Development and Characterization of (Ti,Cr)B₂ based Composites

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Abstract

Process flow sheet for the development of (Ti,Cr)B₂ + MoSi₂ composites by hot pressing have been established. The hot pressing operations have been optimized to obtain near theoretical dense (~99%) pellets. Detailed evaluation of mechanical, physical and oxidation behavior of composites with varying CrB₂ content was carried out. (Ti,Cr)B₂ + MoSi₂ composites has been found to have a higher hardness, better fracture toughness and oxidation resistance compared to monolithic TiB₂. These pellets prepared meet all the specifications for use as control rod material of a high temperature/compact nuclear reactor.

Introduction

Boron and its compounds are extensively used in nuclear industry for application as control rod, human shielding against neutrons and as sensor elements [1,2]. Neutron absorption of boron is sufficiently high in the thermal neutron energy range (~3800 barns for ¹⁰B isotope) to make it a candidate for use in advanced/compact/high temperature nuclear reactors as neutron shielding and control/shutoff rods. At higher energies, the cross section of most other neutron absorber elements becomes very small, often abruptly as in the case of cadmium, whereas the cross-section of ¹⁰B decreases monotonically with respect to increase in neutron energy. Absolute values along the entire energy spectrum are of sufficient magnitude to make it very effective in the intermediate and fast energy range of neutrons. Boron has another advantage over other potential neutron absorber materials as the reaction products namely helium (α) and lithium are formed as stable, non-radioactive isotopes. As they do not emit nuclear radiation, decay-heating problems are minimal during reactor shutdowns and transfer of depleted control rods. Elemental boron and boron based compounds boric acid, boron carbide and titanium diboride are the most important substances widely used in nuclear industry [1,2].

Titanium diboride (TiB₂) based composites are chosen as the candidate material for neutron absorption in high temperature/compact reactors due to its high temperature properties. TiB₂ has high melting point (3200°C), low density (4.52 gm/cm³), good thermal conductivity (65 W/m/K), chemical inertert and moderate oxidation resistance. Covalent nature of the TiB₂ compound coupled with low diffusion coefficient makes it extremely difficult to obtain dense bodies by sintering. In real high temperature applications monolithic TiB₂ directly cannot be used, due to its poor sinterability, oxidation and thermal shock resistance. However, these difficulties can be overcome by adding suitable sinter additives. In the present study focuses on the development of TiB₂ based composite of “(Ti,Cr)B₂+20% MoSi₂,” and evaluation of thermo physical (CTE, electrical resistivity), mechanical (hardness, fracture toughness, flexural strength, hot hardness) and high temperature oxidation (isothermal and continuous) properties.

In addition to the above said composite, authors have also successfully developed and characterized the various refractory and rare earth metal borides (TiB₂, CrB₂, ZrB₂, HfB₂, EuB₆, LaB₆, CeB₆, YB₆, NbB₂) and its composites. More details on synthesis, densification and properties of these borides are found elsewhere [3-15]. Literature reported properties of B₄C, TiB₂, CrB₂ and MoSi₂ are summarized in Table 1[1,2,5,6,7].

Development of (Ti,Cr)B₂ and MoSi₂ composites

(Ti,Cr)B₂ and MoSi₂ are synthesized independently and a mixture of these powders in the required proportion is hot pressed to obtain the dense pellets. However, during the developmental process, synthesis of TiB₂ and CrB₂ were
studied separately to evolve the production process for composite borides. Optimization of process parameters for the production of (Ti,Cr)B₂ and MoSi₂ and hot pressing of the mixture of these powders to obtain dense pellet were also established. Important process steps are explained below:

**Synthesis of pre-alloyed titanium, chromium di-boride [(Ti₀.₈₅Cr₀.₁₅)B₂]**

Our previous studies indicated that synthesis of TiB₂ and CrB₂ require temperatures above 1700°C for obtaining single phase compound [14,15] with minimum impurities of <1%. Synthesis of the pre-alloyed composite boride [(Ti,Cr)B₂] by co-reduction technique in a single step is considered to be advantageous and economical in obtaining a homogenous product with improved properties compared to ex-situ processing route. Hence, synthesis of (Ti,Cr)B₂ was carried out by the following carbothermic reduction in the presence of boron carbide:

\[
2\text{TiO}_2 + \text{B}_4\text{C} + \text{Cr}_2\text{O}_3 + 6\text{C} \rightarrow 2(\text{Ti},\text{Cr})\text{B}_2 + 7\text{CO}\uparrow \quad (1)
\]

This carbide-oxide reaction is the simplest method of preparing compounds, when the reactants are available in pure and finely divided form. As the reactants consist of four solid substances, homogenization of the charge mixture is essential for completion of the reaction. Fine powders of reactants are accurately weighed and mixed thoroughly by planetary mill. Mixed charge is loaded into a graphite crucible and heated in a vacuum induction furnace. Fig.1 shows the schematic and actual photograph of vacuum induction furnace assembly used in the present study. Temperature of the furnace was measured by two color pyrometer. After completion of holding time, the furnace was allowed to cool down to room temperature in vacuum. Synthesized compacts were taken out, crushed and ground to fine particles using WC lined high energy cup grinding mill. XRD of the powders were taken for phase identification and chemical analysis for the major constituents and impurities. Particle size analysis was carried out by laser scattering method. SEM of the powders was carried out to cross check the particle size and morphology.

### Table 1 Comparison of properties of selected materials (B₄C, TiB₂, CrB₂, MoSi₂) [1,2,5,6,7]

<table>
<thead>
<tr>
<th>Property</th>
<th>B₄C</th>
<th>TiB₂</th>
<th>CrB₂</th>
<th>MoSi₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>2450</td>
<td>3200</td>
<td>2200</td>
<td>2030</td>
</tr>
<tr>
<td>Thermal conductivity (W/m/K)</td>
<td>30 - 42</td>
<td>60 - 120</td>
<td>30-35</td>
<td>53.92</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>2.51</td>
<td>4.52</td>
<td>5.2</td>
<td>6.24</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>28</td>
<td>32</td>
<td>11-20</td>
<td>12</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (°C⁻¹)</td>
<td>5 x 10⁻⁶</td>
<td>8.1 x 10⁻⁶</td>
<td>10.5 x 10⁻⁶</td>
<td>8.5 x 10⁻⁶</td>
</tr>
<tr>
<td>Oxidation resistance upto</td>
<td>≤ 800° C</td>
<td>≤1000°C</td>
<td>-</td>
<td>≤1400°C</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>155</td>
<td>240</td>
<td>207-600</td>
<td>-</td>
</tr>
<tr>
<td>Fracture toughness (Kᵥ) MPa.m¹/₂</td>
<td>2-3</td>
<td>5-7</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>Electrical resistivity (µ Ω - cm)</td>
<td>0.1-10 x 10⁻⁶</td>
<td>10 – 30</td>
<td>-</td>
<td>21.6</td>
</tr>
</tbody>
</table>

**Fig.1:** a) Schematic and b) actual photograph of a vacuum induction furnace used for synthesis of (Ti,Cr)B₂ and MoSi₂
Synthesis of molybdenum di-silicide (MoSi$_2$)

MoSi$_2$ used in the present study was synthesized from its elements. Stoichiometric amounts of molybdenum (Mo, Purity: 99.7%) and silicon (Si, Purity: 99%) powders were weighed and thoroughly mixed in a planetary ball mill. The charge was heated in vacuum up to a temperature of 1300°C. Since the formation of MoSi$_2$ ($\Delta H^{\circ}_{298} = -131 \text{ kJ/mol}$) is highly exothermic, abrupt increase in the charge temperature was observed, which indicates the vigorous reaction in the charge.

Consolidation of pellets

Fine powders of (Ti,Cr)B$_2$ and MoSi$_2$ are weighed in the specified proportion and mixed thoroughly in a gyratory mixer. All these operations are carried out using tungsten carbide lined mills to avoid contamination from milling medium during powder processing. Flow sheet for the preparation of composite powders of fine (Ti,Cr)B$_2$ and MoSi$_2$ for boron alloy preparation are presented in Fig.2. Fig.3 and Fig.4 are showing the photographs of planetary and high energy cup grinding mill used for mixing and fine grinding. Particle size distribution and XRD patterns of starting (Ti,Cr)B$_2$, MoSi$_2$ and mixed powder are presented in Fig.5 and Fig.6 (a&b) respectively.

Densification of (Ti,Cr)B$_2$+MoSi$_2$ composites were carried out by hot pressing. For hot pressing experiments, weighed
quantities of (Ti,Cr)B₂ (5, 10 and 15wt.% CrB₂ equivalent powders) and 20 wt.% MoSi₂ powders were mixed thoroughly using a motorized pestle and mortar in dry condition for 1 h. The powders were then uniaxially pressed using a graphite die of 12 mm diameter at 1800°C under pressure (35 MPa) for 1 hour in a vacuum of 0.01 pascal. The densified pellets were ejected from the die and the density measured by Archimedes’ principle. Schematic and actual photograph of hot press used for present study is presented in Fig. 7.

Fig. 5: Particle size distribution of (Tiₐ₉Crₐ₁₅)B₂, MoSi₂ and mixed powder [Reprinted from [6] with permission from Elsevier]

Fig. 6: XRD of a) (Tiₐ₉Crₐ₁₅)B₂ and b) MoSi₂ powder [Reprinted from [6] with permission from Elsevier]

Fig. 7: a) Schematic and b) actual photograph of High Temperature and High Vacuum Hot Press used for consolidation of (Ti,Cr)B₂ + MoSi₂ composite dense pellets
Characterization of pellets

Densified pellets were cut by using electro discharge machine (EDM) and polished to 0.10 \( \mu \text{m} \) finish. X-ray Diffraction (XRD) and Electron Probe Micro Analyser (EPMA) were carried out on the polished surface. Hardness at various temperatures and fracture toughness at room temperature were measured. Thermal conductivity, coefficient of thermal expansion (CTE) and flexural strength were measured using 5mm \( \times \) 5mm \( \times \) 45 mm sized bar samples. Fractured surface was examined in a SEM. Isothermal and continuous oxidation studies were also carried out. Detailed results are given below:

Densification

The density of composites obtained with 5, 10 and 15\% CrB\(_2\) contained (Ti,Cr)B\(_2\)+20\% MoSi\(_2\) composites were 4.43, 4.67 and 4.81 g/cc respectively. Fig. 8a presents the variation of relative density of pellets with respect to CrB\(_2\) content.

Phase identification

TiB\(_2\) and MoSi\(_2\) peaks are mainly identified and CrB\(_2\) peaks are not seen in the XRD pattern (Fig. 8b). (Ti\(_{0.85}\)Cr\(_{0.15}\))B\(_2\)+20\% MoSi\(_2\) composite was analyzed by SEM-EDS and EPMA. In this sample, three regions of interest were identified. These are the light grey matrix of (Ti\(_{0.85}\)Cr\(_{0.15}\))B\(_2\), white phase (MoSi\(_2\)) and tiny black phase mainly contains Cr, Ti, Mo and B (Fig 9a). Both intergranular and transgranular modes of fractures contribute equally to the failure of the (Ti\(_{0.85}\)Cr\(_{0.15}\))B\(_2\)+20\% MoSi\(_2\) composites (SEM images not shown). No grain growth and porosity is observed, indicates the full densification of the composites without grain coarsening.

Mechanical Properties

Fig.8a presents the micro hardness and indentation fracture toughness values of the composites with varying the CrB\(_2\) content. Hardness values of all composites are in the range of 24 to 27 GPa. Fracture toughness values were calculated by using the Anstis empirical relation as follows [16]:

\[
K_c = 0.016 \left( \frac{E}{H} \right)^{1/2} \times \left( \frac{P}{C^{3/2}} \right)
\]

(2)

Where \( K_c \) is the fracture toughness (MPa.m\(^{1/2}\)), \( E \) – Elastic modulus (GPa), \( H \) – hardness (GPa), \( P \) – load (N), \( 2C \) – full crack length (m). Elastic modulus of (Ti\(_{0.85}\)Cr\(_{0.15}\))B\(_2\)+20\% MoSi\(_2\) composite was measured as 522±8GPa at room temperature by ultrasonic method as per the ASTM C1419-99a test procedure. Average indentation fracture toughness of 5, 10 and 15\% CrB\(_2\) contained (Ti,Cr) B\(_2\)+20\% MoSi\(_2\) composites were measured as 2.8±0.2, 3.5±0.6 and 4.5±0.5 MPa.m\(^{1/2}\) respectively. Hardness of (Ti\(_{0.85}\)Cr\(_{0.15}\))B\(_2\)+20\% MoSi\(_2\) sample from 25°C to 1000°C is also measured. As expected, with increase in temperature, decrease in hardness values were noted. Drastic decrease in the hardness value from 30GPa to 16GPa was observed from 25°C to 300°C[6]. Flexural strength was measured at RT, 500 and 900°C for (Ti\(_{0.85}\)Cr\(_{0.15}\))B\(_2\)+20\% MoSi\(_2\) sample. Three samples were tested at each temperature and the average values were 320, 295 and 285 MPa respectively. Similar to hot hardness, decrease in flexural strength values with increase in temperature was noticed. However, decrease
in strength is not significant, indicating the retention of strength at elevated temperature of 900 °C.

Microstructures of (Ti,Cr)B₂+20%MoSi₂ composites with indentation edge cracks are shown in Fig.9b. Both crack deflections and bridging mechanisms were mainly observed in this composite. These mechanisms are responsible for improvement of the fracture toughness [6].

was measured as 2.12, 2.63 and 3.03 μΩ·cm at 100°C, 500°C and 1000°C respectively. Thermal conductivity of (Ti₀.₈₅Cr₀.₁₅)B₂ + 20% MoSi₂ composite measured up to 600°C and is shown in Fig.10b. Thermal conductivity of sample was observed to decrease from room temperature to 300°C and then increase with temperature. This could be the change in the mechanism of thermal conductivity.

Physical Properties

Coefficient of thermal expansion (CTE) and electrical resistivity of (Ti₀.₈₅Cr₀.₁₅)B₂+20% MoSi₂ composite is presented in Fig.10a. CTE values are found to increase with temperature from 6.67 x 10⁻⁶ at 100°C to 7.54 x 10⁻⁶ K⁻¹ at 800°C. These values are marginally lower than that of monolithic TiB₂ which is 8.1 x 10⁻⁶ K⁻¹. Electrical resistivity of the composite

Oxidation Studies

Continuous Oxidation (Non-Isothermal)

TGA plot on continuous oxidation of all (Ti,Cr)B₂+20%MoSi₂ composites in O₂ is given in Fig.11a. In the plot, three different stages of weight gain are observed for all the composites, a) no change in sample weight up to 300°C, b)
a gradual weight gain between 300 to 700°C and c) a steep weight gain above 700°C. Total specific weight gain is less than $25 \times 10^{-5} \text{ kg/m}^2$ and the rate of weight gain is similar for all the composites. It is seen that $(\text{Ti}_0.85\text{Cr}_0.15)\text{B}_2+20\% \text{MoSi}_2$ composite’s total weight gain ($<20 \times 10^{-3} \text{ kg/m}^2$) is least compared with other two composites.

Morphology of the oxidized surface of $(\text{Ti,Cr})\text{B}_2+20\% \text{MoSi}_2$ samples after continuous oxidation up to 1000°C, (TGA) in oxygen are carried out by SEM [6]. $(\text{Ti}_0.95\text{Cr}_0.05)\text{B}_2+20\% \text{MoSi}_2$ oxidized sample is showing the presence of severe cracks on the surface with thick glossy layer. Number of cracks decreased with increase in CrB$_2$ content of $(\text{Ti}_0.90\text{Cr}_0.10)$ B$_2+20\% \text{MoSi}_2$ composite. Fully protective and crack free glassy layer was seen on the surface of $(\text{Ti}_0.85\text{Cr}_0.15)\text{B}_2+20\% \text{MoSi}_2$ composite. This indicates the effectiveness of CrB$_2$ content in the composite on the oxidation behavior.

**Isothermal oxidation**

Weight gain data obtained during isothermal oxidation at 750, 850 and 950°C as a function of time for all the composites are presented in Fig. 11b. Continuous weight gain with time is observed in all the samples and at all temperatures. However the rate of weight gain is different for different composites and temperatures. With increasing CrB$_2$ content, decrease in weight gain rate is observed. Comparing the weight gain between 750 and 950°C, it is noticed that weight gain increases with temperatures for

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sp. wt. gain, Kg/m$^2$ x 10$^3$</th>
<th>Kp$^a$ (Kg$^2$m$^{-4}$ s$^{-1}$)</th>
<th>Km$^b$</th>
<th>m$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>At 750°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{Ti}_0.95\text{Cr}_0.05)\text{B}_2+20% \text{MoSi}_2$</td>
<td>4.73</td>
<td>$1.25 \times 10^{-10}$</td>
<td>$2.69 \times 10^{-12}$</td>
<td>2.687</td>
</tr>
<tr>
<td>$(\text{Ti}_0.90\text{Cr}_0.10)\text{B}_2+20% \text{MoSi}_2$</td>
<td>2.32</td>
<td>$2.32 \times 10^{-11}$</td>
<td>$8.50 \times 10^{-12}$</td>
<td>2.156</td>
</tr>
<tr>
<td>$(\text{Ti}_0.85\text{Cr}_0.15)\text{B}_2+20% \text{MoSi}_2$</td>
<td>3.06</td>
<td>$5.26 \times 10^{-11}$</td>
<td>$3.49 \times 10^{-15}$</td>
<td>3.590</td>
</tr>
<tr>
<td>At 850°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{Ti}_0.95\text{Cr}_0.05)\text{B}_2+20% \text{MoSi}_2$</td>
<td>34.62</td>
<td>$5.24 \times 10^{9}$</td>
<td>$1.55 \times 10^{9}$</td>
<td>2.327</td>
</tr>
<tr>
<td>$(\text{Ti}_0.90\text{Cr}_0.10)\text{B}_2+20% \text{MoSi}_2$</td>
<td>26.07</td>
<td>$3.72 \times 10^{9}$</td>
<td>$3.57 \times 10^{-10}$</td>
<td>2.602</td>
</tr>
<tr>
<td>$(\text{Ti}_0.85\text{Cr}_0.15)\text{B}_2+20% \text{MoSi}_2$</td>
<td>8.17</td>
<td>$1.75 \times 10^{9}$</td>
<td>$6.80 \times 10^{-14}$</td>
<td>4.359</td>
</tr>
<tr>
<td>At 950°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{Ti}_0.95\text{Cr}_0.05)\text{B}_2+20% \text{MoSi}_2$</td>
<td>57.32</td>
<td>$1.46 \times 10^{8}$</td>
<td>$2.69 \times 10^{8}$</td>
<td>1.807</td>
</tr>
<tr>
<td>$(\text{Ti}_0.90\text{Cr}_0.10)\text{B}_2+20% \text{MoSi}_2$</td>
<td>39.58</td>
<td>$9.96 \times 10^{9}$</td>
<td>$8.01 \times 10^{-11}$</td>
<td>3.410</td>
</tr>
<tr>
<td>$(\text{Ti}_0.85\text{Cr}_0.15)\text{B}_2+20% \text{MoSi}_2$</td>
<td>4.58</td>
<td>$2.14 \times 10^{-10}$</td>
<td>$2.43 \times 10^{-11}$</td>
<td>10.953</td>
</tr>
</tbody>
</table>

(*Kp – Parabolic rate constant, Km – Rate constant of general rate equation, m- Slope of general rate equation)
In order to understand the nature of oxidation, the oxidation data was fitted in the general rate equation and parabolic law. Rate constants (Km and Kp) and slope (m) values at different temperatures are presented in Table 2. The nature of oxidation appears to be complete parabolic (m = 2.1 to 2.6) for 5 and 10% CrB2 composites and cubic (m > 3) for 15% CrB2 composite at 750°C. One order higher parabolic rate constants are measured for the same composites at 850°C in the range of 3 to 5 x 10^{-9} Kgm^{-4}s^{-1}. The above parabolic rate constant values at 750 and 850°C indicate that mechanism of oxidation is diffusion controlled. The value of parabolic rate constant is found to decrease with increase of CrB2 content from 5 to 15%, indicating the effectiveness of CrB2 addition in improving the oxidation resistance.

SEM images of oxidized surfaces of all composites (5, 10 and 15% CrB2) at 750, 850 and 950°C for 64h are also carried out. Presence of liquid phase on the surface of (Ti0.85Cr0.15)B2+20% MoSi2 composite was seen (Fig. 12a&b). At 850°C, surface cracks were not seen on the oxidized sample (Fig.12a). At 950°C, more continuous and protective oxide layer was seen (Fig.12b).

To understand the role of various elements during oxidation of (Ti0.85Cr0.15)B2+20% MoSi2 composite, extended oxidation was carried out at 850°C for 256h. Cross section of the 15% CrB2 contained (Ti,Cr)B2+20%MoSi2 oxidized surface after 256h was characterized by SEM-EDS and is presented in Fig.13. The thickness of the oxide layer is <10 μm and the elemental distribution of this layer for Si, Ti, B, Mo, Cr and O is also presented. Outer most layer of oxidized surface is seen to be that of silicon oxide. Only in the top layer of upto 10 μm, there is a deficiency of the metallic elements. This layer is dominated by silicon and oxygen, clearly indicating the migration of silicon towards the outer surface [6].
Conclusions

1. High dense composites (4.81 g/cc) of pre-alloyed (Ti,Cr) B₂+20%MoSi₂ were prepared.
2. Moderate hardness in the range of 24-27 GPa and fracture toughness values in the range of 3-5 MPa•m¹/₂ were recorded.
3. With increased CrB₂ (5 to 15%) content, failure of this composite was found to change from predominantly transgranular to mixed (trans and intergranular) mode.
4. The nature of oxidation of the composite changed from parabolic to cubic with increase of CrB₂ content from 5 to 15%.
5. Protective oxide layers of TiO₂, Cr₂O₃ and SiO₂ were identified on the surface of the oxidized samples at 750 and 850°C. B₂-SiO₅ phase was identified instead of SiO₂ when oxidized at 950°C.

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