CHAPTER 2
CHAPTER 2
LITERATURE SURVEY

2.1 Introduction

The refractoriness and high strength of non oxide structural ceramics make them ideally suited for applications at high temperature. Titanium diboride (TiB₂) is a ceramic that is being considered as the base material for a range of high technological applications [1]. It has many attractive properties, such as exceptional hardness (25–35 GPa at room temperature, more than three times harder than fully hardened structural steel), which is retained up to high temperature, high melting point (>3000°C), good creep resistance, good thermal conductivity (~65 W/m/K), high electrical conductivity (10-30 x 10⁴ S/cm) and considerable chemical stability [2,3]. TiB₂ is very similar to TiC, an important base material for cermets, and many of the boride’s properties (e.g. hardness, thermal conductivity, electrical conductivity and oxidation resistance) are superior to those of TiC. Such combination of properties makes TiB₂ a candidate material for heavy duty wear applications, particularly at elevated temperatures [1-3].

However, the relatively low fracture toughness of monolithic TiB₂ (~5 MPa.m¹⁄²) and its sensitivity to slow subcritical crack growth, limit its use in many engineering applications. The low self-diffusion coefficient makes pure TiB₂ very difficult to densify. These shortcomings are shared by many structural ceramics, e.g. ZrB₂, HfB₂ and SiC, and considerable research efforts are on to improve both the toughness and sinterability of these materials [1-3].

The development of TiB₂ and its composites, and their potential for high temperature structural/nuclear applications are reviewed in this chapter. The phase diagram and crystal structure of TiB₂ are also discussed. Densification, with and without sinter additives, and the microstructures obtained are considered, followed by a summary of data on mechanical, physical and oxidation properties. Important applications of TiB₂ are also listed.

2.1
2.2 Phase diagram and crystal structure

The Ti–B binary phase diagram is shown in Fig. 2.1[3]. Three intermetallic phases, orthorhombic TiB, orthorhombic Ti3B4 and hexagonal TiB2 are present[3]. TiB and Ti3B4 decompose peritectically at 2453K (2180°C) and 2473 K (2200°C) respectively and TiB2 melts congruently at 3498K (3225°C). Whereas Ti3B4 is a line compound but TiB and TiB2 have a narrow homogeneity range. TiB2 exists over a narrow stoichiometry range of 28.5–30 wt% B [3].

Titanium atoms in TiB2 form a hexagonal close packed (HCP) structure. The hexagonal unit cell of single crystal TiB2 \([a=b= 3.029 \text{ Å}, c=3.229 \text{ Å}; \alpha=\beta=90^\circ, \gamma=120^\circ]\) is shown in Fig. 2.2a [7,8]. Ti atoms are located at \((0,0,0)\) and B atoms at \((1/3,2/3,1/2)\) and \((2/3,1/3,1/2)\) lattice sites [3,4]. In analogy with the usual notation of ABABAB for HCP structure, the stacking sequence of Ti will be AAA. Boron (B) atoms are located interstitially between the A-layers, forming a strong covalently bonded hexagonal network structure as shown in Fig. 2.2b. High hardness and elastic modulus of TiB2 as well as its chemical resistance are attributed to its crystal structure and covalent bonding [3-6].
The important physical and mechanical properties of TiB$_2$ are listed in Table 2.1 along with those of other similar engineering ceramics. TiB$_2$ is superior in terms of hardness, toughness and electrical & thermal conductivity [3]. TiB$_2$ combines superior hardness and a high melting point with corrosion resistance. In addition, the TiB$_2$ is electrically conductive, which is important in some electrical applications and also enables the solid bodies formed to be shaped into complex geometry using electrical discharge machining (EDM).

![Hexagonal unit cell of single crystal TiB$_2$ and illustration of hexagonal net of boron atoms.](image)

Fig. 2.2 a) hexagonal unit cell of single crystal TiB$_2$ and b) illustration of hexagonal net of boron atoms. [7,8]

The engineering applications of monolithic TiB$_2$ are restricted due to its poor sinterability and toughness, exaggerated grain growth and a limited oxidation resistance. Since densification has been a major challenge, sintering of monolithic/bulk borides is reviewed in the following section. [3,9].
Table 2.1 Summary of important physical and mechanical properties of TiB$_2$ and other important high temperature ceramics [3,9]

<table>
<thead>
<tr>
<th>Property</th>
<th>TiB$_2$</th>
<th>ZrB$_2$</th>
<th>B$_4$C</th>
<th>SiC</th>
<th>WC</th>
<th>TiC</th>
<th>Si$_3$N$_4$</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure*</td>
<td>Hex</td>
<td>Hex</td>
<td>Rho</td>
<td>Hex</td>
<td>FCC</td>
<td>FCC</td>
<td>Hex</td>
<td>Tet</td>
</tr>
<tr>
<td>Melting point, K</td>
<td>3498</td>
<td>3273</td>
<td>2723</td>
<td>2473</td>
<td>2873</td>
<td>3340</td>
<td>2173</td>
<td>2316</td>
</tr>
<tr>
<td>Density, kg/m$^3$</td>
<td>4520</td>
<td>6100</td>
<td>2520</td>
<td>3200</td>
<td>15700</td>
<td>4930</td>
<td>3440</td>
<td>3990</td>
</tr>
<tr>
<td>Linear thermal expansion $\alpha$, $10^{-6}$ K$^{-1}$</td>
<td>$\alpha_a=6.6$</td>
<td>$\alpha_c=8.6$</td>
<td>6.83</td>
<td>4.5</td>
<td>5.68</td>
<td>5.2-7.3</td>
<td>7.42</td>
<td>2.4</td>
</tr>
<tr>
<td>Electrical resistivity, $\mu$Ω-cm</td>
<td>10-30</td>
<td>9.2</td>
<td>$10^6$</td>
<td>&gt;$10^5$</td>
<td>17</td>
<td>52</td>
<td>$10^{-18}$</td>
<td>$10^{-20}$</td>
</tr>
<tr>
<td>Fracture toughness K$_IC$, MPa.m$^{1/2}$</td>
<td>5-7</td>
<td>3.5</td>
<td>3-3.5</td>
<td>2.5-6</td>
<td>-</td>
<td>4</td>
<td>4-6</td>
<td>2.5-4</td>
</tr>
<tr>
<td>Elastic modulus, GPa</td>
<td>560</td>
<td>350</td>
<td>450</td>
<td>480</td>
<td>720</td>
<td>400</td>
<td>210</td>
<td>400</td>
</tr>
<tr>
<td>Three point flexural strength, MPa</td>
<td>700-1000</td>
<td>305</td>
<td>300</td>
<td>300-800</td>
<td>480-830</td>
<td>240-270</td>
<td>1000-1200</td>
<td>323</td>
</tr>
</tbody>
</table>

* Hex: hexagonal; Rho: rhombohedral/trigonal; FCC: Face centered cubic; Tet: tetragonal

2.3 Processing, microstructure and properties of bulk TiB$_2$

Synthesis of fine powders is the first step in the fabrication of ceramic components by powder metallurgy. The process then proceeds through densification of monolithic TiB$_2$ (without additive) or sintering with metallic and non-metallic additives. The properties of the material obtained are related to the microstructure developed in these steps.

2.3.1 Synthesis of TiB$_2$

Titanium diboride powder can be prepared by a variety of methods [10-16], such as the direct reaction of titanium or its oxides/hydrides, with elemental boron over 1273K (1000°C)[12], carbothermic /aluminothermic/ silicothermic/ magnesiothermic reduction of titanium oxide and boron oxide mixture [12], or hydrogen reduction of boron halides in the presence of the metal or its halides[12], sol-gel [15,16], self-propagating high-temperature
synthesis (SHS) [13], mechanical milling of TiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3} with metallic magnesium [11,12]. Apart from these routes, electrochemical synthesis has been developed to prepare pure titanium diboride.

An example of solid state reaction is the carbothermic reduction of mixture of TiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3} by the reaction

$$\text{TiO}_2 + \text{B}_2\text{O}_3 + 5\text{C} \rightarrow \text{TiB}_2 + 5\text{CO} \quad (2.1)$$

carried out in electric furnaces. However, this reaction is highly endothermic and needs temperatures above 2073K [16]. Another method for large-scale production of titanium diboride is based on the reduction of TiO\textsubscript{2} with carbon and boron carbide (boron carbide method)[10]:

$$2\text{TiO}_2 + \text{B}_4\text{C} + 3\text{C} \rightarrow 2\text{TiB}_2 + 4\text{CO} \quad (2.2)$$

Purity of the product in this method is >99%. Production of pure TiB\textsubscript{2} powders in a large quantity (kilogram scale) on both laboratory and commercial scale using this method is the main advantage. However, this reaction is also highly endothermic and needs temperatures above 2073K [16].

TiB\textsubscript{2} powder is also obtained by the hydrogen reduction of TiCl\textsubscript{4} and BCl\textsubscript{3} mixture as per the reaction:

$$\text{TiCl}_4 + 2\text{BCl}_3 + 5\text{H}_2 \rightarrow \text{TiB}_2 + 10\text{HCl} \quad (2.3)$$

This method is simple and can yield a pure TiB\textsubscript{2} powder. Handling of chlorides is however difficult due to their corrosive nature.

Self-propagating high-temperature synthesis (SHS), reactive synthesis, and combustion synthesis are methods by which ceramic materials can be produced. All these processes involve exothermic reactions between starting powders as a driving force yielding the desired final product. Commonly, these processes comprise an ignition of the reaction, followed by self-
propagating combustion fronts that transform the green body to a solid piece. The ignition temperature for the stoichiometric mixture of TiO₂, H₃BO₃ and Mg/Al was found to be as low as 958K (685°C) [14]. Titanium diboride powder has been synthesized by reaction of Ti and B inorganic precursors followed by heat treatment in argon atmosphere. SHS is simple, low cost, and needs no expensive facilities. TiB₂ can produce at lower temperatures and in very short time. However, the products were reported to be contaminated with metallic titanium, titanium carbide Al₂O₃ or titanium oxide [13,16].

Mechanosynthesis has been shown to be very effective for the preparation of many metals and ceramic materials with high melting point [12]. In the case of TiB₂, another route to form the compound is by reaction of TiO₂ and B₂O₃ with metallic magnesium during extended ball milling performed at room temperature in a tumbling mill for between 10 and 15 h in an inert atmosphere [11,12]. The final products are TiB₂ and MgO. The oxide can be easily removed by leaching in acid, leaving a powder composed of pure TiB₂, as tested by X-ray diffraction (XRD) analysis [12]. This process is a combustive reaction [12] that takes place once the ignition temperature is reached during ball impacts—the conditions reported in literature allow for TiB₂ production only with long milling times (10 to 15 h) due to the chosen conditions for ball milling and the relatively poor energy transfer during ball impacts. However, the products were reported to be contaminated with unreacted reactants.

It is evident that a number of laboratory scale methods have been successfully developed to synthesize micrometer or sub-micrometer sized TiB₂ powder. Success is, however, limited as far as industrial scale production of TiB₂ is concerned. From the sintering/consolidation point of view, emphasis should be placed on obtaining finer TiB₂ powders with a narrow size distribution and with limited impurities. From a classical Herring approach, it can be predicted that a
decrease in particle size by one order of magnitude will produce 3–4 orders of magnitude reduction in sintering time, depending on the dominant densification mechanism (lattice diffusion, grain boundary diffusion) [17,18]. The presence of impurities in the starting powders causes a decrease in sinterability. For example, TiB₂ powders containing >1 wt% oxygen can be densified only to 90% theoretical density, even at higher sintering temperatures (2273K) [19].

2.3.2 Densification and microstructure of monolithic TiB₂

Consolidation methods by powder metallurgy route are i) pressureless sintering, ii) hot pressing and iii) special methods (hot isostatic pressing, microwave sintering, spark plasma sintering, etc.). Pressureless sintering is simple and gets the intricate shapes. However, some of the materials cannot densify by pressureless sintering. In hot pressing, external pressure is applied in order to achieve the full density. In case of hot isostatic pressing, uniform pressure is applied from all the directions. More details of the spark plasma sintering (SPS) are given in the next section.

The densification of transition metal borides such as TiB₂ is inherently difficult because of three characteristics of these compounds: i) high melting point, ii) low self-diffusion coefficient and iii) the comparatively high vapor pressure of the constituents. To obtain good densification, sintering temperatures exceeding 70% of the absolute melting temperature are usually necessary during consolidation to ensure appreciable grain boundary and volume diffusion induced material transport to occur to result in >95% theoretical density [3]. This implies that TiB₂ (Tₘ ≈ 3523K) requires sintering temperatures of 2073-2573K (1800–2300°C). However, borides undergo an abnormal grain growth at high temperatures. The occurrence of microcracking at the grain boundaries is also promoted with the increase in grain size. Thus, it is
very difficult to achieve crack free dense borides by the conventional cold compaction and sintering, as no shape accommodation occurs without an external pressure and large pores tend to coarsen during high temperature sintering [20].

A thin oxygen rich layer (mainly TiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}) is usually present on the surface of TiB\textsubscript{2} powder, irrespective of synthesis route [19]. The presence of oxygen finally results in increase in grain size and coarsening of pores because the presence of oxides increases the surface diffusivity. In order to achieve higher density and to inhibit abnormal grain growth, the total oxygen content of the powder must be limited to <0.5 wt% or strong reducing additives need to be used to remove TiO\textsubscript{x} below 1873K (1600°C) [19].

Table 2.2 [21-32] presents reported data on densification and material property of monolithic TiB\textsubscript{2} (without sinter additive). A point to note in Table 2.2 is that while hot pressing at or above 2073K (1800°C) can produce >95% theoretical density, hipping at 1773-1873K (1500–1600°C) enables the attainment of similar density with good mechanical properties (hardness is ~ 26 GPa and three point flexural strength ~ 450 MPa) [21-23]. Additionally a sintering route, high pressure sintering (HPS) at temperature greater than 2173K (1900°C) and at a pressure of 3 GPa, has been shown to be capable of producing >95% density TiB\textsubscript{2} with good hardness [24] (Table 2.2). In addition to the commercial powders, as utilized in obtaining the results mentioned above, a group of researchers used elemental powders Ti and B in 1 : 2 weight ratio and obtained 95% or higher theoretical density via high pressure self-combustion synthesis (HPCS) route[24]. A better densification result (~98%) was obtained with carbon addition to (Ti+B) elemental powder mix. For comparison, representative data of other high temperature ceramics are also included in Table 2.2 [21-32]. Near theoretical density was obtained for Si\textsubscript{3}N\textsubscript{4}
and Al₂O₃ ceramics when hipping at 1923K and hot pressing at 1823K respectively [30]. Whereas for ZrB₂ only 98% TD was obtained even after hot pressing at 2173K [32].

Ferber and co-workers [33] reported that materials with anisotropic thermal expansion, such as TiB₂, often develop microcracks, relieving localized residual stresses generated during cooling from hot pressing temperature. Such stresses arise primarily from the mismatch of thermal expansion between individual grains and anisotropic thermal expansion. For example, the thermal expansion coefficients of TiB₂ along the crystallographic ‘a’ and ‘c’ axes are 7.19 x 10⁻⁶ and 9.77 x 10⁻⁶ /K respectively. The experimental observations suggested that the critical grain size for microcracking to occur in case of TiB₂ based ceramics is ~15 µm [33].

Baumgartner and Steiger [34] reported almost full densification (99% TD) of titanium diboride powder by pressureless sintering. The high purity micrometer sized titanium diboride powder was produced by the reaction of titanium tetrachloride and boron trichloride gases in the presence of excess hydrogen in arc plasma heating, according to the following reaction:

\[
\text{TiCl}_4 (g) + 2\text{BCl}_3 (g) + 5\text{H}_2 (g) \rightarrow \text{TiB}_2 (s) + 10\text{HCl} (g)
\]  \hspace{1cm} (2.4)

The densification proceeds by self-diffusion and requires a high grain boundary surface area (small grain size) to reach completion. The reported difficulties in achieving full dense titanium diboride by the pressureless sintering of carbothermic powder are attributed to rapid grain growth (activation energy is ~1.02 MJ/mol) before completion of the densification [34]. This is due to the presence of small amount of oxygen as impurity, which enhances the surface diffusion instead of lattice diffusion.

Spark Plasma Sintering (SPS) is a sintering technique with some similarities to conventional hot pressing. However, in SPS, a strong-pulsed current is directly passed through the electrically conducting pressure die instead of using an external heating source. In
appropriate cases, electric current also passes through the sample, implying self-heating of the sample. The unique features of SPS process are the possibilities to apply very high heating rates up to several hundred degrees per minute and subsequently to achieve full densification within minutes. High heating rate (100 K/min) yielded more homogeneous microstructures than those achieved with the slow heating rate (20 K/min), and therefore a rapid reaction yields a more homogeneous microstructure. Hardness and fracture toughness of SPS samples were 29.6±2.5 GPa and 5.2±0.4 MPa.m$^{1/2}$ respectively [35].

Summarizing, size and purity of the starting powders plays a strong role for densification of TiB$_2$ ceramics. >99% TD obtained by using the high purity micrometer sized TiB$_2$ powders, whereas only 90% TD achieved when TiB$_2$ powder contains >1% oxygen as impurity. The literature indicates that high sintering temperatures (>2073$^\circ$C) are required to obtain high density monolithic TiB$_2$. Also, the grain size of TiB$_2$, sintered from commercial powders, is >4 µm, which limits hardness/strength. Additionally, the influence on modulus, strength, electrical and thermal conductivity is most pronounced, if the grain size is large enough to induce microcracking. It should be noted that the strength could be significantly affected by internal stresses, even in the absence of microcracking.
Table 2.2 Density, microstructural characteristics and mechanical properties of TiB₂ and other high temperature ceramics, sintered without additive under various processing conditions

<table>
<thead>
<tr>
<th>Material composition, wt%</th>
<th>Processing conditions*</th>
<th>Sintered density, %TD</th>
<th>Microstructural phases, µm</th>
<th>Hardness, GPa</th>
<th>Fracture toughness K₁c, MPa.m¹/²</th>
<th>Flexural strength*, MPa</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>commercial TiB₂ powder</td>
<td>PS at 2423 K, Ar</td>
<td>93.1</td>
<td>TiB₂</td>
<td>---</td>
<td>5.4</td>
<td>---</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Hipping at 1773 K, 196MPa, 2h,Ar</td>
<td>97.6</td>
<td>1.8 equiaxed</td>
<td>---</td>
<td>3.7</td>
<td>650 (3P)</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Hipping at 1873 K, 200MPa, 2h,Ar</td>
<td>---</td>
<td>GG:2~4-6</td>
<td>26</td>
<td>3.5</td>
<td>450 (3P)</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>HP at 1873 K, 1h, Ar</td>
<td>91.0</td>
<td>4.8 equiaxed</td>
<td>---</td>
<td>4.1</td>
<td>305 (3P)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>HP at 1973 K, 1h, Ar</td>
<td>95.0</td>
<td>5.0 equiaxed</td>
<td>---</td>
<td>4.3</td>
<td>498 (3P)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>HP at 2073 K, 0.5h, Ar</td>
<td>96.0</td>
<td>5.3 equiaxed</td>
<td>---</td>
<td>5.3</td>
<td>545 (3P)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>HP at 2073 K, 1h, Ar</td>
<td>97.0</td>
<td>8.1 equiaxed</td>
<td>---</td>
<td>5.7</td>
<td>558 (3P)</td>
<td>21</td>
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<tr>
<td></td>
<td>HP at 2073 K, 1.5h, Ar</td>
<td>--</td>
<td>10.5</td>
<td>---</td>
<td>6.3</td>
<td>538 (3P)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>HP at 2073 K, 2h, Ar</td>
<td>--</td>
<td>12.7</td>
<td>---</td>
<td>6.8</td>
<td>475 (3P)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>HP at 2173 K, 1h, Ar</td>
<td>--</td>
<td>12.2</td>
<td>---</td>
<td>6.2</td>
<td>521 (3P)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>HP at 2273 K, 1h</td>
<td>--</td>
<td>--</td>
<td>26.7</td>
<td>4.8</td>
<td>498 (3P)</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>HPS at 2250 K, 5min, 3GPa</td>
<td>94.6</td>
<td>1.4 equiaxed</td>
<td>19.2</td>
<td>--</td>
<td>--</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>HPS at 2500 K, 5min, 3GPa</td>
<td>97.1</td>
<td>--</td>
<td>21.7</td>
<td>2.8</td>
<td>--</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>HPS at 2750 K, 5min, 3GPa</td>
<td>98.0</td>
<td>--</td>
<td>24.5</td>
<td>3.2</td>
<td>--</td>
<td>24</td>
</tr>
<tr>
<td>elemental Ti+B (1:2) powders</td>
<td>HPCS at 2250 K</td>
<td>97.8</td>
<td>--</td>
<td>23.6</td>
<td>3.5</td>
<td>--</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>HPCS at 2500 K</td>
<td>98.0</td>
<td>--</td>
<td>24</td>
<td>3.8</td>
<td>--</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>HPCS at 2750 K</td>
<td>98.0</td>
<td>--</td>
<td>23.9</td>
<td>3.6</td>
<td>--</td>
<td>24</td>
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<tr>
<td>Other high temperature ceramics</td>
<td>Al₂O₃</td>
<td>at 1823 K, 45 min</td>
<td>100</td>
<td>2</td>
<td>19.4</td>
<td>4.6</td>
<td>420 (4P)</td>
</tr>
<tr>
<td></td>
<td>B₄C</td>
<td>at 2423 K, 65 min</td>
<td>95.0</td>
<td>6-10</td>
<td>29</td>
<td>2.5</td>
<td>220 (3P)</td>
</tr>
<tr>
<td></td>
<td>β-SiC</td>
<td>at 2223 K, 2h</td>
<td>--</td>
<td>0.8-3</td>
<td>--</td>
<td>2.5</td>
<td>394 (4P)</td>
</tr>
<tr>
<td></td>
<td>Si₃N₄</td>
<td>Hipping at 1923 K,2h,18MPa,Ar</td>
<td>100</td>
<td>--</td>
<td>15.5</td>
<td>4.6</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>WC</td>
<td>PPC at 1873 K, 4 min, 35 MPa</td>
<td>--</td>
<td>5.5</td>
<td>19.2</td>
<td>8.2</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>ZrB₂</td>
<td>HP at 2173 K, 45 min</td>
<td>98</td>
<td>4.0</td>
<td>23</td>
<td>--</td>
<td>565 (4P)</td>
</tr>
</tbody>
</table>

* PS: pressureless sintering; hipping; HP: hot isostatic pressing; 3P: three point bending; 4P: four point bending; HPS: high pressure sintering; HPCS: high pressure self-combustion synthesis; PPC: plasma pressure compaction
2.3.3 Effect of metallic sinter additives

Various sinter additives have been used to reduce sintering temperature and hence restrict grain growth in the densification of TiB$_2$. The influence of metallic binders (as sinter additives) on the densification and properties of TiB$_2$ has been investigated extensively [33,36-43]. Table 2.3 is a summary of these reports, and includes information on some important cermets. High density TiB$_2$ (>99%) has been obtained through small additions 1–2 wt% of Fe, Cr or Ni [33,44-45]. Very high hardness (23–31 GPa) is achieved with a moderate toughness of 4–6 MPa.m$^{1/2}$ and four point flexural strength value > 500 MPa [46]. Except fracture toughness, the properties of TiB$_2$ materials are superior to many other engineering materials. In particular, the hardness of TiB$_2$ at >18 GPa is higher than those of ZrC/TiC/WC (≤14 GPa) based materials. Thus, TiB$_2$ based materials could be expected to show greater resistance to abrasive/sliding wear. Cemented TiB$_2$ has a toughness of 9.2 MPa m$^{1/2}$, which is comparable with WC and TiC based cermets [41].
<table>
<thead>
<tr>
<th>Material composition, wt.%</th>
<th>Processing conditions*</th>
<th>Sintered density, %TD</th>
<th>Microstructural phases, µm</th>
<th>Vickers hardness, Hv, GPa</th>
<th>Indentation toughness, MPa m₁/²</th>
<th>Flexural strength*, MPa</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>TiB₂+0.014Ni</td>
<td>HP at 2523 K, 30MPa, 20min</td>
<td>97.9</td>
<td>1.5 (equiaxed TiB₂ grains of traces of Ni₄B₃,Ni₃B)</td>
<td>23.3</td>
<td>5.8</td>
<td>716 (4P)</td>
<td>37</td>
</tr>
<tr>
<td>TiB₂+0.7Ni</td>
<td>HP at 1823 K, 1h, vacuum</td>
<td>97.9</td>
<td>---</td>
<td>23.3</td>
<td>5.1</td>
<td>716 (4P)</td>
<td>38</td>
</tr>
<tr>
<td>TiB₂+1.4Ni</td>
<td>HP at 1698 K</td>
<td>&gt;99</td>
<td>---</td>
<td>---</td>
<td>6.4</td>
<td>670 (4P)</td>
<td>33</td>
</tr>
<tr>
<td>TiB₂+7.9Ni</td>
<td>HP at 1698 K</td>
<td>&gt;99</td>
<td>---</td>
<td>---</td>
<td>4</td>
<td>420 (4P)</td>
<td>33</td>
</tr>
<tr>
<td>TiB₂+0.017Fe</td>
<td>HP at 1973 K,1h,Ar</td>
<td>99</td>
<td>6.4(equiaxed TiB₂ grains)</td>
<td>---</td>
<td>6.6</td>
<td>520 (3P)</td>
<td>39</td>
</tr>
<tr>
<td>TiB₂+0.5Fe+0.5Cr</td>
<td>PS at 2073 K,2h,Ar</td>
<td>97.6</td>
<td>--</td>
<td>27.0</td>
<td>6.2</td>
<td>506 (4P)</td>
<td>36</td>
</tr>
<tr>
<td>TiB₂+0.5Fe+0.5Cr</td>
<td>PS at 2173 K,2h,Ar</td>
<td>98.6</td>
<td>--</td>
<td>31.3</td>
<td>5.9</td>
<td>262 (4P)</td>
<td>36</td>
</tr>
<tr>
<td>TiB₂+Ti</td>
<td>HP at 2173 K,2h,Ar</td>
<td>99.6</td>
<td>Needle like of TiB₂</td>
<td>19.0</td>
<td>4.5</td>
<td>360 (3P)</td>
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<tr>
<td>TiB₂+14.4Fe+6.1Ni-8TiAl₃</td>
<td>PS+hipping at 1773 K,Ar</td>
<td>--</td>
<td>5.0(TiB₂ grains)</td>
<td>17.8</td>
<td>9.2</td>
<td>1019 (4P)</td>
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<tr>
<td>ZrB₂+4.0Ni</td>
<td>HP at 2123 K,30min</td>
<td>98</td>
<td>--</td>
<td>14.4</td>
<td>2.8</td>
<td>371 (4P)</td>
<td>42</td>
</tr>
<tr>
<td>WC+6.5Co</td>
<td>PS at 1823 K,4h</td>
<td>--</td>
<td>2.5</td>
<td>15.8</td>
<td>10</td>
<td>--</td>
<td>43</td>
</tr>
<tr>
<td>TiC+10Mo₂C+2Si</td>
<td>PS at 1823 K,4h</td>
<td>--</td>
<td>4.2</td>
<td>15.1</td>
<td>6.1</td>
<td>--</td>
<td>43</td>
</tr>
<tr>
<td>TiC+10Ni+10Mo₂C+25Ni</td>
<td>PS at 1823 K,4h</td>
<td>--</td>
<td>2.4</td>
<td>12.7</td>
<td>10</td>
<td>--</td>
<td>43</td>
</tr>
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</table>

*HP: hot pressing; 3P: three point bending; 4P: four point bending; PS pressureless sintering; hipping: hot isostatic pressing
Earlier experiments, using metallic additives such as nickel, iron, cobalt, titanium, stainless steel and manganese have demonstrated that 99% of theoretical density can be achieved by liquid phase sintering (LPS) [33,39,40]. Ferber et al. [33] have used up to 10 wt% Ni to achieve >99% theoretical density by hot pressing (1698K). As regards the densification mechanism, the transition metals (Ni, Co, Cr) react with TiB₂ forming metal borides with a low melting point (approximately 1173–1373K) and these borides also exhibit good wetting behavior. In case of Ni bonded TiB₂, a ternary ‘τ’ phase with the composition, Ni₂₁Ti₂B₆ forms by the dissolution of TiB₂[33]. At 1073K (800°C), the ‘τ’ phase is in equilibrium with Ni, Ni₃B, Ni₃Ti and TiB₂. Typical metal contents required for the optimum liquid phase sintering of TiB₂ are 5–25 wt% (2–12 at%) of either Ni or Co[33]. In order to avoid reactions consuming TiB₂, the borides of Ni or Co have also been used [20]. In LPS, the sintering temperatures have been decreased from 2373 to 1673K (2100 to 1400°C).

Phenomenologically, the liquid phase sintering, as commonly observed with the use of metallic additives in sintering of TiB₂, enhances the mass transport but simultaneously causes exaggerated grain growth. Extensive nickel intermetallic phase (Ni₂₁Ti₂B₆, Ni₃B, Ni₃Ti) formation was also found to have deleterious effect on both fracture strength and fracture toughness. Hence, the strength and toughness are significantly retained for TiB₂ ceramics with a fine grain size (4 µm) and low Ni content (<2 wt%). The microstructures of bulk TiB₂, prepared by liquid phase sintering, are similar to those of other hard metals, such as WC+Co (Hardness ~22 GPa). For example, hardness and fracture toughness of spark plasma sintering (SPS) samples (TiB₂ +2.5%Ti) were 26.8±1.6 GPa and 5.9±0.3 MPa.m¹/₂ respectively[47]. In liquid phase sintered TiB₂, the boride particles form a rigid skeleton of faceted crystals, when it reacts with transition metals such as iron, nickel or cobalt to form the metallic borides Fe₃B, Ni₃B,
Ni$_2$B and Co$_3$B, which can dissolve titanium [48]. Depending upon the wetting behavior, typically influenced by the surface oxidation of the hard phase. Round pores accumulate at particle/matrix interfaces or close to triple pocket. Such pores cannot be completely infiltrated by the liquid phase during sintering. Moreover, the evaporation of Fe, Co or Ni borides potentially cause entrapped gas pores [48].

Relatively small additions (1–5 wt%) of nickel, nickel boride (NiB) and iron have been found to promote liquid phase sintering of TiB$_2$. High density (>94%) was obtained at temperatures >1773K. Significant grain growth was observed in TiB$_2$ samples with Ni, NiB and Fe binders during sintering at 1973K (1700°C)[45]. The grain growth was observed to be closely related to the oxygen content of the samples and sintering temperature. It has been observed by Einarsrud et.al [45] that addition of carbon to act as a strong reducing agent to remove the surface oxides of the particles does inhibit the grain growth. Therefore, to obtain fine grained microstructures it is essential to optimize the sinter additive content and the processing conditions (temperature, time, etc.). A liquid phase sintered microstructure, obtained with TiB$_2$+1.5wt% Ni material is shown in Fig. 2.3a[45]. All the triple pockets appear to contain sintering liquid residue.

Combined addition of various metallic additives has also been investigated [36]. Simultaneous addition of 0.5 wt% Cr and 0.5 wt% Fe was found to enhance the densification of TiB$_2$ up to 98.8%[36]. A typical microstructure of TiB$_2$+0.5Cr+0.5Fe shows equiaxed grain with sizes between 2 and 10 µm (Fig. 2.3b). In Fig. 2.3c, high resolution TEM image reveals the existence of sintering liquid, rich in Fe and Cr[36]. Mechanical properties of the TiB$_2$+0.5Cr+0.5Fe, sintered at 2073K (strength of 506 MPa and a fracture toughness of 6.2 MPa.m$^{1/2}$), were much better than those measured in the TiB$_2$+0.5Cr+0.5Fe sintered at 2173K.
(1900°C)[36]. In the case of 0.5 wt% Fe addition to TiB₂ along with 0.5 wt% Cr, abnormal grain growth was suppressed remarkably and an increase in sintered density was recorded. Microstructural observations confirmed the existence of Fe rich phase at the triple pockets and at grain boundaries [44].

![Image of TEM and SEM images](image)

Fig. 2.3 a) bright field (BF) TEM image showing wetting behavior of liquid phase in TiB₂–1.5Ni (wt. %)[45], b) SEM image of TiB₂–0.5Fe–0.5Cr (wt. %)[45] and c) BF TEM image along with EDS analysis revealing presence of Fe and Cr in sintering liquid residue at triple pocket of TiB₂–0.5Fe–0.5Cr[36]

2.16
Wettability and dissolution of TiB$_2$ in the transient liquid phase have been widely identified as critical factors when sintering with metallic additives. In most cases the hardness is inferior to that of the monolithic TiB$_2$ (Table 2.3). From the perspective of high temperature applications, the presence of metallic binder is not desirable, the low melting point of either sintering liquid or metallic additives leads to incipient fusion and consequent degradation of high temperature properties.

### 2.3.4 Effect of non-metallic sinter additives

The principal objective of non-metallic additives is therefore to improve sinterability of TiB$_2$ without promoting grain growth thus circumventing limitations of metallic additives. Various non-metallic additives (AlN, SiC, Si$_3$N$_4$, CrB$_2$, B$_4$C, TaC) have been used for attaining densification of TiB$_2$ with good mechanical properties [22-26,49,50]. Table 2.4 [22,26,46,49-53] presents the summary of the published results. A comparison of Tables 2.3 and 2.4 indicates that higher amount of non-metallic additives, more than 5–10 wt%, is typically added to densify TiB$_2$, while a smaller amount of metallic additive, even less than 2 wt% was sufficient to obtain dense TiB$_2$. As with the use of metallic binders, a combination of high Vickers hardness (~20–27 GPa) and moderate indentation toughness (~4–7 MPa m$^{1/2}$) and also a modest flexural strength of 500 MPa is obtainable with the use of a variety of non-metallic sinter additives [46].

The addition of non-metallic binders has an important influence on the sinterability and microstructure of the TiB$_2$. Representative SEM images of polished bulk TiB$_2$ ceramics are shown in Fig. 2.4(a–c). All these materials were hot pressed at 2073K (1800°C) for 1h in vacuum. It can be noticed in Fig. 2.4a that monolithic bulk TiB$_2$, without any sinter additive, exhibits coarse grains of sizes around 10 µm [46]. The presence of large pores at multiple grain junctions is also commonly observed.
The pore sizes appear to have reduced with the addition of 2.5 wt % Si₃N₄ to TiB₂ (Fig. 2.4b) [50]. Near full dense microstructure with finer TiB₂ grain sizes of 5 µm or less is observed, when AlN is used as sinter additive with an optimal amount of 5 wt% (Fig. 2.4c) [52]. Evidence of sintering liquid residue at triple pocket is presented in TiB₂+MoSi₂ composite (Fig. 2.4d). As in the case of addition of metallic additive, the liquid phase sintering is reported to occur for TiB₂ with non-metallic additives also. For example with MoSi₂ addition, TiSi₂ forms and liquid TiSi₂ (Tₘ<1733K) is reported to enhance densification of TiB₂ [50]. Similarly, Torizuka et al. [54,55] observed the formation of grain boundary liquid phase (amorphous SiO₂), when SiC was used as an additive. According to Murata et al. [51], TaC and TaN were effective for densification of TiB₂ by formation of (Ti,Ta)B₂ and (Ti,Ta)(C,N) solid solutions when hot pressed at 2273K (2000°C) [52]. The presence of reaction products such as TiN and BN has been observed in TiB₂+Si₃N₄ composite system [52].

Fracture mechanisms are considerably influenced by binder additions, as can be observed in Fig. 2.5. The fracture of monolithic TiB₂ occurred mainly by an intergranular mode along with noticeable evidence of transgranular fracture, apparently owing to high porosity and large grain size. However, TiB₂ with non-metallic sinter additives such as AlN, Si₃N₄ exhibited predominant intergranular fracture (Fig. 2.5 b & c) [36,46,52]. In Fig. 2.5d, it can be noticed that the fracture mode is mixed in case of using metallic binder (0.5Cr+0.5Fe) with large TiB₂ grains, exhibiting transgranular fracture. Sintering additives enhance the density significantly and reduce the grain size by the secondary phase formation. However, the addition of sinter additives, such as AlN, SiC, Si₃N₄, beyond an optimal amount resulted in lowering of the density and reducing the grain size owing to grain boundary phase formation [46,53].

2.18
Table 2.4 Overall summary illustrating influences of non-metallic additives on microstructure and mechanical properties

<table>
<thead>
<tr>
<th>TiB&lt;sub&gt;2&lt;/sub&gt; composite</th>
<th>Processing conditions</th>
<th>Sintered density, %TD</th>
<th>Microstructural phases, µm</th>
<th>Vickers hardness, Hv, GPa</th>
<th>Fracture toughness, MPa m&lt;sup&gt;1/2&lt;/sup&gt;</th>
<th>Flexural strength *, MPa</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influence of Nitride based additives:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0% additive</td>
<td>HP at 2073 K, 60 min, 30MPa, Ar</td>
<td>89.0</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>12.5</td>
<td>4.5</td>
<td>360 (4P)</td>
<td>46</td>
</tr>
<tr>
<td>2.5% AlN</td>
<td></td>
<td>94.0</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;, BN, TiN, Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>16.1</td>
<td>5.0</td>
<td>500 (4P)</td>
<td>46</td>
</tr>
<tr>
<td>5.0% AlN</td>
<td></td>
<td>98.0</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;, BN, TiN, Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, unreacted AlN</td>
<td>22.0</td>
<td>6.8</td>
<td>650 (4P)</td>
<td>46</td>
</tr>
<tr>
<td>10% AlN</td>
<td></td>
<td>88.5</td>
<td></td>
<td>14.0</td>
<td>5.2</td>
<td>500 (4P)</td>
<td>46</td>
</tr>
<tr>
<td>20.0% AlN</td>
<td></td>
<td>87.5</td>
<td></td>
<td>12.1</td>
<td>4.6</td>
<td>400 (4P)</td>
<td>46</td>
</tr>
<tr>
<td>0% additive</td>
<td>HP at 2073 K, 60 min, Ar</td>
<td>90.0</td>
<td>3-7 µm TiB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>23.0</td>
<td>5.8</td>
<td>380 (4P)</td>
<td>52</td>
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<tr>
<td>2.5% Si₃N₄</td>
<td></td>
<td>99.0</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;, TiN, BN</td>
<td>27.0</td>
<td>5.1</td>
<td>810 (4P)</td>
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<tr>
<td>5.0% Si₃N₄</td>
<td></td>
<td>97.5</td>
<td></td>
<td>21.0</td>
<td>4.8</td>
<td>510 (4P)</td>
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<tr>
<td>10% Si₃N₄</td>
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<td>96.0</td>
<td></td>
<td>20.0</td>
<td>4.4</td>
<td>400 (4P)</td>
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<td>…</td>
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<td>…</td>
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<tr>
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<td></td>
<td>90.0</td>
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<td>15</td>
<td>…</td>
<td>…</td>
<td>51</td>
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<tr>
<td>5.0% TiN</td>
<td></td>
<td>96.8</td>
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<td>15</td>
<td>…</td>
<td>…</td>
<td>51</td>
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<td>5.0% ZrN</td>
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<td>15</td>
<td>…</td>
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<td>…</td>
<td>15</td>
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<td></td>
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<tr>
<td>0% additive</td>
<td>PS at 1973 K, vacuum+hipping at 1873 K, 200MPa, Ar</td>
<td>62</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>…</td>
<td>3.3</td>
<td>450(3P)</td>
<td>53</td>
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<tr>
<td>2.5% SiC</td>
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<td>Amorphous SiO&lt;sub&gt;2&lt;/sub&gt;, liquid phase along GB</td>
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<td>4.3</td>
<td>660 (3P)</td>
<td>53</td>
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<tr>
<td>5.0% SiC</td>
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<td>93.0</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;, SiC, TiC</td>
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<td>4.9</td>
<td>850 (3P)</td>
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<tr>
<td>0% additive</td>
<td>HP at 2273 K, 30 min</td>
<td>90.0</td>
<td>…</td>
<td>15</td>
<td>…</td>
<td>…</td>
<td>53</td>
</tr>
<tr>
<td>1.0% TaC</td>
<td></td>
<td>98.0</td>
<td>(TiTa)B&lt;sub&gt;2&lt;/sub&gt;, (Ta, Ti)(C,N) solid soln.</td>
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<td>…</td>
<td>…</td>
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<tr>
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<td></td>
<td>99.4</td>
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<td>15</td>
<td>…</td>
<td>…</td>
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<tr>
<td>5.0% TiC</td>
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<td>…</td>
<td>15</td>
<td>…</td>
<td>…</td>
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<td>…</td>
<td>15</td>
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2.19

Contd…
<table>
<thead>
<tr>
<th>Material composition, wt%</th>
<th>Processing conditions*</th>
<th>Sintered density, %TD</th>
<th>Microstructural phases, µm</th>
<th>Vickers hardness, Hv, GPa</th>
<th>Fracture toughness, MPa m$^{1/2}$</th>
<th>Flexural strength*, MPa</th>
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</tr>
<tr>
<td>0% additive</td>
<td>HP at 2073 K, 60 min, vacuum</td>
<td>97.5</td>
<td>TiB$_2$</td>
<td>26</td>
<td>5.1</td>
<td>...</td>
<td>49,50</td>
</tr>
<tr>
<td>10%MoSi$_2$</td>
<td>HP at 1973 K, 60 min, vacuum</td>
<td>99.3</td>
<td>TiB$_2$,MoSi$_2$, trace TiSi$_2$</td>
<td>27</td>
<td>4.0</td>
<td>...</td>
<td>49,50</td>
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<tr>
<td>20%MoSi$_2$</td>
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<td>98.7</td>
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<td>25</td>
<td>5.0</td>
<td>...</td>
<td>49,50</td>
</tr>
<tr>
<td>10%MoSi$_2$</td>
<td>PS at 2173 K, 120 min, Ar+H$_2$</td>
<td>82.4</td>
<td>...</td>
<td>...</td>
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<td>...</td>
<td>49,50</td>
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<tr>
<td>15%MoSi$_2$</td>
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<td>...</td>
<td>49,50</td>
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<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>49,50</td>
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<tr>
<td>25%MoSi$_2$</td>
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<td>91.3</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>49,50</td>
</tr>
<tr>
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<td>HP at 1923 K, 30MPa, Ar</td>
<td>98.8</td>
<td>TiB$_2$,Ti$_5$Si$_3$</td>
<td>25</td>
<td>4.3</td>
<td>381</td>
<td>89-91</td>
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<tr>
<td>5%TiSi$_2$</td>
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<td>99.6</td>
<td>TiB$_2$,Ti$_5$Si$_3$</td>
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<td>5.8</td>
<td>426</td>
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<tr>
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<td>99.6</td>
<td>TiB$_2$, TiSi$_2$, Ti$_5$Si$_3$</td>
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<td>4.2</td>
<td>338</td>
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<tr>
<td>10%WSi$_2$</td>
<td>1973 K, 60 min</td>
<td>&gt;98</td>
<td>...</td>
<td>...</td>
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<td>Influence of Boride based additives:</td>
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<td></td>
</tr>
<tr>
<td>5.0%ZrB$_2$</td>
<td>HP at 2273 K, 60 min</td>
<td>79.6</td>
<td>...</td>
<td>15</td>
<td>...</td>
<td>...</td>
<td>51</td>
</tr>
<tr>
<td>3.0%CrB$_2$</td>
<td>MW at 2173 K, 30 min, Ar</td>
<td>95.0</td>
<td>...</td>
<td>28.9DPH</td>
<td>6.2</td>
<td>...</td>
<td>26</td>
</tr>
<tr>
<td>3.0%CrB$_2$</td>
<td>MW at 2373 K, 30 min, Ar</td>
<td>98.0</td>
<td>...</td>
<td>27.0DPH</td>
<td>6.1</td>
<td>...</td>
<td>26</td>
</tr>
</tbody>
</table>

*HP: hot pressing; 4P: four point bending; 3P: three point bending; PS: pressureless sintering; hipping: hot isostatic pressing; MW: microwave sintering

It was commonly noted that the optimum non-metallic additive content to achieve near theoretical density in TiB$_2$ is around 5–10 wt%. The influence of sinter additives on density, grain size and mechanical properties is discussed in this section. As will be shown below, optimizing the amount of binder and sintering temperature is critical for obtaining higher densification and improved mechanical properties through a finer grain size.

2.20
Fig. 2.4 SEM Images of TiB\textsubscript{2} specimens hot pressed at 2073K (1800\degree C) for 1h containing a) 0 wt\% sinter additive, b) 2.5 wt\%Si\textsubscript{3}N\textsubscript{4} and c) 5 wt\%AlN, d) TEM image of TiB\textsubscript{2}+20wt\% MoSi\textsubscript{2}, hot pressed at 1973K (1700\degree C) [46,50,52].

The relative density of pure TiB\textsubscript{2} (90\%TD, average grain size ~7 \mu m) increased markedly to >99\%, and a fine microstructure (~3 \mu m) obtained by hot pressing on addition of 2.5 wt\% Si\textsubscript{3}N\textsubscript{4} [52]. Density decreased slightly and the grain size remained approximately constant with higher Si\textsubscript{3}N\textsubscript{4} additions. The hardness of TiB\textsubscript{2} also enhanced, as reported, owing to the higher density. Further increase in Si\textsubscript{3}N\textsubscript{4} content resulted in lower hardness, apparently because of the formation of secondary phases TiN and BN. This trend was also observed for the flexural
strength [52]. In contrast, the fracture toughness decreased steadily as the Si$_3$N$_4$ addition was increased. The high fracture toughness is believed to be related to the fine grain size and high porosity of the specimen. In particular, crack deflection along the grain boundaries and pinning of the propagating cracks by pores were believed to contribute to enhance the fracture toughness. However, it is also possible that the presence of interconnected pores can favor for the initiation of cracks.

Fig. 2.5 SEM Images revealing fracture surface morphology/fracture characteristics of bulk TiB$_2$ containing a) 0 wt.% sinter additive, b) 2.5 wt.% Si$_3$N$_4$, c) 5 wt.% AlN and d) TiB$_2$ with metallic additives[36,46,52]

A thin oxide rich layer is usually present on the surface of non oxide ceramic powders, in case of TiB$_2$, mainly TiO$_2$ and B$_2$O$_3$ were reported [19]. Presence of surface oxide layer is
detrimental for densification due to enhanced surface diffusivity [3]. In order to achieve higher
density strong reducing additives need to be used to remove surface oxides. Following few case
studies address the role of sinter additives on reducing the surface oxides of TiB₂ powders. Table
2.5 presents the reactions that play an important role on reduction of surface oxides of TiB₂
powders.

Park et al. [56] investigated the effect of hot pressing temperature (1773–2073K) on the
densification behavior of TiB₂+2.5wt% Si₃N₄. A considerable increase in density at 1773–
1873K (1500–1600°C) is attributed to the formation of silica (SiO₂) during hot pressing. Such
microstructural evolution suggests that to densify TiB₂ at low temperatures, the elimination of
the oxide layer is necessary and the formation of a liquid phase during sintering is of critical
importance.

The hardness and fracture toughness of the specimens, as a function of the hot pressing
temperature, are also reported in literature [46,56]. These results illustrate that TiB₂ with good
combination of mechanical properties can be densified at temperatures as low as 1873K
(1600°C) with the addition of a small amount of Si₃N₄ sinter additive [56]. AlN has been
reported to have a similar influence on the sinterability and mechanical properties of TiB₂ [46].
When a small amount of AlN (≤5 wt%) was added to TiB₂, the rutile phase (TiO₂), present on
the TiB₂ powder surface was eliminated by a reaction with AlN to form TiN and Al₂O₃,
according to the following reaction:

\[
3\text{TiO}_2 (s) + 4\text{AlN (s)} \rightarrow 3\text{TiN (s)} + 2\text{Al}_2\text{O}_3 (s) + 0.5\text{N}_2 (g)
\]  \hspace{1cm} (2.5)

\[
\text{TiB}_2 (s) + 1.5\text{N}_2 (g) \rightarrow \text{TiN (s)} + 2\text{BN (s)}
\]  \hspace{1cm} (2.6)

The elimination of TiO₂ markedly improved the sinterability and consequently the mechanical
properties of TiB₂. BN formation at grain triple pockets is confirmed in TEM analysis. It should
be pointed out that large AlN additions (>10 wt%) decreased the sinterability and mechanical properties, apparently owing to residual/unreacted Al$_2$O$_3$ or AlN [46].

The effect of ZrO$_2$ and SiC on sinterability and mechanical properties of titanium nitride, titanium carbonitride and titanium diboride was investigated by Torizuka et al. [54] The combined addition of ZrO$_2$ and SiC was found to be effective in improving the sinterability and mechanical properties of TiB$_2$. The density of TiB$_2$ and TiB$_2$+20%ZrO$_2$ after sintering at 1973K (1700°C) was 70%TD. Therefore, the addition of ZrO$_2$ alone had little effect in improving the sinterability of TiB$_2$. Although TiB$_2$ and TiB$_2$+20%ZrO$_2$ lacked sinterability, the addition of SiC was found to be effective in improving the density. For example, the density of TiB$_2$+19.5ZrO$_2$+2.5SiC was 97%TD. It was reported that TiO$_2$, existing on the surface of TiB$_2$ powder, reacts with SiC and formed TiC and SiO$_2$, according to the reaction [53]

$$\text{TiO}_2 + \text{SiC} \rightarrow \text{TiC} + \text{SiO}_2$$

(2.7)

In the case of sintered TiB$_2$+2.5wt% SiC compacts, the added SiC was transformed to SiO$_2$; ~3.5 vol%SiO$_2$ was reported to form as a result of this reaction. The residual amount of TiO$_2$ and B$_2$O$_3$ contributed to lowering the melting point of SiO$_2$ and increasing the liquid volume. The existence of amorphous SiO$_2$ in the microstructure suggests that the densification is enhanced by liquid phase sintering [53].

MoSi$_2$ additions can reduce the hot pressing temperature to 1973K (1700°C), for obtaining the near theoretical density [49,50]. However, no noticeable improvement in mechanical properties was found on addition of 10–20 wt% MoSi$_2$ (Table 2.4). This could be due to the presence of residual/unreacted TiSi$_2$ or MoSi$_2$. As mentioned above, the densification is enhanced by liquid phase sintering, promoted by the formation of a reaction product TiSi$_2$. In a follow-up study detailed transmission electron microscopy, in combination with
thermodynamic analysis, revealed that the most likely reaction pathways for the formation of TiSi$_2$ is [49,50]:

\[
\text{TiB}_2 + 3\text{O}_2 (g) + \text{MoSi}_2 \rightarrow \text{TiSi}_2 + \text{B}_2\text{O}_3 (g) + \text{MoO}_3 (g) \quad (2.8)
\]

\[
5\text{TiO}_2 + 5.714\text{MoSi}_2 \rightarrow 1.143\text{Mo}_5\text{Si}_3 + \text{Ti}_5\text{Si}_3 + 5\text{SiO}_2 \quad (2.9)
\]

Additionally, the maximum density achievable with pressureless sintering was found to be 90–91% with 25 wt% MoSi$_2$ at 2173K (1900°C) [49,50].

Table 2.5 presents the reaction of sinter additives on the role of reduction of surface oxides of TiB$_2$ powders

<table>
<thead>
<tr>
<th>Sinter additive</th>
<th>Mechanism</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$</td>
<td>3TiO$_2$ + Si$_3$N$_4$ $\rightarrow$ 3TiN + 3SiO$_2$ + 1/2N$_2$</td>
<td>56</td>
</tr>
<tr>
<td>TiSi$_2$</td>
<td>7TiO$_2$ + 8TiSi$_2$ $\rightarrow$ 3Ti$_5$Si$_3$ + 7SiO$_2$</td>
<td>89</td>
</tr>
<tr>
<td>AlN</td>
<td>3TiO$_2$ + 4AlN $\rightarrow$ 3TiN + 2Al$_2$O$_3$ + 0.5N$_2$</td>
<td>46</td>
</tr>
<tr>
<td>SiC</td>
<td>TiO$_2$ + SiC $\rightarrow$ TiC + SiO$_2$</td>
<td>53</td>
</tr>
<tr>
<td>MoSi$_2$</td>
<td>5TiO$_2$ + 5.714MoSi$_2$ $\rightarrow$ 1.143Mo$_5$Si$_3$ + Ti$_5$Si$_3$ + 5SiO$_2$</td>
<td>49,50</td>
</tr>
</tbody>
</table>

Besides hot pressing and pressureless sintering, limited investigations of advanced sintering techniques, such as microwave sintering, have been reported for densification of TiB$_2$ and composite with CrB$_2$ addition. Using a 2.45 GHz, 6 kW microwave furnace adapted for inert gas sintering, titanium diboride (TiB$_2$) was rapidly sintered to $>$90% theoretical density at sintering temperatures of 2173 – 2373K (1900–2100°C) with soaking time of 30 min or less [26]. A comparison with conventional sintering indicated that microwave sintering of TiB$_2$ + 3wt% CrB$_2$ occurred at 200K lower temperature and yielded material with significantly improved hardness, grain size and fracture toughness[26].

Thermal stability of monolithic TiB$_2$ is of critical importance and has been widely reported in literature. Oxidation resistance is one of the important properties for the high temperature structural materials to be critically considered. The phenomenological aspects of
2.26

TiB₂ oxidation, surface and subsurface oxide scale formation, and oxidation induced degradation are discussed in the following section.

2.4 High temperature oxidation behavior

High temperature oxidation is sometimes termed ‘dry corrosion’ or ‘scaling’. The oxidation mechanism depends on the temperature, partial pressure of oxygen, duration of exposure, porosity and composition, i.e. addition of sinter additives in the case of TiB₂. Kulpa et al. [57] reported that oxidation of TiB₂ powder in 0.05 ppm oxygen in argon, started below 673 K (400°C) and proceeded with the formation of TiBO₃. The reactions are:

At 673K and 0.05 ppm oxygen

$$4\text{TiB}_2 + 9\text{O}_2 \rightarrow 4\text{TiBO}_3 + 2\text{B}_2\text{O}_3 \quad (2.10)$$

At 673 – 1173 K (400 – 900°C) and 10 ppm O₂:

$$4\text{TiBO}_3 + \text{O}_2 \rightarrow 4\text{TiO}_2 + 2\text{B}_2\text{O}_3 \quad (2.11)$$

It has been experimentally observed [54] that both reactions occur concurrently in the range 673 – 1173 K (400–900°C). A comparison of oxidation resistance of various TiB₂ based materials reveals that monolithic TiB₂ without sinter additive has poor oxidation resistance, compared with TiB₂ containing Cr, Si or Al based sinter additives. These additives can potentially form protective glassy/amorphous Cr₂O₃, SiO₂ [54,58] or Al₂O₃ [46] or borosilicate glass layers [109] on the surface of composites that act as a barrier to diffusion of oxygen to the bulk.

Oxidation rate constant values at various temperatures for monolithic TiB₂ and TiB₂ based materials are compared with those of other structural ceramics in Table 2.6. Up to 1173K
At 900°C, all materials, except TiB₂ cermet and WC followed diffusion controlled kinetics, i.e. parabolic rate law

$$(\Delta w/s)^2 \approx K_P t$$  \hspace{1cm} (2.12)

where $K_P$ is the parabolic oxidation rate constant, $\Delta w$ is the weight gain (kg) in time $t$ (sec) and $s$ the surface area (m²) of the material exposed to oxidizing environment. In the range 1073 – 1273K (800–1000°C), the oxidation of TiB₂ cermet was governed by linear behavior

$$\Delta w/s = K_L t$$  \hspace{1cm} (2.13)

where $K_L$ is the linear oxidation rate constant. Similar linear oxidation behavior was also observed for TiB₂, without any sinter additive [59]. Comparing the data presented in Table 2.6, it can be seen that while the oxidation rate constants of TiB₂ based materials are comparable with those of other ceramics, they are not good enough for extended exposure in air at >1273K (1000°C).

Surface oxide morphologies on monolithic TiB₂ after oxidation under various test conditions are presented in Fig. 2.6[58,59,66]. After oxidation at 1123K (850°C) for 1h, the cracks are noticeable on oxide scale; however, on continued oxidation for 4h at 1123K (850°C), the oxide scale becomes severely fractured and non-protective (Fig. 2.6a and b). It was reported [59] that monolithic TiB₂ in bulk form starts to oxidize in air at around 673 – 773K (400–500°C) and the process was governed by a diffusion controlled mechanism up to 1173K (900°C). The overall oxidation reaction was as follows:

$$TiB_2 + 2.5O_2 \rightarrow TiO_2 + B_2O_3$$

(2.14)
Crystalline B$_2$O$_3$ and TiO$_2$ were identified on the surfaces of monolithic TiB$_2$ after oxidation at 973 and 1073K[59]. The grain morphology at 1073K is clearly revealed in Fig. 2.6c and intergranular cracking is commonly observed after oxidation in air for 10 h.

Table 2.6 Comparison of weight gain and oxidation rate constant of TiB$_2$ based materials with other high temperature ceramic materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Oxidation conditions</th>
<th>Weight gain, kg/m$^2$</th>
<th>Parabolic oxidation rate constant $K_p$, kg$^4$m$^{-4}$s$^{-2}$</th>
<th>Linear oxidation rate constant $K_L$, kg$^2$m$^{-2}$s$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB$_2$ + Fe + Ni + Al cermet</td>
<td>1273 K, 70h, air, Pellet</td>
<td>250</td>
<td>-</td>
<td>9.92x10$^{-7}$</td>
<td>60</td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>1373 K, 8h, air, pellet</td>
<td>60</td>
<td>1.2x10$^{-7}$</td>
<td>-</td>
<td>59</td>
</tr>
<tr>
<td>Al$_2$O$_3$ + 30vol% TiB$_2$</td>
<td>1073 K, 20h, air, pellet</td>
<td>05</td>
<td>6.94x10$^{-10}$</td>
<td>-</td>
<td>59</td>
</tr>
<tr>
<td>HfB$_2$ + 19SiC + 5.8Si$_3$N$_4$ (Vol%)</td>
<td>1773 K, 1h, air, pellet</td>
<td>16</td>
<td>6.91x10$^{-8}$</td>
<td>-</td>
<td>61</td>
</tr>
<tr>
<td>SiC + 3 wt% AlN</td>
<td>1673 K, 192h, air, pellet</td>
<td>19.9</td>
<td>3.67x10$^{-9}$</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>WC + 18wt%Co</td>
<td>973 K, 8h, air, pellet</td>
<td>280</td>
<td>-</td>
<td>1.36x10$^{-5}$</td>
<td>63</td>
</tr>
<tr>
<td>AlN + 10TiB$_2$ + 10TiSi$_2$(wt%)</td>
<td>1723 K, 3h, air, pellet</td>
<td>41</td>
<td>1.65x10$^{-7}$</td>
<td>-</td>
<td>64</td>
</tr>
<tr>
<td>MoSi$_2$</td>
<td>1473 K, 75h, air, pellet</td>
<td>01</td>
<td>2.29x10$^{-12}$</td>
<td>-</td>
<td>65</td>
</tr>
</tbody>
</table>

The large volume expansion (~7 vol%) that occurred during the oxidation of TiB$_2$ to TiO$_2$ subsequently caused cracking in the oxide layer, resulting in an increase in the active area for oxidation by allowing oxygen ingress through surface cracks in the oxide layer. Linear oxidation behavior was also noted for longer periods (8–13h) of oxidation at 1273 and 1373K[59]. It was also observed that the oxide scale was composed of highly textured TiO$_2$.  

2.28
crystals, as revealed in Fig. 2.6d. At high temperatures (>1273K) for longer periods, monolithic TiB₂ exhibits linear oxidation behavior owing to the increase in the active area for oxidation.

![SEM images](image)

Fig. 2.6 SEM images revealing nature of oxide scale as well as severity of cracking and oxide scale morphology on oxidized surface of monolithic TiB₂, after oxidation at 1123K for a) 1h and for b) 4h, at 1073K for c) 10h and at 1273K for d) 30h [58,59,66]

Koh et al. [67] investigated the oxidation behavior of hot pressed TiB₂+2.5wt% Si₃N₄ at temperatures between 1073 and 1473K for up to 10h in air. TiB₂+2.5wt% Si₃N₄ exhibited better oxidation resistance at high temperatures (<1273K) owing to protective oxide layer formation on the surface. At temperature <1273K, parabolic weight gains were recorded as a result of the formation of TiO₂ and B₂O₃ on the surface. The oxide layer was severely cracked during post
oxidation cooling owing to the thermal expansion mismatch between the oxide layer and the underlying bulk material (Fig. 2.7a). At temperatures >1273K, crystalline TiO₂ was identified along with volatile B₂O₃. In this case, the surface was covered with only thick crystalline TiO₂ layer. Fig. 2.7b shows the spheroidal crystalline phase of TiO₂ on the oxidized surface (1273K, air) of TiB₂+2.5wt%Si₃N₄.

Fig. 2.7 SEM images of severely cracked oxide film on oxidized surfaces of TiB₂+2.5 wt.% Si₃N₄, exposed to air for 10h at a) 1073K and b) 1273K[67]

In understanding the oxidation resistance property, it is also important to study the morphology of subsurface oxide scale. Fig. 2.8 illustrates the subsurface oxide scale formation of TiB₂ after oxidation at 1073 and 1273K [67]. At the lower temperature (1073K) a thick B₂O₃ top layer (~ 50 μm thickness), above a rather thin TiO₂ layer (~ 10 μm thickness) was formed (Fig. 2.8a). Owing to evaporation of B₂O₃ layer during oxidation treatment at T~1273K, only TiO₂ layer was found to be present at the subsurface region after oxidation at 1273K (1000°C). Also, to be noted is the formation of a rather thick TiO₂ layer of ~100 μm thickness at 1273K (1000°C) (Fig. 2.8b). Such a thick layer was observed to be heavily cracked, which implies the non-protectiveness of this oxide scale. However, on oxidation of TiB₂ with MoSi₂ additive at
1123K (850°C), the presence of glassy B₂O₃ could not have been detected by XRD, because of its non-crystallinity [66].

![Diagram of oxide scale formation](image)

Fig 2.8 Illustration of formation of subsurface oxide scale on fracture surface of TiB₂, oxidized in air at a) 1073K (800°C) for 10h and b) 1273K (1000°C) for 2h[67]

The oxidation behavior of hot pressed TiB₂+12.1 wt%B₄C+2.1 wt%Ni is similar to that of monolithic TiB₂ up to 1173K (900°C), the parabolic kinetics indicating a diffusion limited reaction[68]. At 1273K (1000°C), the best fit of the oxidation data was obtained with the Ginstling–Brounshtein equation[68]:

\[
(1-2/3 \alpha) - (1-\alpha)^{2/3} \approx kt
\]

(2.15)

where \(\alpha\approx\Delta w/s\), which considers a three-dimensional diffusion process associated with a decrease in the reaction surfaces, owing to the growth of a product layer around the reactants (spherical particles). As regards the kinetics, the formation of B₂O₃ was detected initially, because of the small radius of the boron atom [69,70]. Its diffusion to the surface is more rapid than the diffusion of the metal atom of the boride and this leads to the formation of large amounts of B₂O₃. The glassy nature of the B₂O₃ film provides additional diffusion barrier for atmospheric oxygen during oxidation.
While oxidation studies have been conducted on a few TiB₂ based materials, the attempts to improve oxidation resistance on an engineering scale are very limited. In an innovative approach, TiB₂ materials were coated with SiO₂ by exposing the specimens in a bed of SiC powder in a flowing H₂ containing 0.1%H₂O at 1723K (1450°C) for 2h [58]. The coating was found to be effective in suppressing the oxidation of TiB₂ at 1473K for 10h. The oxidation rate of coated TiB₂ (at 1473K for 10h) was decreased by about a factor of 10, because of the reduced oxygen transport through the coating and also because of the consumption of oxygen via reaction with Ti₂O₃ to form TiO₂ (Ti₂O₃ was formed during coating with SiO₂ by exposing the specimens in a bed of SiC powder in a flowing H₂ containing 0.1%H₂O at 1723K for 2h). When TiB₂ specimen without a coating was exposed at 1073K (800°C) for 10 h, the surface was covered with crystalline B₂O₃ layer, as shown in Fig. 2.8a. Beneath this B₂O₃ layer, crystalline TiO₂ (rutile) was formed. The TiO₂ layer was severely cracked owing to the thermal expansion mismatch between the oxide layer and underlying TiB₂, as mentioned earlier.

The oxidation of TiB₂ can exert a negative influence on the mechanical and physical properties and on the performance of components, made of TiB₂ ceramics. Therefore, one of the important criteria to define the oxidation resistance of a material is the strength retention property of the material after oxidation. Flexural strength of TiB₂ specimens without and with the SiO₂ coating (after treatment in a bed of SiC powder) was measured and the data were plotted in Fig. 2.9 [58]. Without the coating, the strength reduced remarkably after oxidation for 10h above 1273K (1000°C). It was reported [58] that the formation of a thick oxide layer and the presence of cracks were direct causes for this reduction in strength. When TiB₂ specimen was coated with SiO₂ layer, the strength decreased to a much lower extent. Besides, when the coated specimen was oxidized at 1073K (800°C) for 10 h, the reduction in strength was minimal.
Some of the important engineering applications of TiB$_2$ are presented in the next section.

Fig. 2.9 Flexural strength of TiB$_2$ specimens after oxidation in air for 10h at various temperatures A) without and B) with SiO$_2$ coating layer [58]

### 2.5 Applications of bulk TiB$_2$ materials

TiB$_2$ can be used as control rod and shielding material in nuclear reactors because it contains boron, which has the ability to absorb fast and slow neutrons without forming any long lived radionuclide. Absorption cross section of TiB$_2$ for fast neutrons can be enhanced by using compounds which are enriched in $^{10}$B isotope during the synthesis of TiB$_2$. Natural boron contains about 19% $^{10}$B and remaining is $^{11}$B [1-3]. TiB$_2$ is also a candidate material for high temperature structural applications like sharp leading edge of hypersonic re-entry vehicles,
cutting tools and molten metal crucibles. Apart from re-entry vehicles these materials are
candidates for other extreme environment encountered in metal processing industries.

Some of the structural ceramics are considered as potential materials for armor
applications owing to their low density, superior hardness and high compressive strength, which
enable erosion and ‘defeat of the projectiles’. The desirable characteristics of ceramics, in
particular, which are beneficial for the defeat of projectiles, include the combination of high
compressive yield strength or hardness, high tensile spall strength, high fracture toughness and
high poison’s ratio. In this context, the spall strength of a material can be defined. The stress or
strain, at which a further increase in stress or strain causes the material to deform inelastically is
Hugoniot Elastic Limit (HEL). Alternatively, the spall strength can be described as the stress,
where a material loses its cohesiveness under shock induced tension [72].

Over more than three decades, ballistic performance and dynamic behavior studies have
been performed on various ceramics (AlN, Al₂O₃, B₄C, SiC, TiB₂, WC and ZrO₂). As far as
armor applications are concerned, TiB₂ exhibits favorable properties, such as high impact
velocity for dwell/penetration transition and deformation induced hardening. Dandekar et al. [73]
assessed the strength properties of TiB₂ under plane shock wave loading in terms of its spall
threshold and the shear stress, when a shock compressive stress of 60 GPa was applied. The
break, i.e. cusp in the shock wave loading profile of TiB₂ at 4.5–7.0 GPa is of mechanical nature
and its effect is to decrease the spall threshold values at stresses above the cusp, but below the
accepted HEL value of 13–17 GPa. The spall strength of TiB₂ decreases with increasing impact
stress and becomes negligible at the HEL. Two phase ceramics of titanium diboride/alumina with
a range of phase assemblage and phase morphologies have been developed. For armor
applications, these materials exhibit a wide range of fracture toughness values, which are often higher than the constituent ceramic phase, in bulk monolithic form [74].

As far as other applications are concerned, TiB$_2$ is an attractive material for the aluminum industry, because of its wettability and low solubility in molten aluminum and its good electrical conductivity. The wettability of the TiB$_2$/carbon composite material increased as the TiB$_2$ content increased [75]. Pure hot pressed TiB$_2$ is completely wetted by aluminum with contact angle of zero in a cryolite melt at 1253K (980°C) [75].

TiB$_2$ is extensively used as evaporation boats for vapor coating of aluminum. Fang et al. [76] developed porous TiB$_2$ electrodes for the alkali metal thermoelectric converter (AMTEC). The electrical performance of these new electrodes was found to be superior to that of the other electrodes, such as TiN or Mo. Because of its chemical inertness, TiB$_2$ can be expected to show a long time stable operation. Although TiB$_2$ shows its potential in electrode applications for aluminum extraction, extensive study with various TiB$_2$ materials (sintered with different sinter aid) is however limited. It is expected that the good wetting property of TiB$_2$ by aluminum can be affected by the presence of sinter aid.

Other important applications of TiB$_2$, such as an electrical contact barrier for Si in the semiconductor industry, have also been proposed. However, boron diffusion from TiB$_2$ into underlying silicon was observed above 1273K (1000°C), which limits its wider application[76].

2.6 Literature on sintering aids used in the present study

In the present study, various silicides TiSi$_2$, CrSi$_2$, WSi$_2$, MoSi$_2$ and CrB$_2$ were used. Important physical and mechanical properties of these materials are listed in Table 2.7 [77-88].
Summary of these materials, which were used as sinter aids in TiB₂ or other materials are listed in Table 1.1 (Page no: 1.5).
### Table 2.7: Important physical and mechanical properties of various silicides and CrB₂ [77-88]

<table>
<thead>
<tr>
<th>Property</th>
<th>TiSi₂</th>
<th>CrSi₂</th>
<th>CrB₂</th>
<th>Ti₅Si₃</th>
<th>WSi₂</th>
<th>W₅Si₃</th>
<th>MoSi₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Orthorhombic</td>
<td>Hexagonal</td>
<td>Hexagonal</td>
<td>Hexagonal</td>
<td>Hexagonal/Tetragonal</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>4150</td>
<td>4600</td>
<td>5200</td>
<td>4320</td>
<td>9250</td>
<td>14520</td>
<td>6300</td>
</tr>
<tr>
<td>Melting point, K</td>
<td>1813</td>
<td>1750</td>
<td>2473</td>
<td>2403</td>
<td>2437</td>
<td>2597</td>
<td>2323</td>
</tr>
<tr>
<td>Hardness, GPa</td>
<td>8-10</td>
<td>11</td>
<td>11-20</td>
<td>9 - 10</td>
<td>13</td>
<td>7-10</td>
<td>13</td>
</tr>
<tr>
<td>Fracture toughness, MPa.m¹/²</td>
<td>2 - 3</td>
<td>-</td>
<td>-</td>
<td>2 - 4</td>
<td>3.7</td>
<td>-</td>
<td>2-2.5</td>
</tr>
<tr>
<td>Elastic modulus, GPA</td>
<td>250</td>
<td>354.6</td>
<td>210</td>
<td>150</td>
<td>468</td>
<td>312</td>
<td>384</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>-</td>
<td>-</td>
<td>600</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, x10⁶ K⁻¹</td>
<td>10.4</td>
<td>αₐ=9.2, αₖ=7.4</td>
<td>6-8</td>
<td>αₐ = 5.1, αₖ = 22.2</td>
<td>8.5</td>
<td>αₐ=5.0, αₖ=16.3</td>
<td>8.4</td>
</tr>
<tr>
<td>Thermal conductivity, W/m/K</td>
<td>-</td>
<td>10</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Electrical resistivity, μΩ·cm²</td>
<td>&lt;15/123</td>
<td>70 x 10³</td>
<td>30</td>
<td>55</td>
<td>20-80</td>
<td>50-60</td>
<td>21</td>
</tr>
<tr>
<td>Oxidation resistance, °C</td>
<td>-</td>
<td>1200</td>
<td>1000</td>
<td>-</td>
<td>1000</td>
<td>2000</td>
<td>1400</td>
</tr>
</tbody>
</table>

In view of the above concerns, present study focused on the densification of TiB₂ using different additives. Objective of the sinter additive is twofold, one is to lower the sintering temperature to obtain dense body without losing much of its inherent mechanical/physical properties and other is to improve the oxidation resistance by formation of a protective oxide layer.
One of the major focus areas of recent research is to solve the processing related problems pertaining to the requirement of extremely high sintering temperatures. In this regard, uses of metallic (Telle, 1994; Basu, 2006; Ferber, 1983; Kang, 2001; Kang, 1989; Einarsrud, 1997) as well as ceramic (Basu, 2006; Opila, 2004; Biswas, 2006; Torizuka, 1996; Torizuka, 1992; Murata, 1967; Bellosi, 2006; Monteverde, 2005) sinter-additives have been considered with good results [110-115]. However, incorporation of secondary phases is not devoid of serious drawbacks (Telle, 1994; Basu, 2006) [110-113]. Another important aspect is improving the fracture toughness of borides by microstructural tailoring and incorporation of various reinforcements. However, the important aspect that needs to be considered is that the composition and microstructural design should not have negative impacts over the high temperature performance [110-115].

To date, material researchers have focused on UHTCs (Borides and MAX phase composites) in terms of powders and bulk synthesis, microstructure characterization, physical and mechanical properties evaluation, oxidation and ablation testing, as well as the impact resistance. The powder synthesis is aimed at solving the problem of poor sinterability through modifying the particle morphology and reducing the grains to nano-size. The use of precursor method has also enabled the ability to prepare rod-like and plate-like grains with relative ease. Additionally, in order to enhance the sintering ability, selective sintering additives are necessary to produce low temperature liquid phases in the samples or lowering the grain boundary Gibbs free energy. Generally, the intrinsic strength and modulus of borides are high enough for use in the aircrafts. However, the shortcomings of these ceramics are their brittleness and low damage tolerance, which will have an adverse effect on their wider applications [115].
Nevertheless, the introduction of graphite, carbon fiber, or silicon carbide fiber has contributed to the effectiveness and reliability of borides and carbides. Recently, it has been considered that the microstructure design through texturing is very important to increase their physical and mechanical properties. For instance, Sakka and coworkers [115-117] at NIMS have recently succeeded in using the Strong Magnetic Field Alignment (SMFA) method to design textured microstructures of UHTCs (e.g., ZrB₂, HfB₂ and B₄C) with improved mechanical properties. The oxidation resistance and ablation resistance have also been significantly enhanced through combining silicon carbide and transition metal silicides. [115-117].

2.7 Summary

A significant research activity has been invested to use several sinter-additives and to optimize sintering conditions in order to improve sinterability and mechanical properties of monolithic TiB₂. In particular, an extensive and critical literature analysis has been reported on the role of metallic binders (e.g. Ni, Fe, Cu, Co, Ti) in the densification of TiB₂. More than 99% TD was achieved by liquid phase sintering. However, the presence of metallic binder is not desirable for high temperature structural applications. Therefore, studies related to the use of non-metallic sinter-additives have also been pursued. Several ceramic additives such as AlN, SiC, Si₃N₄, CrB₂, B₄C, TaC were used for attaining the densification of TiB₂ with better mechanical properties. As regards the fabrication routes, it has been noted that hot pressing and pressureless sintering with limited effort of using microwave sintering are employed to densify borides. Despite significant efforts in material development, bulk TiB₂ materials have not yet penetrated into commercial market in a big way. The bottleneck for such limitation is the processing difficulties and poor mechanical properties in terms of fracture toughness.
One of the promising applications of TiB$_2$ includes high temperature structural materials. As mentioned earlier, room temperature mechanical properties (hardness, toughness, strength, E-modulus) are measured for a large number of bulk TiB$_2$, sintered using various metallic/ non-metallic additives. Such property measurement at high temperature is lacking. Also, lacking is the measurements of thermal properties (thermal conductivity, thermal expansion coefficient) at high temperature as well as thermal shock resistance property. It can be noted that TiB$_2$ could be an excellent choice for applications requiring heat dissipation at high temperatures due to its high thermal conductivity. The oxidation resistance of TiB$_2$ is affected by temperature, partial pressure of oxygen, time of exposure, porosity and sintering additives. It is reported that oxidation resistance of TiB$_2$ could be improved by coating a protective amorphous SiO$_2$ layer on the surface of borides. Finally the recent trends in this field are also presented.

2.8 References


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2.44


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