Synopsis

Title: Studies on the synthesis, densification and oxidation of zirconium diboride based materials

1. Introduction

Zirconium diboride (ZrB$_2$) is considered a leading material in the category of ultra high temperature ceramics (UHTC) due to very high melting point (3245°C), high thermal conductivity (57.9 Wm$^{-1}$K$^{-1}$), good thermal shock resistance, low coefficient of thermal expansion (5.9x10$^{-6}$ oC$^{-1}$), retention of strength at elevated temperatures and stability in extreme environments [1-3]. ZrB$_2$ is considered a candidate material for hypersonic flight, atmospheric re-entry and rocket propulsion [1, 4, 5]. It gets wetted but not attacked by molten metals and hence used for holding molten metal and as thermo-well tubes in metal processing [6]. Good electrical conductivity makes it suitable for electrode application in Hall -Heroult cell and electric discharge machining [7-9].

Zirconium diboride has two major limitations, (1) poor sinterability and (2) low fracture toughness. Densification of monolithic ZrB$_2$ is very difficult due to strong covalent bonding and low self-diffusion [1, 10]. In this study, efforts were made to overcome these limitations by using suitable sinter additives. Zirconium diboride can be densified by liquid phase sintering or by solid phase sintering. Titanium disilicide (TiSi$_2$) and Chromium disilicide (CrSi$_2$) have been selected as sinter additives for liquid phase sintering process. These silicides have low melting point and thus can be useful in liquid phase sintering.

For solid state sintering, Europium hexaboride (EuB$_6$) was selected as sinter additive. EuB$_6$ is a boron rich boride and thus can introduce structural defects (interstitial point defects) in ZrB$_2$ lattice on formation of solid solution. Presence of point defects would result in enhanced diffusion and thus may be helpful in densification.

Additives are also expected to improve fracture toughness by crack deflection which could be due to presence of second phase. TiSi$_2$ and CrSi$_2$ are expected to increase the oxidation resistance of ZrB$_2$ by formation of silica based protective layer. Effect of EuB$_6$ on oxidation behavior of ZrB$_2$ is not reported till date. In this study, investigations were carried out in this direction.
Objective:

The first objective of present study is to carry out detailed investigation on synthesis of \( \text{ZrB}_2 \) by boron carbide reduction of \( \text{ZrO}_2 \) in presence of carbon according to reaction (1).

\[
\text{ZrO}_2 + \frac{1}{2}\text{B}_4\text{C} + \frac{3}{2}\text{C} \rightarrow \text{ZrB}_2 + 2\text{CO} \quad \cdots \cdots \cdots (1)
\]

Though this synthesis route has been used by some researchers [11, 12], detailed results are not available in the open literature. Detailed investigations were therefore planned to study the influence of process parameters on the product quality.

The second objective is to carry out investigation on densification of \( \text{ZrB}_2 \). Effect of sinter additives (\( \text{TiSi}_2, \text{CrSi}_2, \text{EuB}_6 \)) on densification of \( \text{ZrB}_2 \) was studied.

The third objective of this study is to carry out oxidation study of \( \text{ZrB}_2 \) based composites. \( \text{ZrB}_2 \) is candidate for high temperature applications and thus oxidation resistance is of vital importance.

2. Experimental Procedure

Raw materials used for synthesis of \( \text{ZrB}_2 \) were \( \text{ZrO}_2 \) (99% purity; 8.34 \( \mu \text{m} \) median diameter), boron carbide powder (78.5% B, 19.5%C, <1% O, 0.02% Fe, 0.02% Si, 5.34 \( \mu \text{m} \) median diameter; supplied by M/S Boron Carbide India) and petroleum coke (C-99.4%, 13.9 \( \mu \text{m} \) median dia., supplied by M/S Assam Carbon, India). All the raw materials were dried in an oven at 100\(^\circ\)C to remove moisture content before use.

For synthesis of \( \text{ZrB}_2 \) powders, weighed quantities of \( \text{ZrO}_2 \), boron carbide and petroleum coke in various ratios were mixed thoroughly, pelletized and heated in an induction furnace at fixed temperature between 1200 and 1875 \(^\circ\)C. Major phases of powders were identified by XRD and impurities were analyzed by chemical methods. Similar procedure was used for synthesis of \( \text{EuB}_6 \) and \( \text{HfB}_2 \) powder.

For densification, weighed quantities of fine zirconium diboride and sinter additives (\( \text{TiSi}_2/\text{CrSi}_2/\text{EuB}_6/\text{HfB}_2 \)) were mixed thoroughly, filled into a graphite die and hot pressed at temperatures of 1650 \(^\circ\)C to 1850\(^\circ\)C under a pressure of 20 to 35 MPa for 60 minutes in a high vacuum (\( 1 \times 10^{-5} \text{ mbar} \)) chamber. Hardness was measured on the polished surface at a load of 100 g and dwell time of 10 sec. The indentation fracture toughness (\( K_{IC} \)) data were evaluated by crack length measurement of the crack pattern formed around Vickers indents. Fractured surface of dense pellets was analyzed by scanning electron microscope.
Oxidation tests were conducted in a resistance heated furnace. The samples were oxidized for different time intervals (0.5, 1, 2, 4, 8, 16, 32, and 64 h) at 900 °C. The samples were weighed before and after exposure, to determine the weight change during the oxidation process. The oxidation products were identified using XRD. The morphology and nature of oxide layer was elucidated by observing the surface in a scanning electron microscope (SEM).

3. Results and discussion

This chapter summarizes the results obtained during the various experiments giving details of starting powder preparations till microstructural and mechanical characterization. This chapter is divided into three major sections representative for the three phases in the research: section-3.1 on synthesis of boride powders, section-3.2 on densification, mechanical properties and microstructure and section- 3.3 on oxidation study of prepared composites.

3.1 Synthesis

Experiments were carried out to study the effect of process parameters on synthesis of boride powders. ZrB₂, EuB₆, and HfB₂ powders were synthesized by boron carbide reduction of respective oxides.

3.1.1 ZrB₂ synthesis

Studies were carried out to prepare pure ZrB₂ containing oxygen less than 1.0 wt%. Oxygen is an impurity in boride powders, which reduces its sinterability.

A stoichiometric charge mixture (according to reaction 1) was heated at various temperatures from 1200°C to 1800°C and weight loss during the experiment is recorded.

\[
\text{ZrO}_2 + \frac{1}{2}\text{B}_4\text{C} + \frac{3}{2}\text{C} \rightarrow \text{ZrB}_2 + 2\text{CO} \]

Weight loss in the reaction is due to formation of carbon mono-oxide. The theoretical weight loss after completion of reaction is 33 wt % of charge. The observed weight loss gives indication for completion of reaction.

The obtained product was analyzed by XRD and chemical analysis. Results on synthesis of ZrB₂ is summarized in Table-1
Table 1 Effect of temperature and charge composition on ZrB₂ synthesis

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Molar ratio ZrO₂: B₄C: C</th>
<th>Temperature (°C)</th>
<th>Weight loss (wt.%)</th>
<th>Phases present in XRD pattern</th>
<th>Carbon (wt.%)</th>
<th>Oxygen (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2: 1: 3</td>
<td>1200</td>
<td>18.47</td>
<td>ZrB₂, ZrO₂</td>
<td>9.7</td>
<td>5.2</td>
</tr>
<tr>
<td>2.</td>
<td>2: 1: 3</td>
<td>1400</td>
<td>27.15</td>
<td>ZrB₂, ZrO₂</td>
<td>8.2</td>
<td>2.4</td>
</tr>
<tr>
<td>3.</td>
<td>2: 1: 3</td>
<td>1650</td>
<td>30.28</td>
<td>ZrB₂, ZrB, ZrO₂, C</td>
<td>7.3</td>
<td>2.4</td>
</tr>
<tr>
<td>4.</td>
<td>2: 1: 3</td>
<td>1700</td>
<td>31.66</td>
<td>ZrB₂, ZrB, C</td>
<td>3.5</td>
<td>2.0</td>
</tr>
<tr>
<td>5.</td>
<td>2: 1: 3</td>
<td>1800</td>
<td>33.04</td>
<td>ZrB₂, ZrB, C</td>
<td>3.2</td>
<td>0.5</td>
</tr>
<tr>
<td>6.</td>
<td>2: 1.1: 2.7</td>
<td>1800</td>
<td>32.67</td>
<td>ZrB₂</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>7.</td>
<td>2: 1.1: 2.7</td>
<td>1875</td>
<td>33.01</td>
<td>ZrB₂</td>
<td>0.06</td>
<td>0.5</td>
</tr>
</tbody>
</table>

It was found that weight loss is close to theoretical loss (33 wt.%) at 1800 °C but the product is composed of ZrB₂, ZrB and carbon phases. The presence of boron deficient phase (ZrB) even after the treatment at 1800 °C indicates the loss of boron from the charge, which could occur by following reaction.

\[
\text{ZrO}_2 + \frac{3}{4}\text{B}_4\text{C} = \text{ZrB}_2 + \frac{1}{2}\text{B}_2\text{O}_3 + \frac{1}{2}\text{CO} + \frac{1}{4}\text{C} \quad \ldots
d\ldots
d\ldots
d(2)
\]

Single phase ZrB₂ was obtained by modifying the charge composition by increasing the B₄C content and reducing the carbon content in the charge. To further reduce the carbon and oxygen content in the product, the synthesis temperature was increased to 1875 °C.
3.1.2 EuB₆ synthesis

In this study, EuB₆ was used as sinter additive to ZrB₂. It was synthesized by reduction of Eu₂O₃ by B₄C according to reaction (3).

$$\text{Eu}_2\text{O}_3 + 3\text{B}_4\text{C} \rightarrow 2\text{EuB}_6 + 3\text{CO}$$ \hspace{1cm} (3)

Stochiometric mixture as per reaction (3) was heated between 1200 to 1400°C in vacuum for 2 hours and then the product was analyzed by XRD and chemical analysis. At 1200°C, weight loss is only 2.65% and product is composed of both EuB₆ and Eu₂O₃ phases. At 1300 °C, loss in weight is 19.56 %, which is higher than the theoretical loss of 16.23%. Though the product contains only EuB₆, its carbon and oxygen content is high at 3.8 and 2.1% respectively. On increasing synthesis temperature to 1400 °C, oxygen content of the product was decreased to 0.4% and relatively pure EuB₆ has been formed. Product obtained at 1400 °C contains 2.6% carbon. The higher carbon content and higher weight loss could be due to the formation of volatile boron oxide during reaction. To reduce carbon in the product, the charge was modified by adding elemental boron and lowering B₄C addition. Carbon content was reduced to 0.7 % by using modified charge.

3.1.3 HfB₂ synthesis

In this study, HfB₂ was used as sinter additive to ZrB₂. It was synthesized by reduction of HfO₂ by B₄C in presence of carbon according to reaction (4).

$$\text{HfO}_2 + \frac{1}{2}\text{B}_4\text{C} + \frac{3}{2}\text{C} \rightarrow \text{HfB}_2 + 2\text{CO}$$ \hspace{1cm} (4)

The synthesis was carried out at 1875 °C in vacuum. The product obtained was found to be pure HfB₂ containing 0.5% Oxygen and 0.4 % Carbon.

3.2 Densification, mechanical properties and microstructure

This section describes the results on densification, mechanical properties and microstructural characterization of prepared composites. Densification studies were carried out on monolithic ZrB₂ by pressureless sintering and hot pressing. Effect of sinter additives on densification, mechanical properties and microstructure were investigated.
3.2.1 Monolithic ZrB₂

Pressureless sintering experiments were carried out in vacuum induction furnace in the temperature range of 1800-2000°C. Pressureless sintering has resulted in maximum density of 78% only. In Hot pressing ZrB₂ was densified to near theoretical density at 1850°C and 35 MPa pressure. Hardness and fracture toughness values were measured as 23.95 GPa and 3.31 MPa.m¹⁄² respectively. Fractured surface of the dense bodies revealed that intergranular fracture is predominant mechanism. Regular faceted grains of 4-6 micron are visible.

3.2.2 Effect of TiSi₂ addition

Effect of TiSi₂ on densification of ZrB₂ was investigated. Addition of 10% TiSi₂ lowered the hot pressing temperature to 1650°C from 1850°C, which was required for monolithic ZrB₂. The enhanced sintering is attributed to liquid phase sintering resulted by formation of ZrSi₂ which forms during hot pressing. Formation of ZrSi₂ phase was observed by XRD analysis and SEM –EDS analysis of hot pressed sample. ZrSi₂ has low melting point (1620 °C) and hence results in liquid phase sintering. XRD pattern of the dense pellets indicated the presence of crystalline ZrB₂ and ZrSi₂. Zirconium disilicide is formed during sintering by the following reaction.

\[ \text{ZrB}_2 + \text{TiSi}_2 \rightarrow \text{ZrSi}_2 + \text{TiB}_2 \]  (6)

The reaction is thermodynamically feasible at temperatures higher than 1100 K. TiB₂ was not observed as separate phase as it formed solid solution with ZrB₂. The formation of solid solution was confirmed by elemental analysis of different phases observed in microstructure.

Hardness of ZrB₂ + 10%TiSi₂ sample is measured as 19.5 GPa which is lower than that of monolithic ZrB₂ (23.91 GPa). The lower hardness is due to the presence of relatively soft phase ZrSi₂ which was formed during hot pressing. To compensate the hardness reduction, HfB₂ was added and two more samples of composition (a) ZrB₂+10%TiSi₂+10%HfB₂ and (b) ZrB₂+10%TiSi₂+20%HfB₂ were also prepared. Near theoretical density was obtained in both the samples at 1650 °C and 20 MPa. Hardness of ZrB₂+10%TiSi₂+10%HfB₂ was measured as 23.08 GPa, which is comparable to that of monolithic ZrB₂.
Fracture toughness of ZrB$_2$ + 10%TiSi$_2$ was measured as 6.36 MPa.m$^{1/2}$ which is higher than that of the monolithic ZrB$_2$. The increased fracture toughness is due to crack deflection. Thermal expansion mismatch between the matrix and second phase results in residual stresses which causes crack deflection. Crack deflections were found in the microstructure.

3.2.3 Effect of CrSi$_2$ addition

Effect of CrSi$_2$ addition on densification and properties of ZrB$_2$ was studied. It was observed that CrSi$_2$ has similar effects as TiSi$_2$ on densification and properties of ZrB$_2$. Addition of CrSi$_2$ lowered the densification temperature, lowered the hardness and increased the fracture toughness.

3.2.4 Effect of EuB$_6$ addition

Effect of EuB$_6$ addition on densification and properties of ZrB$_2$ was investigated. EuB$_6$ is a boron rich additive, which is expected to create structural defects (interstitial point defects) in ZrB$_2$ lattice on formation of solid solution and thus can enhance the densification. Addition of 2.5 weight% EuB$_6$ resulted in densification of 98.3% $\rho_{th}$ at a temperature of 1750 °C and a pressure of 35 MPa. Composites with 5% EuB$_6$ was also hot pressed up to 98.1% density at similar processing conditions. A density of 96.0% was achieved in ZrB$_2$+10%EuB$_6$ composite. In case of monolithic ZrB$_2$, a near full density (99.8% TD) was obtained at a higher temperature and pressure of 1850 °C and 35 MPa respectively. In this case, the hot pressing temperature was lower by 100°C. Addition of EuB$_6$ to ZrB$_2$ results in the formation of solid solution of ZrB$_2$ and EuB$_6$. On the formation of ZrB$_2$-EuB$_6$ solid solution, Eu will go to Zr site and Boron will go to boron site. Due to large number of boron atoms from EuB$_6$, there will be formation of point defects in ZrB$_2$. The point defects are known to enhance the diffusional mass transfer and thus assist in densification at slightly lower temperature. Formation of solid solution was confirmed by elemental analysis (EDS) of phases present in microstructure and change in lattice parameter measured by XRD. BSE image of ZrB$_2$ + 10%EuB$_6$ sample (Fig.1) has shown the presence of light gray matrix in which dark gray phase is dispersed. In EDS spectra, dark gray phase was analyzed to contain only Zr and B indicating that it is ZrB$_2$. The light gray matrix was analyzed to contain Zr, Eu and B indicating the formation of ZrB$_2$-EuB$_6$ solid solution. XRD pattern of the dense pellet of ZrB$_2$+10%EuB$_6$ indicates the presence of crystalline ZrB$_2$, EuB$_6$ and carbon. Presence of EuB$_6$ in XRD pattern indicates that the ZrB$_2$ and EuB$_6$ does not form complete solid solution and so EuB$_6$ is also present as second phase in the composite.
Hardness of monolithic sample was measured as 23.91 GPa, which increased to 24.8 GPa with the addition of 2.5wt% EuB₆. The increase in hardness is due to the formation of solid solution.

Fig.1 (A) BSE image of ZrB₂+ 5%EuB₆ (B) EDS spectra of phase marked as 1 in (A), (C) EDS spectra of phase marked as 2 in (A), and (D) EDS spectra of phase marked as 3 in (A),
3.3 Oxidation study

Non oxide ceramics are susceptible to oxidation at high temperatures. For any high temperature application in air, the material must be resistant to oxidation. In this study, oxidation test were carried out at 900 °C in air for different time interval. Following sub-sections will describe the results obtained by oxidation test of different composites.

3.3.1 Monolithic ZrB₂

The weight gain data obtained during oxidation at 900 °C as a function of time for monolithic ZrB₂ is presented in Fig 2. It shows that weight gain is linear indicating non-protective nature of oxide. The test was stopped after 32 hours as the oxide layer was broken and spalled off from the sample.

![Fig. 2 Specific weight gain vs. time plot for monolithic ZrB₂ at 900 °C in air](image)

3.3.2 Effect of TiSi₂ and HfB₂ addition

The weight gain data obtained during oxidation at 900 °C as a function of time for ZrB₂ composites containing TiSi₂ and HfB₂ are presented in Fig.3. Continuous weight gain with time is observed in all the samples. In case of composites, the rate of oxidation was found to decrease with
increase in time which indicates the formation of protective layer. In monolithic ZrB₂, oxidation rate was found to be constant. Samples containing HfB₂ has shown highest oxidation resistance.

![Graph showing specific weight gain vs time for ZrB₂ and its composites.](image)

Fig. 3 Specific weight gain vs time plot for ZrB₂ based composites.

Better oxidation resistance of the composite samples is attributed to the formation of silica based glassy layer. SEM microstructures of oxidized surfaces evidently showed the formation of protective glassy phase. The glassy phase was analysed by EDS to contain mainly silicon (~ 46 at%) and oxygen (~52 at%). Zirconium (~ 0.8 at%) and titanium (~0.2 at%) are also present in very small quantity.

### 3.3.3 Effect of CrSi₂ and HfB₂ addition

Oxidation study of ZrB₂ +10%CrSi₂ and ZrB₂+10%CrSi₂+10%HfB₂ samples were carried out at 900 °C for 64 hour. Both the samples have shown continuous weight gain with time. However, the rate of oxidation is found to decrease with increase in time which indicates the formation of protective layer. The final weight gain in ZrB₂+10%CrSi₂ sample is 0.0397 kg/m² after 64 hours whereas in ZrB₂+10%CrSi₂+10%HfB₂ sample is 0.0171 kg/m² which is lower. The lower weight gain in the HfB₂ containing sample could be attributed to lower diffusivity of oxygen ion through HfO₂ [13,14].
3.3.5 Effect of EuB₆ addition

Oxidation study of ZrB₂ +2.5%EuB₆, ZrB₂ +5%EuB₆ and ZrB₂ +10%EuB₆ samples were carried out at 900 °C for 64 hour. All the three samples have shown continuous weight gain with time (Fig.4). In the initial 8 hours, the weight gain is very small which increases during the exposure at 8-16 hour and then the rate of oxidation gets decreased. The decrease in rate of oxidation after 16 hour is due to the formation of a protective layer. The oxidized layer was analyzed by EDS to contain mainly zirconium (~21.67 at%) Europium (6.49 at %) and oxygen (~71.84 at%).

![Graph showing specific weight gain vs time in ZrB₂ based composite samples oxidized at 900°C](image)

Fig. 4 Specific weight gain vs time in ZrB₂ based composite samples oxidized at 900°C

4. Conclusion

The major findings of the present thesis have been summarized below.

- Heating of stoichiometric charge for synthesis of ZrB₂ by boron carbide reduction of zirconia in presence of carbon results in formation of ZrB phase along with ZrB₂. This boron deficient phase is formed due to loss of boron in the form of its volatile oxides.
- The boron deficient phase ZrB can be avoided and single phase ZrB₂ can be obtained by adjusting the molar ratio of charge by increasing B₄C and reducing carbon.
Synthesis of pure ZrB₂ by this method requires a temperature of 1875 °C. The High temperature is required due to low diffusivity of all the elements through boride phase which is predominantly covalently bonded.

Synthesis of single phase EuB₆ is possible by using the stoichiometric charge but the product contains around 2% carbon which can be reduced by addition of elemental boron in the charge mixture.

Synthesis of pure EuB₆ is possible at temperature of 1400 °C, which is relatively lower than that required for ZrB₂.

Pressureless sintering of Monolithic ZrB₂ results in maximum density of 78% at 2000 °C. Near theoretical density of Monolithic ZrB₂ can be obtained by hot pressing at 1850 °C and 35 MPa pressure for 2 hour.

Addition of TiSi₂ or CrSi₂ lowers the hot pressing temperature by 200 °C. This decrease is attributed to liquid phase sintering caused by reaction product ZrSi₂ which forms during hot pressing.

Addition of EuB₆ lowers the hot pressing temperature by 100 °C. This is due to the formation of solid solution of ZrB₂ and EuB₆ which in turn results in the formation of point defects and diffusion is enhanced.

TiSi₂ and CrSi₂ addition results in formation of ZrSi₂ which is responsible of liquid phase sintering.

EuB₆ is only partially soluble in ZrB₂ and also exist as a distinct phase in the material.

TiSi₂ and CrSi₂ addition has resulted in lower hardness whereas EuB₆ addition has increased the hardness.

Fracture toughness values of all composite samples are higher than the monolithic sample. This is due to crack deflection caused by the presence of second phase in microstructure.

Monolithic ZrB₂ does not have good oxidation resistance at 900 °C. Linear oxidation kinetics was observed in case of monolithic ZrB₂.

TiSi₂, CrSi₂ addition as well as EuB₆ addition has improved the oxidation resistance of ZrB₂ at the temperature of 900 °C. The good oxidation resistance is due to the formation of protective oxide layer.
5. References:


