The Oxidation Behavior of ZrB$_2$-based Mixed Boride

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Abstract. Zirconium diboride based composites containing silicon carbide with relative densities in excess of 99% were produced by hot-pressing. Oxidation test was conducted in air at 1500 °C. ZrB$_2$-SiC composite showed relatively low oxidation resistance due to the non-uniform surface silica-rich layer. But in case of mixed boride-SiC composites further improvement of the oxidation performance were observed due to the phase separation in the surface silica-rich layer.

Introduction

Ceramic borides, carbides and nitrides are characterized by high melting points, high mechanical properties and relatively good oxidation resistance in extreme environments. This family of ceramic materials is known to be as Ultra High Temperature Ceramics (UHTCs) [1, 2]. The oxidation of ZrB$_2$ has been studied by number of investigators [3, 4]. Many attempts have been made to enhance the oxidation resistance of ZrB$_2$-based materials through appropriate additives. Considerably, the most common additive is SiC, which enhance oxidation resistance by forming a silica-rich scale [4, 5] and limits diboride grain growth [6]. Modification of the chemical composition of the oxide surface layer is one of the efficient ways of controlling oxidation resistance of non-oxide ceramics [2]. It is known from the literature that borate and silicate glass containing group IV-VI transition metal oxide show strong tendency to phase separation [7]. Therefore, this study has been focused on the improvement of the oxidation resistance by modifying surface glass scale.

Experimental Procedure

Processing. Commercially available ZrB$_2$ (Grade A, H.C Starck), NbB$_2$ (Japan New Metal Co., LDT), TaB$_2$ (Japan New Metal Co., LDT) and SiC (H.C. Starck, UF25) were used to prepare the materials. Three compositions, their designation, and processing history are summarized in Table 1. To reduce the particle size in some batches, as-received ZrB$_2$, NbB$_2$ and TaB$_2$ were vibration milled, respectively. Powders were milled in ethanol for 2 h using steel balls. During the milling 4 wt. % of Fe impurity was introduced because of wear of the steel balls. Fe impurity was successfully removed by an acid treatment. Subsequently, milled powders were ball-milled in ethanol for 24 hours with SiC. The solvent of the powder mixtures were dried on hot-plate with continuous string, and the resulting dried powder mixtures were ground. Thus, obtained milled powders were hot-pressed (Thermal Technology Inc, Astro Hot Press) in BN-coated graphite dies. Powder compacted were heated under Ar flow at 1800 °C with an average heating rate of ~20°C/min. When the die temperature reached 1800 °C, a uniaxial load of 32 MPa was applied and dwelled for 2 h at 1800 °C, and then the furnace was cooled at a cooling rate of ~20 °C/min to room temperature.

Oxidation. The oxidation test was carried by exposing the sample under air atmosphere after diamond-polishing to a 1 μm using routine metallographic methods. Prior to oxidation, specimens were cleaned with acetone in an ultrasonic bath. Each specimen was heated a heating rate ~5 °C/min to the 1500 °C and held for 30 min in a tube furnace.
Table 1. Summary of UHTC compositions, designations, processing and relative density

<table>
<thead>
<tr>
<th>Composition</th>
<th>Designation</th>
<th>Processing</th>
<th>Density (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB&lt;sub&gt;2&lt;/sub&gt; – 30 vol. %</td>
<td>ZS</td>
<td>1800°C, 32 MPa</td>
<td>99</td>
</tr>
<tr>
<td>SiC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Zr&lt;sub&gt;0.7&lt;/sub&gt;Nb&lt;sub&gt;0.3&lt;/sub&gt;)B&lt;sub&gt;2&lt;/sub&gt; – 30</td>
<td>ZNS</td>
<td>1800°C, 32 MPa</td>
<td>99</td>
</tr>
<tr>
<td>vol. % SiC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Zr&lt;sub&gt;0.7&lt;/sub&gt;Ta&lt;sub&gt;0.3&lt;/sub&gt;)B&lt;sub&gt;2&lt;/sub&gt; – 30</td>
<td>ZTS</td>
<td>1800°C, 32 MPa</td>
<td>99</td>
</tr>
<tr>
<td>vol. % SiC</td>
<td></td>
<td></td>
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</tbody>
</table>

<sup>a</sup> Based on rule-of-mixture

Result and discussion

Bulk densities for the hot pressed billets were measured and the results showed 5.27 g/cm<sup>3</sup> (ZS), 5.3 g/cm<sup>3</sup> (ZNS) and 6.29 g/cm<sup>3</sup> (ZTS), respectively. Using a rule of mixture calculation, and assuming that the true densities 6.09 g/cm<sup>3</sup> for ZrB<sub>2</sub>, 6.61 g/cm<sup>3</sup> for NbB<sub>2</sub>, 11.7 g/cm<sup>3</sup> for TaB<sub>2</sub> and 3.21 g/cm<sup>3</sup> for SiC. Based on this true density, all samples had >99% relative densities. XRD showed (data not shown) metal boride – SiC composites were successfully fabricated at 1800 °C. In case Nb, Ta doping, the slight shift of peaks was observed, which clarify the solid solution of Nb and Ta atoms into the Zr lattice site. SEM analysis did not reveal any obvious porosity in the microstructure, which supports the results of the density measurement and vibration milling was effective to enhance sintering driving force due to the reduced particle size. In case of ZS, average grain size of ZrB<sub>2</sub> was 2–6 µm while average grain size of ZNS, ZTS were 0.8–5µm and 0.6–4 µm respectively. This result indicated that by adding NbB<sub>2</sub> and TaB<sub>2</sub>, average grain size of ZrB<sub>2</sub>-transition metal boride solid solution became small.

Oxidation of three samples at 1500 °C for 30 min in air produced structures that consist of three layers: (1) surface silica-rich layer, (2) a SiC-depleted layer, and (3) un-reacted layer. The formation of three layers is consistent with previous investigation [5, 8, 9]. Fig. 1 is a SEM image of the top surface of the oxidized materials at 1500 °C, for 30 min.

![Fig. 1. SEM images of oxidized top surface of materials: (a) ZS, (b) ZNS, and (c) ZTS](image-url)
It is shown that in non-uniform surface silica-rich layer was observed. This may be due to wetting characteristics or low viscosity of surface silica-rich layer owing to relative low temperature compared with melting point of $\text{SiO}_2$ that might enhance the local oxidation rate. But in case ZNS and ZTS, surface silica-rich layer was uniformly distributed and expected parabolic oxidation behavior. Materials containing NbB$_2$, TaB$_2$ might be less oxidation than ZS, which is the result of phase separation in surface silica-rich layer induced by Nb-, Ta- contained oxide. Similar to previous investigation[10], the presence of light spots of surface silica rich layer in Fig. 1 (b) and (c) distributed in a silica-rich matrix is an indication of high temperature glass phase separation. The light spots were Nb-, Ta- contained oxide from the analysis by EDS. Both increased liquidus temperatures and viscosities, which are characteristic features of phase separations, are good for a decrease in oxygen diffusivity through surface silica-rich layer. And cross-sectional analysis showed (data not shown) similar results with top surface analysis. ZS showed relatively thick surface silica-rich layer and SiC-depleted layers due to the non-uniform surface Si containing layer. In contrast, ZNS and ZTS showed thin surface silica-rich layer and SiC-depleted layer due to the uniform surface silica-rich layer.

Summary

Billet of ZrB$_2$ containing SiC particulate addition of 30 mol % of NbB$_2$ and TaB$_2$ were produced using hot pressing of commercial powders. Nearly full densification was achieved relatively low temperature due to the size reduction of starting borides powder via vibration milling. In case of ZS, relatively poor oxidation resistance was observed due to the non-uniform distribution of surface silica rich layer. But in case of ZNS and ZTS, improved oxidation resistance was observed due to the uniform distribution of surface silica-rich layer. Oxidation of the mixed boride borides (ZNS, ZTS) results in the formation of corresponding oxide in the surface silica-rich layer. It should be emphasized that the oxidation resistance of mixed boride was higher than that of that ZrB$_2$ ceramics due the phase separation phenomena.

References

SiAlONs and Non-oxides

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