FABRICATION AND OXIDATION BEHAVIOR OF REACTIVELY HOT Pressed TaB2-SiC Ceramics

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Abstract. The synthesis route, microstructure, mechanical properties and oxidation behavior of TaB2-SiC composite fabricated by reactive hot pressing using Ta/B4C/Si as precursors were investigated. The reaction sequence of TaB2-SiC composite was studied thorough series of heat treatment ranging from 1000 to 1900 °C in Ar. Based on the reaction sequence analysis, TaB2-SiC composite was reactively hot pressed at 1900 °C. Its elastic modulus, flexural strength, Vickers hardness and fracture toughness were 487 GPa, 542 MPa, 17.9 GPa and 3.63 MPam1/2, respectively. The oxidation behavior of the TaB2-SiC composites at 1500 °C in air exhibited passive oxidation with parabolic kinetic.

1. INTRODUCTION

Transition metal boride, carbide and nitride have been classified as ultra-high temperature ceramics (UHTCs). UHTCs possess unique properties such as high melting point (>3200 °C), high mechanical properties and good oxidation resistance [1]. Among UHTCs, tantalum diboride has a high melting point (3200 °C), high hardness (24.5 GPa) and good thermal conductivity [2]. This combination of properties makes TaB2-based ceramics potentially useful in applications for thermal protection system (TPS) on hypersonic aerospace vehicles and reusable atmospheric re-entry vehicles. Many attempts have been made to enhance the oxidation resistance of transition-metal boride (ZrB2, HfB2) through appropriate additives [3-5]. For temperatures above 1200 °C, the addition of SiC provides improved oxidation resistance by forming a SiO2-rich protective layer [3,5]. To date, oxidation behavior of tantalum diboride has not been studied as extensively as other transition metal diborides such as ZrB2 and HfB2.

Transition-metal borides typically need relatively high temperature (>1900 °C) and high pressure (>30 MPa) to obtain fully densified samples because of strong covalent bonding and low diffusion coefficient [1]. Therefore, metallic additives have been used to promote liquid-phase formation that can reduce densification temperature, but it can deteriorate the high temperature properties [6]. Recently, pressureless sintering of transition-metal borides has been widely investigated by using WC, B4C, C and MoSi2 [7-9]. Another alternative advantageous method is reactive hot pressing (RHP), which involves both the synthesis and densification under single-step process leading to high-density ceramics at reduced temperatures and lower impurity contents compared with non-reactive process [10-12].

In this paper, the reaction sequence, microstructure, mechanical properties and oxidation behavior...
of reactively hot pressed TaB$_2$-SiC composite are investigated.

2. EXPERIMENT

The precursor powders were Ta (-325 mesh, Sigma–Aldrich, USA), B$_2$C (Grade HS, ~0.8 μm, H. C. Stack, Germany) and Si (-325 mesh, Sigma–Aldrich, USA). The chemical reaction can be expressed by the following equation, used to prepare the TaB$_2$-SiC composite:

$$2 \text{Ta} + \text{B}_2\text{C} + \text{Si} \rightarrow 2\text{TaB}_2 + \text{SiC}.$$  (1)

The volume contents of TaB$_2$ and SiC were 74.4 vol.% and 25.6 vol.%, respectively. The theoretical density of the composite with respect to the rule of mixture is 9.12 g/cm$^3$. The precursor powders were ball-milled in ethanol for 24 h using ZrO$_2$ balls. In order to investigate the reaction sequences and sintering conditions of the TaB$_2$-SiC, pressureless heat treatment was conducted. The powder mixtures were pressed into disc shaped pellets and heat treated in the temperature range of 1000 to 1900 °C for 1 h under an Ar atmosphere with a heating rate of 10 °C/min. Under the above basic experimental conditions the composites were sintered using reactive hot pressing at 1900 °C for 1 h under a pressure of 32 MPa in an Ar atmosphere.

Phase composition was determined by X-ray diffractometry (XRD, Rigaku D/MAM-IIIC). The microstructures of each specimen were observed using a scanning electron microscope (SEM Philips XL 30). The polished samples were subjected to an oxidation test in Air. The specimen was heat treated at 1500 °C for 30 min in a tube furnace with a heating rate of 5 °C/min. The oxidation behavior was also studied using thermal gravimetric analysis (TGA, SETARAM). Elastic modulus ($E$) was measured by the resonance frequency method (ASTM E1876-1, 2001). Hardness and fracture toughness of the sample were determined using Vickers indentation at a load of 2 kg and a dwell time of 15 s. The fracture toughness was estimated through the following equation [13]:

$$K_{IC} = 0.0319 \frac{P}{a^{1/2}},$$

where $P$ is the applied load, $a$ is the mean indentation half-diagonal length, and $I$ is the crack length. The flexural strength was measured by three point bending method.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic calculations

Fig. 1 shows Gibbs free energy of the possible reaction in the Ta/B$_2$C/Si system based on the thermodynamic calculation. The large negative Gibbs energy values indicated the thermodynamic possibility of the reaction. In light of thermodynamic calculation, every possible reaction has negative Gibbs free energy values, indicating that the reactions are thermodynamically favourable.

$$\text{Ta} + 2 \text{B}\_2 \rightarrow \text{TaB}_2,$$  (2)

$$\text{Ta} + \text{B}_2\text{C} \rightarrow \text{TaC} + 4\text{B},$$  (3)
3.2. The powder synthesis via solid-state precursors

Fig. 2 shows the XRD results of the samples heat-treated at different temperatures. The samples heat treated at 1000 °C revealed the formation of a cubic phase of TaC, in addition to Si and Ta peaks. The result indicates that the reaction between Ta and B\textsubscript{4}C occurs at 1000 °C. At a suitable reaction temperature, it is assumed that B and C atoms from B\textsubscript{4}C diffuse faster than those of Ta and Si. Among these reactions, the diffusion rate of C is higher than that of B and C easily reacts with Ta [10,11]. As a result, it is evident that the formation of TaC occurs at a temperature lower than 1000 °C and occurs faster than the formation of TaB\textsubscript{2}. The formation of TaB\textsubscript{2} occurs at a relatively higher temperature (1400 °C) through a reaction between Ta and B or residual B\textsubscript{4}C. By analyzing the reaction sequence, it can be evidently concluded that reactions (2) and (3) or (4) may occur in two steps. Further increase in the reaction temperature results in the formation of TaB\textsubscript{2} as the main phase, based on the peak intensity, as can be seen in Fig. 2. The XRD pattern of the sample reacted at 1900 °C showed the formation of the final composites TaB\textsubscript{2} and SiC without any secondary phase. As a result, it can be concluded that the powder reaction takes place in two steps, in which the reaction initiated the formation of TaC and at higher temperature, simultaneous reactions take place by reaction (5) and (6) and formed TaB\textsubscript{2}, SiC and elimination of TaC.

### Table 1. Relative density and mechanical properties of the reactively hot pressed samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative density (% T.D.)</th>
<th>Elastic modulus (GPa)</th>
<th>Flexural strength (MPa)</th>
<th>Vickers hardness (GPa)</th>
<th>Fracture toughness (MPa m\textsuperscript{1/2})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaB\textsubscript{2}-SiC</td>
<td>98.6</td>
<td>468</td>
<td>608±64</td>
<td>19.1±0.4</td>
<td>3.35±0.38</td>
<td>This study</td>
</tr>
<tr>
<td>HfB\textsubscript{2}-SiC</td>
<td>99.8</td>
<td>-</td>
<td>692±58</td>
<td>18.3±0.3</td>
<td>5.23±0.17</td>
<td>5</td>
</tr>
<tr>
<td>ZrB\textsubscript{2}-SiC</td>
<td>~99</td>
<td>510</td>
<td>800±115</td>
<td>27±2.2</td>
<td>2.12±0.06</td>
<td>12</td>
</tr>
</tbody>
</table>
3.3. Microstructure
Fig. 3 shows the microstructure of TaB$_2$-SiC composite densified at 1900 °C for 1 h. As discussed above, during the reaction process the diffusion rates of Ta and Si atoms are slow and the compound formation is mainly controlled based on the diffusion rate and reactivity of boron and carbon. Due to the large particle size of the Ta precursor powder, the resultant product TaB$_2$ also formed with similar size grains, as shown in Fig. 3. Thus, the distributions of the in situ-formed TaB$_2$ and SiC phases in the composites are not homogenous with large TaB$_2$ (light phase) particles and non-uniform distribution of SiC (dark phase). Size and morphology of formed TaB$_2$ and SiC is related to its original particle size and shape.

3.4. Oxidation behavior
Fig. 4 shows the results of isothermal TGA analysis of TaB$_2$-SiC composite at 1500 °C in air and inset gives a cross-sectional analysis of the oxidized TaB$_2$-SiC composite (1500 °C for 30 min, in air) showing a layered structure: SiO$_2$ layer (I), SiC-depleted layer (II) and un-reacted TaB$_2$-SiC layer. The formation of layered structure is consistent with observations of other investigators who have studied ZrB$_2$-SiC and HfB$_2$-SiC composites[1,3,5]. As shown in Fig. 4, the TaB$_2$-SiC composite exhibited passive oxidation protection with parabolic mass gain kinetics during the isothermal analysis at 1500 °C. At high temperatures (above 1300 °C), the SiC phase begins oxidizing, resulting in the formation of a silica-rich glassy layer on the surface by reaction (8).

\[
\text{SiC}(s) + 3/2 \text{O}_2(g) \rightarrow \text{SiO}_2(l) + \text{CO}(g). \tag{8}
\]

The surface silica rich layer prohibits the transport of oxygen through the inner oxide scales and makes it possible for a TaB$_2$-SiC composite to show parabolic mass gain kinetics.

3.5. Mechanical properties
The relative density and mechanical properties of reactively hot pressed TaB$_2$-SiC composite were compared to those of HfB$_2$ and ZrB$_2$ [5,12] (Table 1). Elastic modulus, flexural strength, Vickers hardness of TaB$_2$-SiC composite are slightly lower than those of HfB$_2$ and ZrB$_2$-SiC composite. Direct comparison seems unjustified in this case because of the difference in the volume fraction of boride and silicon carbide, sample preparation method, testing methods and specimen sizes being tested. In general, the mechanical properties of TaB$_2$ are comparable to those of ZrB$_2$ and HfB$_2$ [5,12], which makes it a promising candidate material for ultra-high temperature applications such as propulsion systems.

4. CONCLUSIONS
This study reports on reactive powder synthesis via solid-state precursors, microstructure, oxidation behavior and mechanical properties of TaB$_2$-SiC composite. The reactions of the powder mixture commenced at 1000 °C and finished at 1900 °C. In an ambient oxidation test, TaB$_2$-SiC showed parabolic oxidation behavior at 1500 °C. The mechanical properties for the reactively hot pressed TaB$_2$-SiC composite were comparable to the reported value. To our knowledge, this is the first time to investigate reaction mechanisms and oxidation behavior of TaB$_2$-SiC fabricated by reactive hot pressing. Future work will focus on evaluating the oxidation behavior of TaB$_2$-SiC in extreme conditions (> 2000 °C) by using an oxyacetylene torch.

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