

Oxidation behaviour and strength of B₄C–30 wt % SiC composite materials

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The oxidation behaviour and the effect of oxidation on the room-temperature flexural strength of B₄C–30 wt % SiC composite material were investigated. The weight changes of the samples exposed to air at temperatures between 500 and 1000 °C were continuously monitored with a microbalance. At temperatures below 800 °C, the weight change of the specimen was negligible. As the temperature was increased to 800 °C, parabolic weight gain was observed. The rate of the weight gain increased with exposure temperature. The oxidation product formed on the surface was found to be a crystalline boric oxide (B₂O₃) by X-ray analyses. The oxide layer was severely cracked due to the thermal expansion mismatch between the oxide layer and the substrate. However, the room-temperature flexural strength was increased when the samples were exposed at temperature between 700 and 900 °C, apparently due to the blunting of strength-limiting defects at the surface. When the temperature was higher than 1000 °C, a severe reduction in strength was observed. The reliability of the composite material was also improved significantly by such exposures.

1. Introduction

Boron carbide (B₄C) is a useful ceramic material for engineering applications because of its high hardness, high elastic modulus, and low specific gravity. The unique combination of these properties led to the development of B₄C-based wear parts and armour materials. Nuclear properties, such as high cross-section for neutron absorption and resistance to irradiation, made this material attractive for neutron absorbing material [1–5]. However, like other covalent bonding materials, the production of high-density B₄C by pressureless sintering is very difficult. Accordingly, hot pressing has generally been employed to obtain dense B₄C bodies. The addition of sintering aids, such as carbon, Al₂O₃, and TiB₂, was also effective in improving the density of the material up to 95% theoretical by suppressing the coarsening of the grains during sintering [6, 7]. Making a composite material by adding a large amount of SiC was found to be another effective method to improve the density while maintaining the physical properties of B₄C [8].

Engineering ceramic materials are often exposed to harsh environments including high temperature and corrosive atmospheres. Therefore, the high-temperature stability of this material, especially its oxidation behaviour, is one of the most important properties to be understood clearly before the actual application of these materials [9]. According to previous research on

the oxidation behaviour of B₄C, parabolic weight gain occurred in the temperature range 800–1100 °C as a result of the B₂O₃ formation on the surface. As the temperature increased further, a rapid weight loss was detected due to the evaporation of B₂O₃ formed on the surface. The flexural strengths of the specimens were reported to decrease steadily during the oxidation processes at all temperatures investigated [10, 11].

The strength of non-oxide ceramics is strongly affected by the oxidation process. When the oxide layer formed on the surface has the thermal expansion coefficient higher than that of the substrate, a severe reduction in strength was observed due to the residual tensile stress at the surface [12]. A moderate increase in strength is expected for the opposite case. The strength is also influenced by the modification of the surface morphology. Our previous investigations on the stability of Silicon-based materials (SiC, Si₃N₄, and SiC whisker-reinforced Al₂O₃) at elevated temperature have shown that the strength of those materials increased whenever a thin oxide layer was formed on the surface [13–18]. The increases in strength were attributed to the blunting of the strength-limiting surface flaws with the SiO₂ layer formed by the oxidation process. As the oxide layer became thicker, new defects such as bubbles and pits were formed in the oxide layer or at the interface between the oxide layer and the substrate, negating the benign flaw-blunting effect [19].

In the present work, the oxidation behaviour of sintered B_4C -30 wt % SiC composite material was investigated by monitoring the weight changes of the specimens during high-temperature exposure. The effects of oxidation on the room-temperature flexural strength and on the reliability of this material were also determined. The changes in microstructure and surface composition were observed and correlated to the oxidation behaviour and the strength of the specimens.

2. Experimental procedure

The starting materials used in this experiment were B_4C (Grade HS, Starck, Germany) and SiC powder (Grade A10, Starck, Germany). After mixing in methanol, the powder was isostatically pressed with the pressure of 70 MPa. The green bodies were sintered at 2100 °C for 2 h in a flowing argon atmosphere. The density of the sintered body was higher than 98% theoretical.

The oxidation behaviour of the material in air at elevated temperatures was determined by continuously monitoring the weight changes of the samples (3 mm × 4 mm × 0.4 mm) with a microbalance (TGA 7, Perkin-Elmer, USA). The sensitivity of the balance was 0.1 µg. A platinum wire and a crucible were used to suspend the sample from the balance. The air was introduced from the top of the vertical tube furnace at a constant speed of 1.3 cm s⁻¹ (STP) and with a total pressure of 0.1 MPa.

The specimens for the mechanical test with dimensions of 3.0 mm × 4.0 mm × 25 mm were cut out from the sintered body. The tensile surfaces of the bend bar were polished with diamond pastes down to a grit size of 1 µm. The edges of the tensile surface of each specimen were slightly bevelled on a 6 µm grit diamond wheel. After grinding and polishing, the specimens were cleaned in ultrasonically agitated baths of acetone and isopropyl alcohol. Groups of samples were oxidized in air at temperatures of 500–1000 °C for various periods of time. Five flexure bars were exposed to each set of conditions. Four-point flexure tests were performed at room temperature on the exposed samples, with a crosshead speed of 0.03 mm s⁻¹, and inner and outer spans of 10.0 and 20.0 mm, respectively. The reliability of the specimens was determined by calculating the Weibull modulus of the specimens.

The microstructures of the samples before and after oxidation for various periods of time were examined by a scanning electron microscopy (XL20, Philips, The Netherlands). The reaction products formed on the surface were identified using an X-ray diffractometer (XRD, D/MAX 2A, Rigaku, Japan), and an energy-dispersive X-ray spectrometer (EDS, PV9900, Philips, The Netherlands).

3. Results and discussion

The weight changes of the B_4C -30 wt % SiC composite material exposed to air were strongly dependent on the exposure temperature, as shown in Fig. 1.

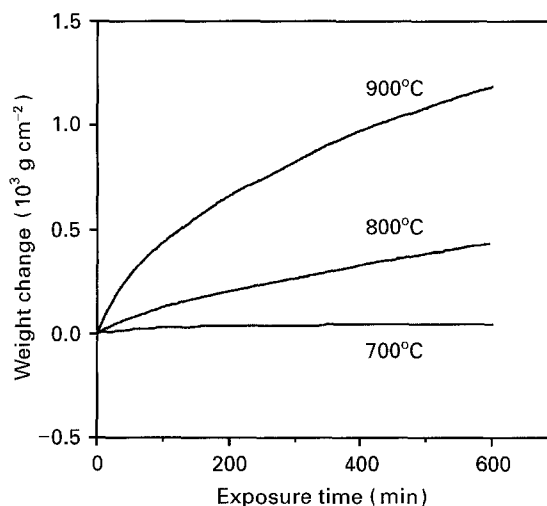


Figure 1 Weight changes of the B_4C -30 wt % SiC composite materials exposed to air at elevated temperatures. At temperatures higher than 700 °C, parabolic weight gains were observed, indicating the formation of dense oxide layer on the sample surface.

Up to 700 °C, the weight changes were negligible. As the temperature was increased to 800 °C, a parabolic weight gain was observed, indicating the formation of dense layer on the sample surface. With further increase of temperature, the weight gain rate became remarkably higher as shown in Fig. 1.

Scanning electron micrographs of the samples before and after exposure to air at various temperature are shown in Fig. 2. From the polished surface of the sample before exposure, a fine mixture of B_4C and SiC was observed clearly as shown in Fig. 2a. The darker phase was identified as B_4C by EDS analyses. When the sample was exposed to air at 700 °C for 5 h, the surface became rough, as shown in Fig. 2b. However, interestingly enough, the top of the surface was smooth, indicating that there was a material loss by the oxidation process. In other words, the surface became rough not by the oxide formation but by the evaporation of one species from the surface. As the exposure temperature was increased to 800 °C a continuous layer was formed on the surface, Fig. 2c. The layer was severely cracked, apparently due to the difference in thermal expansion coefficient of the oxide layer and that of the B_4C -SiC substrate material. When the samples were exposed to higher temperatures (900 °C), larger cracks were developed as shown in Fig. 2d, implying the formation of thicker oxide layers.

X-ray diffraction patterns representative of B_4C -SiC samples before and after exposure at various temperatures in air are shown in Fig. 3a–c. Before exposure (Fig. 3a), only B–C compounds (B_4C , $B_{13}C_2$, and B_8C) and SiC peaks were detected, as expected. When the samples were exposed to air at 700 °C for 5 h, one peak of B_2O_3 was detected, as shown in Fig. 3b, suggesting a small amount of crystalline B_2O_3 was formed on the surface. As the oxidation temperature was increased to 800 °C, many strong peaks of B_2O_3 were detected as shown in Fig. 3c. With further increase in the temperatures to 900 and 1000 °C, similar diffraction patterns to that in Fig. 3c were observed.

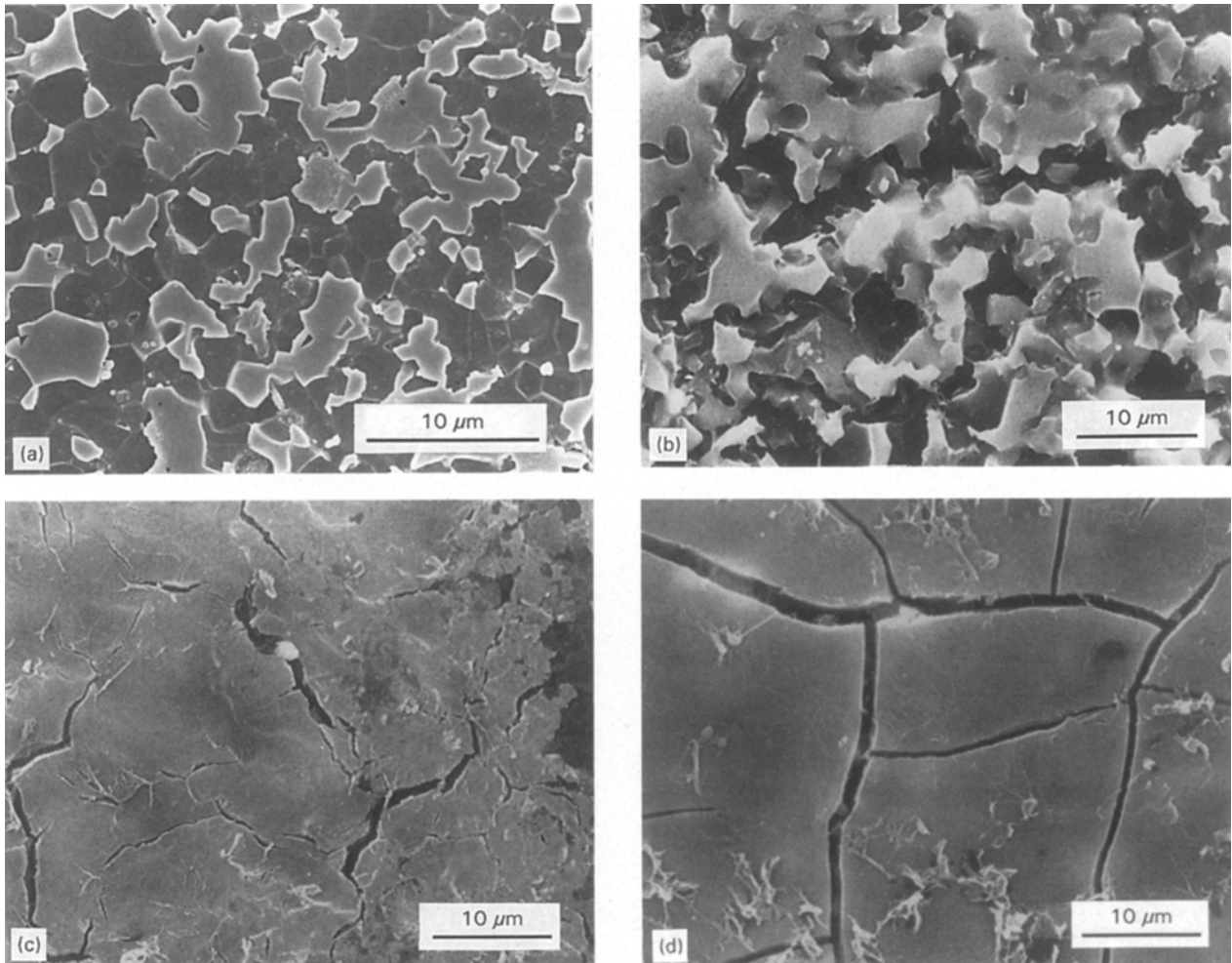


Figure 2 Scanning electron micrographs of the samples, (a) before exposure, and after exposure for 5 h at (b) 700 °C, (c) 800 °C, (d) 900 °C showing a continuous layer and cracks on it.

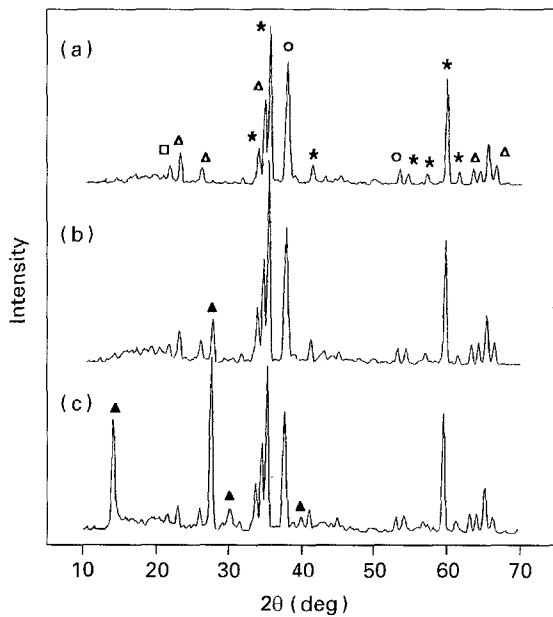
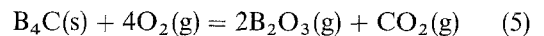
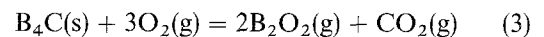
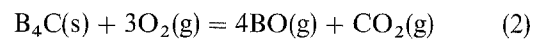
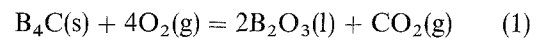


Figure 3 X-ray diffraction patterns of B_4C -SiC samples; (a) before exposure, (b) after exposure at 700 °C, and (c) at 800 °C. (○) B_4C , (Δ) $B_{13}C_2$, (□) B_8C , (★) SiC, and (▲) B_2O_3 .

From these experimental results on weight gain, surface morphology and composition changes of the specimens, it is predicted that the composite material exhibits two different types of oxidation behaviour

depending on the exposure temperature. The observed weight changes of the specimens are results of B_4C oxidation, because SiC is extremely resistant to oxidation in this temperature range [20]. The parabolic weight gains occur at temperatures higher than 800 °C as a result of the formation of a continuous oxide layer, while no weight change takes place at temperatures ≤ 700 °C due to the combined effect of the B_2O_3 formation and the B_4C evaporation. When B_4C is exposed to air in temperature range investigated in this research, the following reactions are favourable thermodynamically [21, 22].



There are two types of oxidation reactions; the weight gain reaction of Reaction 1 and the weight loss reactions of Reactions 2–5. When the oxygen partial pressure, P_{O_2} , is high enough, a B_2O_3 layer is formed on the surface by Reaction 1, resulting in the parabolic weight gain of the sample (passive oxidation). On the other hand, if the P_{O_2} is not high enough, Reactions 2–5 would occur, resulting in linear weight loss of the

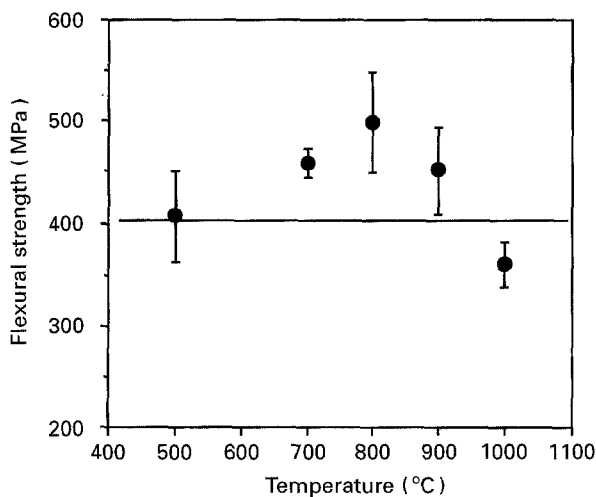


Figure 4 Room-temperature flexural strengths of the B_4C -SiC composite material exposed to air at various temperatures for 5 h.

sample (active oxidation). The transition P_{O_2} from active to passive oxidation at 1000 K was calculated to be about 10^{-10} atm following Wagner's analysis [23]. Therefore, the environment employed in this research, ambient air, is well within the passive oxidation region. Accordingly, the oxidation of B_4C is expected to proceed by Reaction 1. This was actually observed when the samples were exposed to air at temperatures higher than 800 °C. However, the samples exposed to air at temperatures below 700 °C exhibited no apparent signs of Reaction 1, except one weak peak in the X-ray diffraction pattern. This behaviour is believed to be due to the fact that the thermodynamic equilibrium is not achieved at these temperature ranges. Even though Reaction 1 is most favourable thermodynamically, Reactions 2–5 are also favourable. Therefore, if Reaction 1 does not proceed rapidly enough for the sample to be fully covered with a continuous B_2O_3 layer, active oxidation of B_4C would occur by Reactions 2–5. In this case, the evaporation of B_4C and the formation of B_2O_3 islands at the surface, occur simultaneously. The inertness of SiC in the composite material induced the surface morphology of the specimen as shown in Fig. 2b.

The room-temperature flexural strengths of the B_4C -SiC composite material were influenced by the oxidation processes. The effect of the oxidation temperature on strength is shown in Fig. 4. When the specimens were exposed at temperatures up to 500 °C for 5 h, the strength was not affected. However, as the temperature was increased to above 700 °C, increase in strength was observed. When the temperature was increased further to 1000 °C, reductions in strength were observed. The strength was also influenced by the exposure time as shown in Fig. 5. The maximum strength of the specimens was detected when the samples were exposed to 800 °C for 5 h. These results demonstrate that the room-temperature strength of B_4C -SiC composite material can be improved by the formation of an oxide layer on the surface if the oxidation conditions are properly controlled.

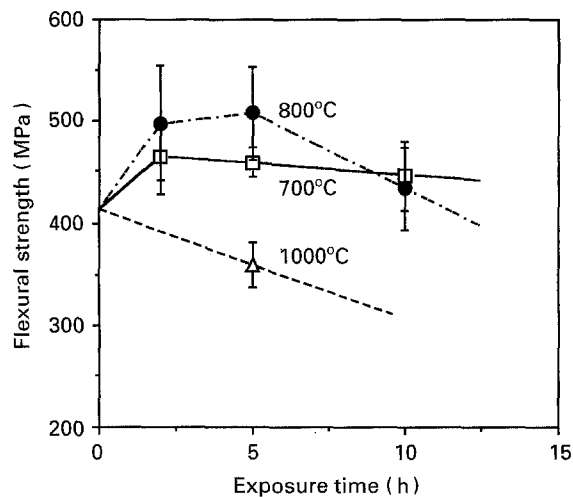


Figure 5 Room-temperature flexural strengths of the B_4C -SiC composite material exposed to air for different periods of time. The highest strength was observed after exposure at 800 °C for 5 h.

When the thermal expansion coefficient of the oxide layer on the surface is higher than that of the substrate, residual tensile stress is developed on the oxide layer during cooling. Cracks are developed on the oxide layer if the residual stress is higher than the strength of the layer. The severely cracked layer on the surface shown in Fig. 2c and d reflected the large difference in the thermal expansion coefficient of the B_2O_3 layer ($\sim 14 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) and that of the B_4C -SiC substrate material ($\sim 4.6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$). Generally, when cracks are developed on the surface of a material, reductions in strength were observed due to the stress concentration at the crack tips in addition to the residual tensile stress. The cracks generated in the oxide layer may even propagate in the substrate if the interfacial strength between the substrate and the oxide layer is sufficiently high [12]. In this case, reduction in strength is most severe. On the other hand, if the oxide layer formed on the surface is effective in blunting the existing flaws, the strength of the material tends to increase. This strengthening behaviour has been observed in SiC, Si_3N_4 and Al_2O_3 -SiC_w composite material when these materials were exposed to a controlled oxidation atmosphere of H_2 - H_2O or Ar- O_2 environments [13, 16, 17].

According to the scanning electron micrographs, in most cases, the fracture origins before exposure were the surface defects, as shown in Fig. 6a. Such defects were believed to be filled in with fluid B_2O_3 formed during the oxidation process. A typical fracture surface after oxidation is seen in Fig. 6b, showing the dense B_2O_3 layer of about 10 μm thickness. Therefore, observed increase in strength by the oxidation process is deemed to be a result of the dominance of the crack-blunting effect over the residual tensile stress or the stress concentration at the crack tips in the oxide layer.

The formation of an oxide layer was also effective in improving the reliability of the B_4C -SiC composite material, as shown in Fig. 7. The Weibull modulus of the specimen before exposure was 6.6, indicating the wide scattering of the flexural strength. On exposure

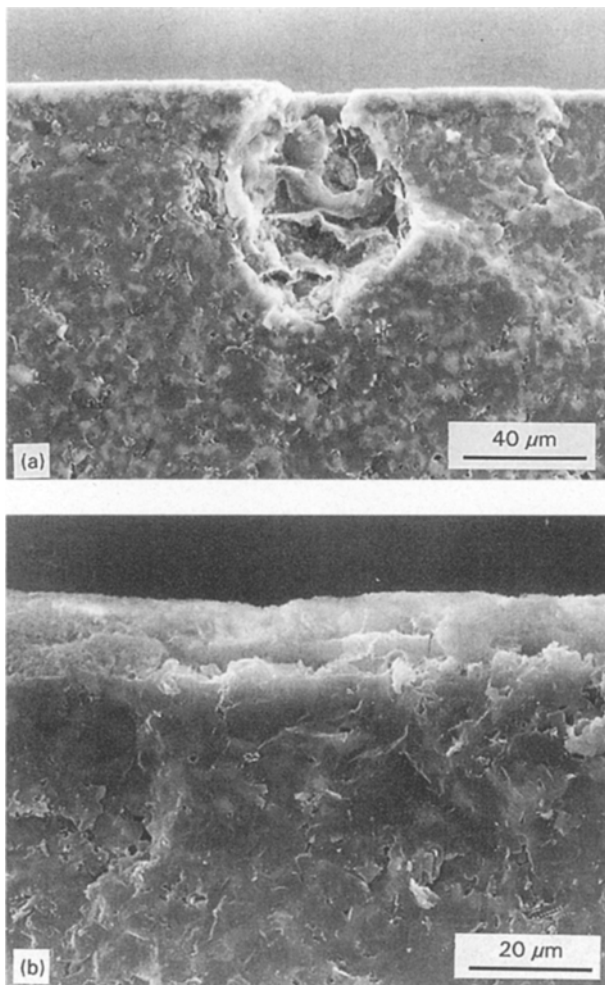


Figure 6 Scanning electron micrographs of the fracture surface of the samples, (a) before exposure, showing the fracture origin on the surface, and (b) after exposure at 800 °C for 5 h, showing the oxide layer formed on the surface.

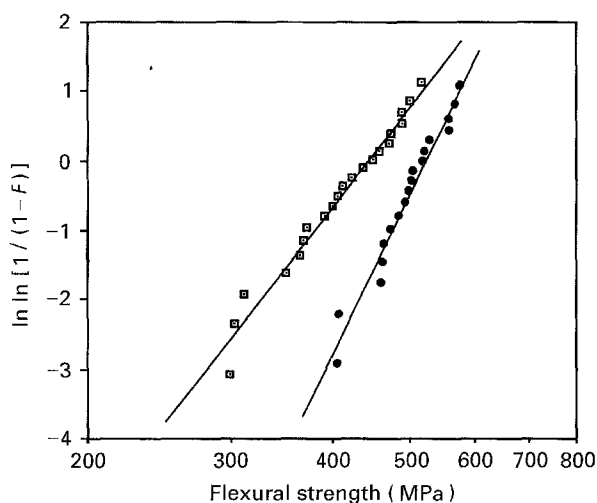


Figure 7 Weibull modulus of the specimen (\square) before ($m = 6.6$) and (\bullet) after ($m = 10.5$) exposure to air at 800 °C for 5 h. The reliability of the B_4C -SiC composite material was improved remarkably by the oxidation process.

to air at 800 °C for 5 h (under which condition the highest strength was detected), the Weibull modulus was increased to 10.5. This improvement in the reliability implies that the variations in the severity of

the fracture origin were reduced significantly, supporting evidence that strengthening effects originated from the blunting of surface defects with the fluid B_2O_3 .

4. Conclusion

The oxidation behaviour and the flexural strength of B_4C -30 wt % SiC composite material exposed to air at elevated temperatures were investigated. Samples were oxidized at temperatures between 500 and 1000 °C. Changes in weight, composition, microstructure, and room-temperature flexural strength were monitored. The weight changes and strengths of the samples were strongly dependent on the exposure temperature. At temperatures ≤ 700 °C, the weight changes were negligible due to the combined effects of the volatilization of B_4C and the formation of B_2O_3 islands on the sample surface. At temperatures higher than 700 °C, parabolic weight gains were detected as a result of the formation of a liquid oxide layer. The oxide layers were severely cracked due to the thermal expansion mismatch between the oxide layer and the substrate. Despite the formation of cracks on the surface, increase in room-temperature flexural strength was observed, apparently due to the blunting of surface defects by the fluid B_2O_3 . The oxidation process was also effective in improving the reliability of the material by reducing the variations in the severity of the fracture origins at the surface.

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