RESEARCH REPORT

Ceramic, Composite, and Optical Materials Center – October 2017

Project: Synthesis of Sinterable Boride Powders and Ceramics
PI: Richard A. Haber, Rutgers University
Researcher: Azmi Mert Celik, Graduate Student

Long Range Goals:

- Synthesis of high purity, sinterable titanium diboride (TiB₂) powders and their utilization in composites in order to improve hardness and fracture toughness of brittle hard ceramics such as boron carbide (B₄C) and silicon carbide (SiC).
- Advancing a better knowledge of reaction kinetics and ultimate mechanical properties of bulk ceramics fabricated using synthesized boride powders.

1. Background

Advancing knowledge on synthesis, characterization, and development of transition metal diborides has a significant role due to their potential uses in refractory, cutting tools, crucibles, aerospace, and defense industries thanks to their excellent mechanical and physical properties such as high hardness, high elastic modulus, low density, good chemical and wear resistance, and high thermal and electrical conductivity values\(^1\)-\(^8\). Transition metal diborides, TMB₂ (TM= Ti, Zr, Hf), exhibit a basic hexagonal AlB₂ type crystal structure with P6/mmm space group as shown in Figure 1 below\(^1,2,5\).

Figure 1. (a) hexagonal unit cell of single crystal TiB₂: a=b=3.029 Å, c=3.229 Å, α=β=90°, γ=120°; 1 formula unit per cell, Ti at (0,0,0), B at (1/3,2/3,1/2) and (2/3,1/3,1/2)
and (b) illustration of hexagonal net of boron atoms: Ti are situated half c axis above and below boron network; c axis is perpendicular to paper.$^{1,5}$

Titanium diboride ($\text{TiB}_2$) is one of the hardest materials known. The melting temperature of $\text{TiB}_2$ is around 3225°C and thermal conductivity is 60-120 W/mK and electrical resistivity is $10-30 \times 10^{-6} \ \Omega\text{cm}$, and it has a Vickers hardness of 25-35 GPa at room temperature.$^9$ $\text{TiB}_2$ has a simple hexagonal crystal structure and it has a low theoretical density (4.52 g/cm$^3$)$^{10}$. Titanium diboride also have good corrosion, oxidation, and high thermal resistance values. Those properties make $\text{TiB}_2$ an important hard material that can be used as armor, crucibles, coating for cutting tools, and wear resistance parts.$^{11}$ Three different intermetallic phases are present in the Ti-B system: orthorhombic $\text{TiB}$, orthorhombic $\text{Ti}_3\text{B}_4$, and hexagonal $\text{TiB}_2$. The high congruent melting point of titanium diboride (3225°C) and its stability at high temperatures make it a potential candidate material for ultra-high temperature applications.$^{1,2,7}$ Figure 2 shows the binary equilibrium phase diagram of Ti-B system.$^{12}$

![Figure 2. The equilibrium phase diagram of binary Ti-B system$^{12}$.](image)
Another hard material, Zirconium diboride (ZrB$_2$) also has similar properties, such as high melting point (3000 ºC), high hardness (22 GPa), high thermal conductivity (60-140 W/mK), high electrical resistivity (9.2x10$^{-6}$ Ωcm), good corrosion resistance, and excellent chemical stability$^{13}$. There are some ways to produce TiB$_2$ and ZrB$_2$. Pure titanium metal and boron powder can be used as starting materials, but the high cost of this process makes it non-preferred at the commercial scale. P. Millet and T. Hwang have synthesized TiB$_2$ and ZrB$_2$ from titania, zirconia and amorphous boron powders at low temperature$^{11}$. Mono phase TiB$_2$ has been created by the self-propagating high-temperature synthesis (SHS) from elemental powder mixtures of Ti and B in argon atmosphere$^{14}$. TiB$_2$ can also be produced by using boric acid (B$_2$O$_3$), titanium dioxide and carbon powders. The reaction for this method$^{10}$:

$$\text{TiO}_2 (s) + 5\text{C} (s) + \text{B}_2\text{O}_3 (s) \rightarrow \text{TiB}_2 (s) + 5\text{CO} (g).$$

Whereas, one of the most efficient ways of producing TiB$_2$, or ZrB$_2$ is using titania, or zirconia, boron carbide (B$_4$C) and carbon powders. Borothermic reduction of titanium dioxide$^{10,15}$:

$$2\text{TiO}_2 (s) + \text{B}_4\text{C} (s) + 3\text{C} (s) \rightarrow 2\text{TiB}_2 (s) + 4\text{CO} (g).$$

Similarly, reaction for zirconium diboride$^{16}$:

$$2\text{ZrO}_2 (s) + \text{B}_4\text{C} (s) + 3\text{C} (s) \rightarrow 2\text{ZrB}_2 (s) + 4\text{CO} (g).$$

Hafnium diboride (HfB$_2$) is another Ultra High Temperature Ceramic (UHTC) thanks to its high melting point (3380 ºC), high thermal conductivity (51.6 W/mK), and good thermal shock resistance. Potential uses of HfB$_2$ are hypersonic flight material, atmospheric re-entry and rocket propulsion$^{17}$. It is produced by using the similar reaction with others, starting with hafnium dioxide, boron carbide, and carbon powders$^{17}$. Boron carbide determines the size of final TiB$_2$ product; therefore if initial B$_4$C is fine enough, phase-pure and submicron-sized TiB$_2$ can be synthesized$^{18}$.

2. Experimental
Titanium dioxide (Degussa P-25), boron carbide (H.C. Starck HD-20) and carbon (Carbon Lampblack) powders have been used as starting materials to synthesize TiB$_2$ in this work. Powder mixture was reacted at 1800 ºC in argon atmosphere for 30 min. The reaction is$^{10,15}$:

$$2\text{TiO}_2(s) + \text{B}_4\text{C}(s) + 3\text{C}(s) \rightarrow 2\text{TiB}_2(s) + 4\text{CO}(g).$$

ZrB$_2$ precursor was also prepared by using the same method. Similarly, the reaction for ZrB$_2$ is$^{16}$:

$$2\text{ZrO}_2(s) + \text{B}_4\text{C}(s) + 3\text{C}(s) \rightarrow 2\text{ZrB}_2(s) + 4\text{CO}(g).$$

The reaction for HfB$_2$ precursor$^{17}$:

$$2\text{HfO}_2(s) + \text{B}_4\text{C}(s) + 3\text{C}(s) \rightarrow 2\text{HfB}_2(s) + 4\text{CO}(g).$$

The different steps involved in the production and characterization of Titanium diboride samples are shown in the Figure 3.

**Figure 3.** Schematic of steps involved in synthesis and characterization of TiB$_2$ samples.

Synthesized TiB$_2$ powders were characterized using X-Ray Diffraction (XRD) with PANalytical X-ray Diffractometer Model PW3040/60, Cu Kα radiation. Powder morphology was observed using Scanning Electron Microscope (Zeiss Sigma Field
LECO TC600 oxygen/nitrogen analyzer was used to determine oxygen content of powders. TiB$_2$ powders were densified in various temperatures and dwelling times by using Spark Plasma Sintering (Thermal Technology SPS, 10-4) without the help of sintering additives. Heating rate and applied pressure were 150°C/min and 50 MPa, respectively.

![Figure 4. Schematic of Spark Plasma Sintering.](image)

The bulk densities were measured for spark plasma sintered disk samples using the Archimedes’ method. Elastic properties of bulk samples were calculated using ultrasound analysis. Disk samples were cut into small pieces and then polished using Buehler EcoMet250 Grinder/Polisher to investigate microstructure. Microstructure analysis on samples were conducted using Field Emission Scanning Electron Microscope (FEM-SEM).
(Zeiss Sigma FESEM with Oxford INCA PentaFETx3 EDS System – Model 8100), and EBSD were done on selected samples to determine crystal orientation of polycrystal grains. Optical imaging was performed using Keyence VHX-5000 Digital Microscope. Microhardness measurements were carried out using LECO M-400-G3 Hardness Tester with Vickers indenter tip. Cross-section ion milling experiments were performed with HITACHI IM4000Plus Ion Milling System.

3. Results and Discussion

TiB$_2$ precursor has been prepared and reacted at 1800°C for 30 min. XRD and SEM analyses were done on reacted TiB$_2$ powder. According to XRD analysis data that is shown below in Figure 5, TiB$_2$ formation was confirmed, and TiB$_2$ powders contain little amount of oxygen impurities.

![Figure 5. XRD pattern of reacted TiB$_2$ powder (1800 °C, 30 min).](image)

FESEM analysis was done on both H.C. Starck and synthesized powders to be able to compare powder morphologies. As can be seen in Figure 6, particle size of H.C.
Starck powders is much bigger and particles do not have uniform shape. On the other hand, synthesized powders are submicron-sized and they exhibit uniform hexagonal morphology. Using in-house synthesized powders, bulk ceramics with better properties can be produced.

Figure 6. FESEM micrographs of commercial (H.C.Starck Grade F) powders at (a) 10 KX, and (b) 25 KX, and in-house synthesized powders at (c) 10 KX, and (d) 25 KX.

Presence of TiO₂ and B₂O₃ oxide layers on powder surface is a common obstacle for densification of TiB₂ along with strong covalent bonding and low self-diffusion coefficient\(^\textit{19}\). LECO analysis confirmed that oxygen content of Rutgers-synthesized TiB₂ powders is about 0.50 wt% while it is above 1.50 wt% for H.C.Starck Grade F TiB₂ powders. Due to their coarser particle size and higher oxygen content, densification of H.C. Starck powders is difficult and limited without sintering additives\(^\textit{20}\).

Ultrasound analysis and was done on bulk ceramics to calculate Elastic modulus values. Relative densities were calculated using Archimedes’ method. The results were combined and shown in Figure 7 as a function of dwelling time during SPS. Density and
Elastic modulus of synthesized powders are significantly higher than those of H.C.Starck powders. As mentioned above, it can easily be seen that purity and particle size have major effect on densification of boride powders. Elastic properties of bulk ceramics are also improved remarkably when better quality, i.e. in-house synthesized powders used. Near fully-densified titanium diboride ceramics with $E = 541$ GPa, and $\rho = 99.43\% \rho_{th}$ were sintered from synthesized powders at 1750$^\circ$C and 45 minutes dwelling time, while H.C.Starck powders can only be densified up to $\rho = 95.39\% \rho_{th}$ with $E = 468$ GPa.

![Graph showing Elastic modulus and Relative Density values](image)

**Figure 7.** Elastic modulus (black symbols) and relative density (red symbols) values of bulk ceramics spark plasma sintered at 1750$^\circ$C at various dwelling times.

In this project, another commercial powder, Momentive HCT-F TiB$_2$ was also used for comparison. Figure 8 shows the comparison between relative density values of spark plasma sintered bulk ceramics produced using three different TiB$_2$ powders;

- Rutgers-synthesized,
- H.C.Starck Grade F,
- Momentive HCT-F.
Spark plasma sintering conditions were 1750ºC, 50 MPa, 150ºC/min, three different holding times: 5, 15, and 45 minutes.

Figure 8. Relative density values of bulk ceramics spark plasma sintered at 1750ºC at various dwelling times.

Figure 9 plots the Young’s modulus values of same bulk samples. It is obvious that better density results in better elastic properties. Even though, there is a dramatic increase in elastic modulus of commercial powders from 5 minutes to 45 minutes, only 85% of theoretical elastic modulus can be achieved. On the other hand, in-house synthesized powders not only can be densified to near fully relative density values, but also they exhibit very high relative elastic modulus.
Figure 9. Young’s modulus values of bulk ceramics spark plasma sintered at 1750ºC at various dwelling times.

FESEM micrographs of densified TiB$_2$ ceramics at 2.5 KX magnification were shown in Figure 10. Ceramics sintered using H.C. Starck powders are more porous and their particle size is bigger as expected. Figure 10a and 10b exhibit microstructure of ceramics sintered using H.C. Starck powders for 5 minutes and 45 minutes dwelling times, respectively. Micrographs of ceramics produced from in-house synthesized TiB$_2$ powders are shown in Figure 10c and 10d with same dwelling times, 5 minutes (Fig. 10c) and 45 minutes (Fig. 10d). It is clearly seen that synthesized powders can be densified fully while ceramics manufactured using H.C.Starck powders have ~5% porosity. The effect of porosity and grain growth were mentioned and shown in Figure 7.
FESEM micrographs of bulk ceramics made from commercial (H.C. Starck) powders sintered at 1750°C for (a) 5 min, and (b) 45 min, and from in-house synthesized powders for (c) 5 min, and (d) 45 min.

FESEM micrographs of in-house synthesized and densified TiB$_2$ ceramics (1750°C, 45 min) were demonstrated in Figure 11. Images are taken at four different magnification values.

EBSD analyses were done on the same sample to determine the variation in crystal orientation and investigate a possible preferred orientation. Figure 12 proves that crystals has grown and distributed randomly. Random distribution of crystals provides good properties throughout the TiB$_2$ ceramics.
**Figure 1.** FESEM micrographs of dense TiB$_2$ ceramics spark plasma sintered at 1750°C and 45 minutes using in-house synthesized TiB$_2$ powders at various magnification values: (a) 1 KX, (b) 5 KX, (c) 10 KX, and (d) 25 KX.

**Figure 2.** EBSD crystal orientation maps of dense TiB$_2$ ceramics SPS’d at 1750°C and 45 minutes using in-house synthesized TiB$_2$ powders at various magnification values: (a) 2.5 KX, and (b) 5 KX.
Hardness values along with relative densities and elastic moduli for various samples (SPS’d at 1750°C, 15min, 30min and 45min using in-house synthesized powder) are shown in Table 1. Denser samples exhibit better hardness as expected.

**Table 1.** Vickers hardness values at 200g load

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% ρ&lt;sub&gt;th&lt;/sub&gt;</th>
<th>E (GPa)</th>
<th>H&lt;sub&gt;v&lt;/sub&gt; (GPa) [200g load]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RU15</td>
<td>97.74</td>
<td>504</td>
<td>26.2</td>
</tr>
<tr>
<td>RU30</td>
<td>98.32</td>
<td>522</td>
<td>27.9</td>
</tr>
<tr>
<td>RU45</td>
<td>99.43</td>
<td>541</td>
<td>29.3</td>
</tr>
</tbody>
</table>

However, higher porosity of the samples and higher loads caused catastrophic damage to indented samples, thus microhardness measurements were not applicable to some of RU (bulk samples made from in-house synthesized powders) and SF (densified H.C. Starck Grade F) samples. FESEM micrographs in Figure 13 show the above-mentioned damage in samples during hardness tests. Intergranular fracture is distinguishable in samples where the indentation was applied.
Figure 13. FESEM micrographs of the damage on RU45 (SPS’d at 1750°C and 45 minutes using in-house synthesized TiB$_2$ powders) caused by 1 kg micro-indentation load at various magnification values: (a) 2.5 KX, and (b) 5 KX.

To understand the reasons behind the damage, cross-section ion milling was performed on bulk samples. Figure 14 shows the optical images of cross-sectioned samples taken with Keyence VHX-5000 Digital Microscope. Detailed microstructure of cross-sectioned areas are shown in Figure 15.
Figure 14. (a) 20X optical image of cross-sectioned SPS disk sample. (b) 3D optical image of cross-section area. (c) depth measurements on cross-section profile.
Figure 15. FESEM micrographs of cross-sectioned (RU15CS) sample at 500X and 5KX magnifications.

The top image in Figure 15 is a combination of 15 different FESEM images taken at 500X and (a), (b), (c), (d), (e) and (f) are detailed microstructures taken at 5KX magnification. It is obvious that the surface of the sample has more porosity than the areas close to the center. Previous micro-indentation experiments were done on top surface (around area a) and indenter tip caused intergranular fracture on samples
mentioned above. Nano-indentation is utilized to measure hardness of monolithic TiB$_2$ samples without causing damage. Results will be reported in the next CCOMC update.

The precursor for B$_4$C-TiB$_2$ composite powders was also prepared using the borothermic reduction reaction of titanium dioxide with excess amounts of B$_4$C shown below:

$$2\text{TiO}_2(s) + (1+x) \text{B}_4\text{C}(s) + 3\text{C}(s) \rightarrow 2\text{TiB}_2(s) + x \text{B}_4\text{C}(s) + 4\text{CO(g)}.$$ 

Possible results after running this precursor are shown in Figure 16. Considering the particle size of B$_4$C is much bigger than that of TiO$_2$, TiB$_2$ coating on B$_4$C is more favorable than B$_4$C coating on TiB$_2$. Phase separation can also occur depending on the mixing homogeneity.

![Figure 16. Possible reaction scenarios in TiB$_2$ precursors with excess B$_4$C](image)

Instead of regular P25, Evonik W740X (40 wt% P25 TiO$_2$ and 60 wt% water) suspension was used for this experiment. Titania suspension was mixed with H.C. Starck HD20 B$_4$C and C lampblack powders and reacted at 1800ºC for 30 minutes. Precursor was calculated to have 10 wt% TiB$_2$ – 90 wt% B$_4$C mixture after synthesis.

![Figure 17. Schematic of experimental steps in synthesizing B$_4$C-TiB$_2$ composite powders.](image)

XRD patterns for precursor and reacted powders are shown in Fig. 18 (a) and (b). Results show that TiB$_2$ particles were formed within B$_4$C. Figure 19 shows the
morphology of powders before and after synthesis. Trace amounts of unreacted carbon remained on powders. Sintering experiments were not yet done using these powders.

Figure 18. X-Ray Diffraction patterns of B₄C-TiB₂ (a) precursor, (b) reacted composite powders
In-house synthesized TiB$_2$ powders were also utilized in fabrication of B$_4$C-TiB$_2$ composite ceramics. Commercial B$_4$C powders (H.C. Starck Grade HD20) and Rutgers-synthesized TiB$_2$ (synthesis conditions: 1800°C, 30 min under flowing Ar) were ball milled in ethanol using SiC balls for 24 hours and the mixtures were then spark plasma sintered at 1950°C for 5, 20 and 45 mins in Argon atmosphere under 50 MPa pressure. Table 2 shows density values of B$_4$C-TiB$_2$ composites, all samples exhibit good densification, and short dwelling time such as 5 minutes is sufficient to achieve fully dense bulk samples.

Table 2. Density values of various compositions of B$_4$C-TiB$_2$ composites

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Composition (wt%)</th>
<th>Sintering conditions (°C, MPa, min)</th>
<th>Bulk density, $\rho$ (g/cm$^3$)</th>
<th>Relative density, $\rho_{rel}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5TB95BC-5</td>
<td>95 5</td>
<td>1950, 50, 5</td>
<td>2.55</td>
<td>99.1 ± 0.10</td>
</tr>
<tr>
<td>5TB95BC-20</td>
<td>95 5</td>
<td>1950, 50, 20</td>
<td>2.54</td>
<td>98.5 ± 0.15</td>
</tr>
<tr>
<td>10TB90BC-5</td>
<td>90 10</td>
<td>1950, 50, 5</td>
<td>2.60</td>
<td>98.7 ± 0.15</td>
</tr>
<tr>
<td>10TB90BC-20</td>
<td>90 10</td>
<td>1950, 50, 20</td>
<td>2.59</td>
<td>98.4 ± 0.38</td>
</tr>
<tr>
<td>10TB90BC-45</td>
<td>90 10</td>
<td>1950, 50, 45</td>
<td>2.61</td>
<td>99.1 ± 0.09</td>
</tr>
<tr>
<td>15TB85BC-5</td>
<td>85 15</td>
<td>1950, 50, 5</td>
<td>2.68</td>
<td>99.3 ± 0.32</td>
</tr>
<tr>
<td>15TB85BC-20</td>
<td>85 15</td>
<td>1950, 50, 20</td>
<td>2.67</td>
<td>99.1 ± 0.04</td>
</tr>
</tbody>
</table>

Figure 19. FESEM micrographs of B$_4$C-TiB$_2$ (a) precursor, (b) reacted composite powders
Microstructures of monolithic HD20 B$_4$C and HD20 B$_4$C-10 wt% TiB$_2$ (5 mins) composites are shown below in Fig. 20. Fully dense composites with homogeneous microstructure were sintered via SPS.

![Microstructures](image1.jpg)

**Figure 20.** Microstructures of (a),(b) monolithic HD20, (c),(d) HD20-10 wt% TiB$_2$ composite

Figure 21 demonstrates optical microscopy images of 1 kg load Vickers indents on monolithic HD20 B$_4$C and HD20-10 wt% TiB$_2$ composite. Figure 22 shows hardness values of monolithic HD20 B$_4$C and HD20-10 wt% TiB$_2$ composite, HCl washing of starting B$_4$C powders and ball milling the mixture in ethanol media further increased the hardness of the composite. Hardness was increased from 29.9 ± 2.3 GPa to 32.9 ± 1.5 GPa with the addition of 10wt% TiB$_2$ into B$_4$C, it corresponds to a 10 percent improvement over monolithic B$_4$C. Comparison of crack lengths shows that TiB$_2$ addition also improves the fracture toughness of B$_4$C ceramics.
Figure 21. Optical microscopy images of 1 kg Vickers indents on (a) monolithic HD20 B₄C, (b) HD20-10 wt% TiB₂ composite

Figure 22. Vickers hardness values of monolithic HD20 B₄C and HD20-10 wt% TiB₂ composites
4. Future Work

- Hot pressing will be performed as the feasibility study to commercial scale.
- Nano-indentation measurement is utilized to determine hardness of monolithic TiB$_2$ samples. Hardness results will be discussed in the next CCOMC update.
- Detailed FESEM analysis will be done to examine the effects of grain growth during sintering on mechanical properties of monolithic TiB$_2$ ceramics.
- Various synthesis conditions, such as temperature and time will be examined.
- Hardness measurements of B$_4$C-5wt% TiB$_2$ and B$_4$C-15wt% TiB$_2$ samples will be performed.
- Nano-indentation will be used to measure hardness values of B$_4$C and TiB$_2$ in B$_4$C-TiB$_2$ composites.
- Fracture toughness measurements will be done to confirm improvement in K$_{IC}$ of B$_4$C-TiB$_2$ composites.
- Knowledge on effects of various SPS conditions, such as sintering temperature, applied pressure, dwelling time, and heating rate will be acquired.

5. References

5. Munro, R. G. *Journal of Research of the National Institute of Standards and Technology* 2000, 105, 709.


