CHAPTER 1

INTRODUCTION, OBJECTIVES AND WORK PLAN OF PRESENT STUDY

1.1 Introduction

Structural ceramics are suitable for high temperature applications due to their high melting point and retention of strength up to high temperatures. Titanium diboride (TiB₂) is a structural ceramic material that is attracting attention as the base material for a range of high technological applications [1-5]. TiB₂ has many attractive properties, including exceptional hardness (approximately 25–35 GPa at room temperature which makes it more than three times harder than fully hardened structural steel), which is retained up to high temperature. It has high melting point (~3500K), good creep resistance, good thermal conductivity (65 W/m/K), high electrical conductivity and considerable chemical stability [5]. This combination of properties makes TiB₂ a candidate material for heavy duty wear applications, at elevated temperatures. TiB₂ can also be used as control rod and shielding material in nuclear reactors because it contains boron and which has ability to absorb fast and slow neutrons without forming long lived radionuclide. Absorption cross section of TiB₂ for fast neutrons can be enhanced by having compounds with enriched B¹⁰ isotope during the synthesis of TiB₂. Natural boron contains about 19% B¹⁰ isotope and remaining is B¹¹ [1-8].

For high temperature applications, chemical stability is an important factor. TiB₂ is more stable in contact with pure iron as compared to WC or Si₃N₄. TiB₂ based materials should therefore be preferable for engineering applications as compared to WC based materials for high temperature applications [5]. Its chemical inertness at high temperatures and good electrical conductivity (~10⁵ S/cm) make TiB₂ an excellent candidate for special electrical applications, e.g. cathodes for aluminum electrosmelting (Hall-Heroult process) [5,8-10].
However, monolithic TiB$_2$ has relatively low fracture toughness ($<5$ MPa.m$^{1/2}$), it’s sensitive to slow subcritical crack growth and its oxidation resistance is only moderate. These characteristics limit its use in many engineering applications. The self-diffusion coefficient of monolithic TiB$_2$ is also low and this makes it very difficult to densify [4,5]. One option to improve the sinterability/toughness of boride and carbide materials leads to an important class of composite structural materials, popularly known as cermets, wherein a metallic binder is used to obtain dense bulk materials. TiB$_2$ based cermets typically contain TiB$_2$ as the major phase, bonded with a metallic phase (Co–Ni). Cemented borides with a metallic binder have been developed in the TiB$_2$–Fe system. These materials are novel lower density and higher hardness substitutes for the WC–Co system [1-10].

Metallic additives like Ni, Fe, Cr, Al have been used to densify TiB$_2$ with retention of room temperature properties, but the presence of metallic additives in TiB$_2$ is not acceptable for high temperature applications. The presence of metallic binder is problematic due to the low melting point of either metallic additives or sintering reaction product which may lead to incipient fusion and consequent degradation of high temperature properties [4,5]. In view of the above, research has progressed towards the densification of TiB$_2$ using non-metallic sinter additives like oxides (Al$_2$O$_3$, ZrO$_2$), carbides (B$_4$C, SiC, TiC, WC), nitrides (AlN, Si$_3$N$_4$), silicides (MoSi$_2$, TiSi$_2$), and borides (CrB$_2$, ZrB$_2$). Among these additives, silicides have attracted considerable interest due to their compatibility with borides to densify at lower temperatures [5,8]. Silicides were considered as possible additives because of their ability to reduce the surface oxides thereby enhancing densification. Moreover silicides are also expected to improve high temperature oxidation resistance by the formation of a protective glassy layer on the surface which would impede further oxidation.
As reinforcement, TiB$_2$ is also incorporated in several ceramic microstructures to obtain improved mechanical properties. The addition of TiB$_2$ to an Al$_2$O$_3$ or Si$_3$N$_4$ matrix considerably increases hardness, strength, fracture toughness and electrical conductivity. Such composites have been used in wear parts, cutting tools and heat exchangers. These electro-conductive toughened ceramics can be shaped by electro discharge machining (EDM) to manufacture complex components, greatly increasing the number of potential industrial applications [5,8].

1.2 Objectives

Though some work has been reported earlier with the addition of TiSi$_2$, WSi$_2$, MoSi$_2$ and CrB$_2$ in pressureless/ microwave sintering and hot pressing of TiB$_2$ composites, detailed studies on the preparation and characterization of TiB$_2$+WSi$_2$, TiB$_2$+CrB$_2$,TiB$_2$+CrSi$_2$ and combined addition of MoSi$_2$ and CrB$_2$ composite have not been reported so far. Available Literature data on these composites are summarized in Table 1.1. The objective of present study is to synthesize and consolidate TiB$_2$ with various ceramic additives such as silicides, borides and a combination of borides and silicides (CrSi$_2$, TiSi$_2$, WSi$_2$, CrB$_2$, CrB$_2$ + MoSi$_2$ to TiB$_2$). This study also includes the compound such as pre alloyed (TiCr)B$_2$ with the aim of investigating the advantages and properties of composite formed with this additive. The ultimate aim of this thesis is to arrive at a high performance TiB$_2$ material which should have high density, high fracture toughness and superior oxidation resistance as compared to the conventional TiB$_2$.

1.3 Work Plan

Figure 1.1 summarizes the scheme of the present study i.e. synthesis of start materials, the additives that have been studied, the effect of silicide additives on densification and oxidation behaviour of TiB$_2$ and on the physical and mechanical properties. All these are presented in this thesis in seven chapters.
Fig. 1.1 Scheme for the present thesis work
Table 1.1 Summary on the available literature data of the similar TiB₂ composites

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sinter additive</th>
<th>Processing conditions</th>
<th>Densification results</th>
<th>Mechanical properties</th>
<th>Physical properties</th>
<th>Oxidation results</th>
<th>Ref. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiSi₂</td>
<td>HP 1650°C, 30MPa, Ar</td>
<td>&gt;99%TD and reaction product: Ti₅Si₃</td>
<td>Hv - 23-25 GPa K_Ic - 4-6 MPa m¹/²</td>
<td>Elastic Modulus: 470-520 GPa</td>
<td>Near parabolic covered with SiO₂, borosilicate glass and TiO₂</td>
<td>Raju et.al [11-13]</td>
</tr>
<tr>
<td>2</td>
<td>CrSi₂</td>
<td>No work reported</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>WSi₂</td>
<td>1700°C, 60 min</td>
<td>&gt;98%TD</td>
<td>Not studied</td>
<td>Resistant to aluminum liquid corrosion</td>
<td>Lu et.al. [14]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>MoSi₂</td>
<td>HP 1700°C, 60 min, vacuum</td>
<td>&gt;98%TD and reaction product: TiSi₂</td>
<td>Hv - 25-27 GPa K_Ic - 4-5 MPa m¹/²</td>
<td>TC: 50 W/m/K</td>
<td>Very poor due to Pesting of MoSi₂</td>
<td>Murthy et.al. [4,15]</td>
</tr>
<tr>
<td>5</td>
<td>CrB₂</td>
<td>MW at 2100°C, 30 min, Ar</td>
<td>98%TD</td>
<td>27.0 DPH K_Ic - 6.1 MPa.m¹/²</td>
<td>Not studied</td>
<td></td>
<td>Holcombe et.al [16]</td>
</tr>
<tr>
<td>6</td>
<td>CrB₂+MoSi₂</td>
<td>No work reported</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(TiCr)B₂</td>
<td>No work reported</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(TiCr)B₂+MoSi₂</td>
<td>No work reported</td>
<td></td>
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</table>
Detailed literature survey on the synthesis and consolidation of TiB$_2$ is presented in chapter 2. Effect of various metallic and non-metallic additives on densification and thermomechanical behaviour of TiB$_2$ with attendant merits and de-merits are enumerated. The potential applications of this material and need for a high performance TiB$_2$ composite is emphasised in chapter-2. Chapter 3 presents the experimental procedures. Results and discussions are presented in Chapters 4, 5 and 6 respectively. Synthesis of starting powders such as TiB$_2$, CrB$_2$ and MoSi$_2$ is described in chapter 4. Chapter 5 is divided into three sub-sections, which include consolidation by pressureless sintering and hot pressing, physical and mechanical properties and microstructural characterization. Isothermal and continuous oxidation studies and its results are presented in chapter 6. Major findings of the present thesis are summarized in chapter 7. Future scope of the work is also included in chapter 7.

1.4 Summary

Titanium diboride (TiB$_2$) is a structural ceramic material that is attracting attention as the base material for a range of high technological applications. However, consolidation of TiB$_2$ is difficult due to low self-diffusion coefficient and existence of surface oxides on the powder particles. Silicides were considered as possible additives because of their ability to reduce the surface oxides thereby enhancing densification. Moreover silicides are also expected to improve high temperature oxidation resistance by the formation of a protective glassy layer on the surface which would impede further oxidation. The outline of the thesis is brought out below:

Synthesis of borides by a process (boron carbide reduction) which avoid elemental constituent process is amenable to control the yields product consistently and robust for execution. A persistent challenge in the use of (TiB$_2$) borides is getting in the form of
consolidated dense bodies. The inapplicability of cold compaction and sintering is established and the superiority of hot pressing for consolidation is also demonstrated for obtaining the dense composites. Possible mechanisms for densification by hot pressing are brought out. Technological useful properties of the consolidated composites have been measured and the oxidation resistance of these composites also has been evaluated. The role of various additives in consolidation and their influence on the properties including oxidation resistance also has been brought out.

1.5 References


1.7


