the oxidized B<sub>4</sub>C pellets showed that B<sub>2</sub>O<sub>3</sub> phase formed during the oxidation tests conducted, in the air, at the indicated temperatures (Figure 5). As mentioned above, this phase is liquid over 450°C and around 1000°C, the vapor pressure of this phase increases significantly.

Thermodynamic stability of the products resulting from chemical reaction of B<sub>4</sub>C with oxygen can be determined by considering the Standard Gibbs Free Energy changes ( $\Delta G^\circ$ ) of the oxidation reactions. Table 1 indicates the reaction and  $\Delta G^\circ$  values of the reaction calculated by using data from the literature.  $\Delta G^\circ$  values given in Table 1 state that the oxides of B<sub>4</sub>C are thermodynamically stable as oxidation/corrosion product [14]. CO<sub>2</sub> is the corrosion product of the B<sub>4</sub>C compound and it is in the gas phase at all temperatures.

Kinetic behavior can be described by the following expression,

$$X^n = k.t \quad (2)$$

where “X” is the weight change of the material per unit surface area ( $\Delta m / A$ ) or the thickness of the scale layer, “t”, the time (experiment duration) and “k” the kinetic coefficient of the relationship between (X) and (t). In other words, “k” indicates the “rate” of the reaction, “n” is an exponential coefficient related to the mechanism of the reaction. The coefficient “n” can take values such as 1, 2, 3, indicating that the dependence of ( $\Delta m/A$ ) on (t) is linear, parabolic or cubic, respectively.

In many high-temperature oxidation studies, it has been observed that if the corrosion products formed on the substrate are solids at low vapor pressure, thicknesses of the solid product (scale) increase with time according to the “parabolic” kinetics [15]. In order to examine the kinetic behavior of B<sub>4</sub>C samples, the weight change data in Figure 4 are rearranged to plot graphs so that the kinetic coefficient is 2. These new graphs are shown in Figure 6. In Figure 6, the squared values of the specific weight changes [ $(\Delta m/A)^2$ ] are plotted as a function of the experiment duration (t). Thus, if the weight gains are “parabolic”, the lines in

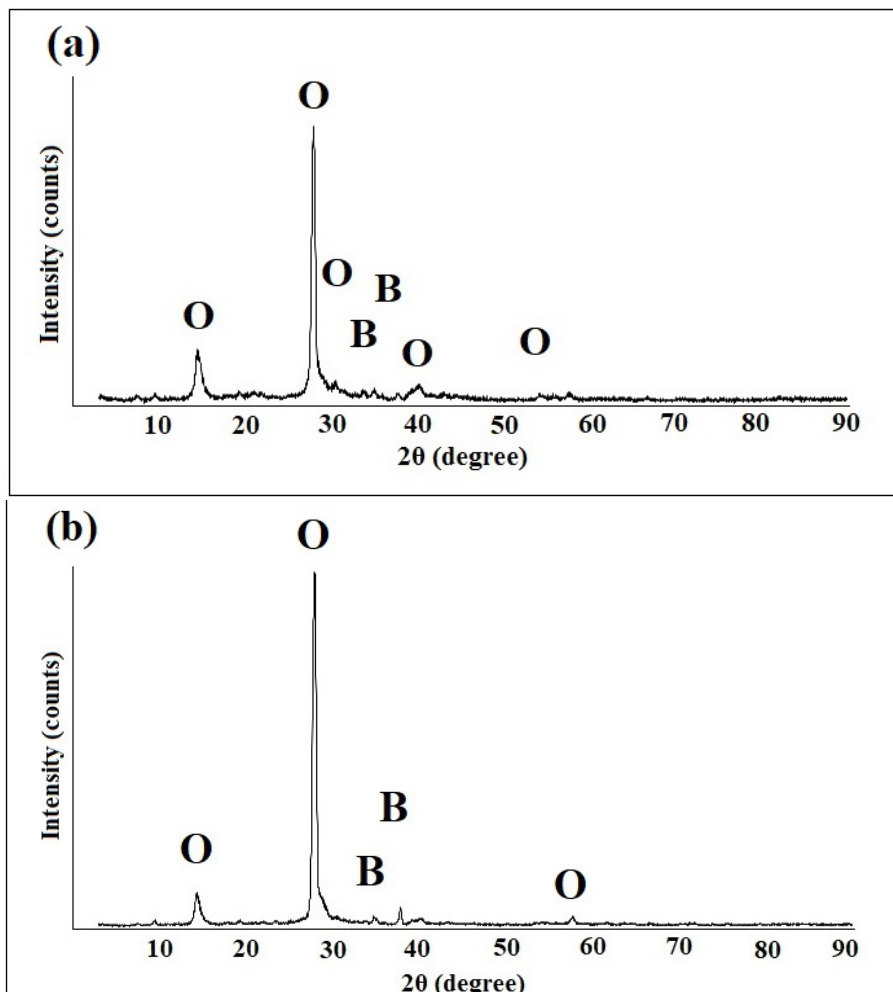
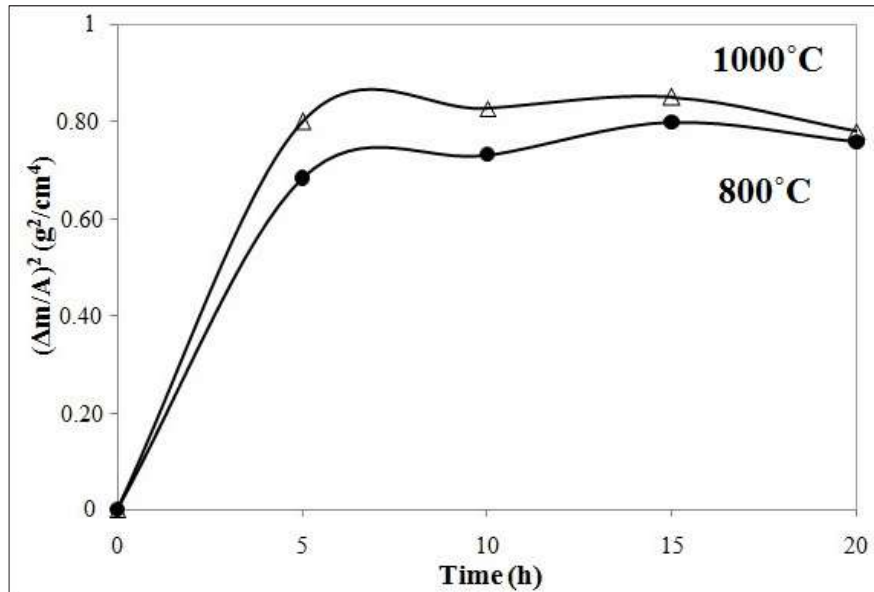


Figure 5. XRD patterns of the B<sub>4</sub>C pellets oxidized at (a) 800°C and (b) 1000°C for 20 h (B: B<sub>4</sub>C, O: B<sub>2</sub>O<sub>3</sub>)

**Table 1.** Oxidation reactions and standart Gibbs free energy changes ( $\Delta G^\circ$ ) [14].

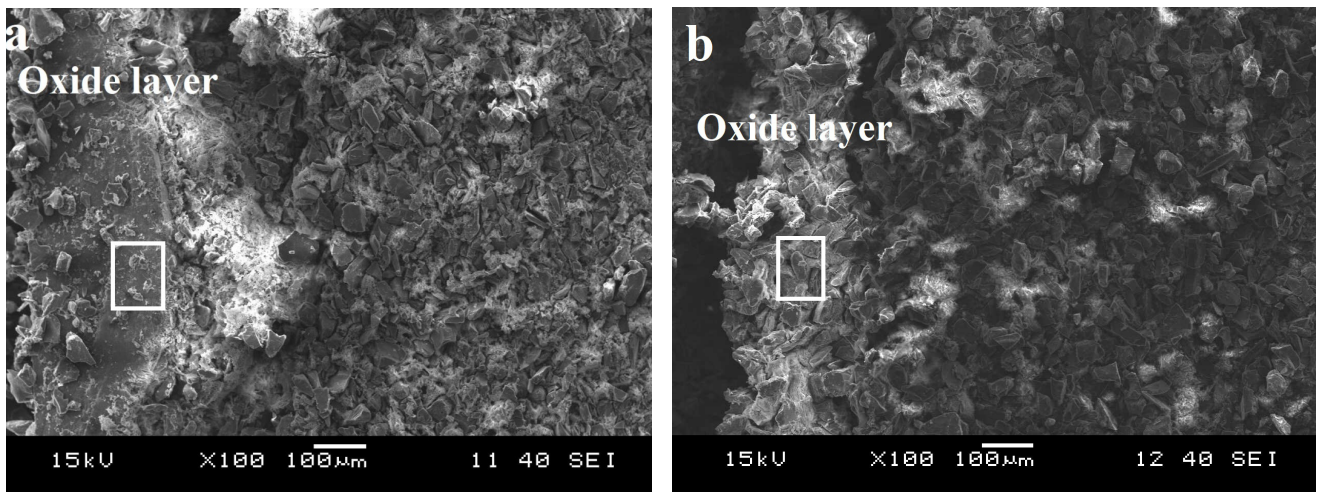
Oxidation Reaction	$\Delta G^\circ$ (kJ)	
	800°C	1000°C
$B_4C(s) + 4O_2(g) \rightarrow 2B_2O_3(l) + CO_2(g)$	-2368,8	-2286,0

**Figure 6.** Weight change per unit area squared  $[(\Delta m/A)^2]$  vs experiment duration(t) for  $B_4C$ .

these graphs should be linear. For the oxidation tests in which experimental data were collected for less than 5 hours, it can be said that  $B_4C$  samples showed a parabolic behavior.  $B_4C$  samples did not form solid oxide phases and showed a limited parabolic behavior for a shorter time period of about 5 hours. The rate of weight gain of the  $B_4C$  samples also decreased with increasing time as can be seen from the slopes of the lines in the graphs. Experimental data obtained at 1000°C showed that the amount of oxidation products increased with the increasing temperature. At these temperatures, kinetics of the oxidation reactions did not seem to be parabolic. As the rate of weight gain with time decreased, after long-term oxidation, net weight losses were observed. This type of oxidation behavior can be explained by the removal of a

gas product, probably the boron oxide vapor from the samples. Besides volatilization of boron oxide, C-containing gas phase products are also believed to play an important role in the weight loss of  $B_4C$ .

Figures 7 a and b show the cross-sectional microstructures of the samples after oxidation at (a) 800°C and (b) 1000°C for 20 h. Due to the mechanical stress during sample preparation, except the oxide layer formed on the surface of pelleted  $B_4C$  samples some  $B_4C$  particles were separated from inside regions. In this case, while the roughness of the inner part is high the outer part of the oxide layer seems flat. EDS analysis of the white square area in Figure 7a showed that the area contained 28.663% B, 63.431% C and 7.906% O by weight. In Figure 7a it can be seen that there

**Figure 7.** SEM images of the  $B_4C$  pellets after oxidation at (a) 800°C for 10 h and (b) 1000°C for 10 h.

is a denser oxide layer over the sample surface. The formation of  $B_2O_3$  phases leads to this denser layer. EDS analysis of the white square area in Figure 7b showed that the composition of the area was 45.187% B, 38.412% C and 16.401% O by weight. SEM/EDS analyses of the oxidized  $B_4C$  sample showed areas appearing "white" in the SEM pictures. It is known that such "white" colors indicate the presence of electrically insulating structures. Since B and O elements were detected by EDS at the same location, it was concluded that boron oxide formed in the samples during oxidation.

#### 4. Conclusions

This study reports the cyclic oxidation behavior of cold pressed  $B_4C$  pellets that were oxidized under air conditions at 800°C and 1000°C for 5, 10, 15 and 20 hours. The results can be summarized as follows:

- After first 5-hours oxidation tests a rapid weight gain was observed. Weight gain at 1000°C is higher than at 800°C.
- After 10 and 15-hours oxidation tests, the rate of the weight gain decreased because of the volatilization of  $B_2O_3$  (g) and C-containing ( $CO$ ,  $CO_2$ ) products. According to the SEM/EDS results dense  $B_2O_3$  (s) oxide layer was formed on the surface of the  $B_4C$  pellet.
- $B_2O_3$  solid phase was even detected by XRD after 20-hours oxidation for both temperatures.

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