Study of the TiO$_2$–H$_2$O–B$_2$O$_3$ Ternary System at 7.7 GPa and High Temperatures

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The TiO$_2$–H$_2$O–B$_2$O$_3$ ternary system was studied at high pressure (7.7 GPa) and high temperatures, and a phase diagram is proposed. Depending on the initial stoichiometric conditions, Raman spectral analysis identified rutile, TiO$_2$-II, H$_2$BO$_3$, HBO$_2$, and B$_2$O$_3$ as the crystalline stable phases, and an amorphous phase constituted by B, Ti, and O. The eutectic point of this system was identified to be at around 400 °C. Two piercing points were located at around 600 and 1100 °C, identified by the stabilization of HBO$_2$ rather than H$_3$BO$_3$, B$_2$O$_3$, and Ti$_2$O$_3$ rather than HBO$_2$, respectively. This study shows that TiB$_2$ sintering at high pressure can be compromised by the presence of oxide-bearing phases that decrease the eutectic point of the system. This phenomenon can produce a liquid that works as a medium for transporting material, producing grain growth, which compromises the boride properties.

Introduction

Borides have been studied extensively due to their potential applications in electrodes, cutting tools, armor materials, and as reinforcing phase in metal-matrix composites. They have exceptional thermal stability, hardness, and mechanical properties under practical applications. However, the presence of oxygen-bearing phases such as boron oxide (B$_2$O$_3$), boric acid (H$_3$BO$_3$), and metaboric acid (HBO$_2$) at the sintering process strongly influences the tribological properties of the borides. Several studies have shown that the presence of these phases causes the anomalous increasing of the boride grain, compromising the density and hardness of the ceramic. The plausible mechanism responsible for such effect is not completely understood. Therefore, the study of the behavior of boron-, oxygen-bearing phases at the sintering conditions is very important.

Until recently, the majority of the experimental studies on the pressure–temperature stability relation of oxygen-, boron-bearing minerals, under hydrous or anhydrous conditions, were developed especially with a geological interest through phase diagram studies. Kracek developed the first studies in a binary system near ambient pressure, in which the end members were B$_2$O$_3$ and H$_2$O. He observed that at this pressure the melting point of B$_2$O$_3$ is around 450 °C, and there is full fluid miscibility between the components H$_2$O and B$_2$O$_3$. In this system, the solid binary phases are H$_3$BO$_3$ (sassolite) and HBO$_2$ (metaborite) that can occur as cubic (HBO$_2$-I), monoclinic (HBO$_2$-II), or orthorhombic (HBO$_2$-III). At 1 atm, cubic, monoclinic, and orthorhombic metaboric acid melt at 236, 200, and 176 °C, respectively. H$_2$BO$_3$ melts incongruently to cubic metaboric acid at 169 °C at 1 atm. Pereira et al. observed that when submitted to high pressure, H$_2$BO$_3$ breaks down to cubic metaboric acid and water. The addition of other materials, such as SiO$_2$ and Al$_2$O$_3$ to the B–O–H system was made by Rockett and Foster, Pichavant, Gielisse and Foster. At 1 atm, B$_2$O$_3$ is completely miscible in the system B$_2$O$_3$–SiO$_2$ and B$_2$O$_3$–Al$_2$O$_3$ above the liquidus. However, a tendency to B-rich-liquid versus B-poor-liquid immiscibility can be observed. It occurs mainly by the presence of metastable liquid–liquid immiscibility reported in the B$_2$O$_3$–SiO$_2$ and B$_2$O$_3$–M$_2$O$_3$ (M = alkali metal) binary systems, and in the SiO$_2$–B$_2$O$_3$–(Na$_2$O,K$_2$O) ternary system. Stable liquid–liquid immiscibility is known to occur in the ternary systems SiO$_2$–B$_2$O$_3$–MO (M = Ca, Ba). In all these systems, except the SiO$_2$–B$_2$O$_3$–H$_2$O, there is

always a hydrous and/or an anhydrous ternary phase. Among them, anhydrous Al–O–B-bearing phases have shown many applications in material science.

Contrasting to this background, few studies have been made in the B–Ti–O system. Finch et al.\(^1\) suggest that oxygen content is one of the main limitations to obtain high densification during hot pressing sintering of TiB\(_2\). For powders of TiB\(_2\) containing more than 1 wt % oxygen, only 75 to 90% of the theoretical density is reached after the sintering process by vacuum hot-pressing (1400 to 1700 °C). Baik and Becher\(^2\) made several densification studies in this ceramic material. They noticed that under hot-pressing densification process, the presence of oxygen, as the B\(_2\)O\(_3\) phase, makes the TiB\(_2\) grain to grow fast by an evaporation–condensation kinetics process, limiting the maximum attainable densification. They suggest that samples with 1.7 wt % oxygen can reach only 85% of the theoretical density, while samples with 0.7 wt % reach around 95%. Under pressureless sintering, they suggest that B\(_2\)O\(_3\) is evaporated due to its low vapor pressure, and oxygen is only present as TiO\(_2\). In this case, the samples can reach the maximum of the theoretical density; however, the fast grain growth still occurs and is caused by a surface diffusivity process. Pavlikov et al.\(^3\) worked at 1 atm in the B\(_2\)O\(_3–\)TiO\(_2\) system and identified an eutectic point between 400 and 450 °C. They suggested a possible liquid–liquid immiscibility close to the liquidus.

As a consequence of the high difficulty to obtain well-sintered boride compacts, alternative sintering techniques have been proposed in the literature.\(^4\) Among these techniques, high-pressure sintering can be a very interesting option. This technique promotes an improvement of the powder compaction and allows the use of lower temperatures and shorter sintering times. This possibility is very important to control grain growth and its deleterious effects, mainly over the mechanical properties of the sintered body.

In this way, the study of the phase diagram under high pressure and high temperature of the phases usually observed in the boride powder is of great interest.

As far as we know, there are no published studies of the system TiO\(_2–\)H\(_2\)O–B\(_2\)O\(_3\) under high pressure and high temperature. We believe the stable phases present in this system play a decisive role in the sintering mechanism of TiB\(_2\). In this work, we investigate this system at 7.7 GPa to study the possible stabilization of a ternary phase and the miscibility of those components and liquids, and we propose a schematic phase diagram for this system.

**Experimental Methodology**

**Starting Material.** The starting materials used were a stoichiometric mixture of crystalline H\(_3\)BO\(_3\) + crystalline HBO\(_2\) (II) + vitreous B\(_2\)O\(_3\) + H\(_2\)O and TiO\(_2\) (anatase + rutile). The Raman spectra of these phases are shown in Figure 1. Crystalline HBO\(_2\) (II) was obtained by partial dehydration of H\(_3\)BO\(_3\) (P. A.) at 1 atm and 120 °C for one week. Vitreous B\(_2\)O\(_3\) was obtained by total dehydration of H\(_3\)BO\(_3\) at 1000 °C for 3 days. After obtaining these two components, each one was mixed and finely ground with TiO\(_2\) in a stoichiometric proportion. HBO\(_2\) + TiO\(_2\) was heated for 2 days at 1 atm and 120 °C, and vitreous B\(_2\)O\(_3\) + TiO\(_2\) was heated for 1 day at 1 atm and 1000 °C. Mixtures with H\(_3\)BO\(_3\) and TiO\(_2\) were also prepared. All mixtures were kept in the oven at 100 °C before the experiment. At this temperature, H\(_3\)BO\(_3\) does not degrade, and the addition of water in the mixtures is avoided. As HBO\(_2\) and B\(_2\)O\(_3\) easily absorb water and transform to H\(_3\)BO\(_3\), Raman spectroscopy was used to estimate the phases present in the mixtures before the experiments. However, even taking maximum care, B\(_2\)O\(_3\) invariably reacts with water, introducing uncertainties in the B\(_2\)O\(_3–\)H\(_2\)O ratios. The compositions of all starting materials are listed in Table 1 in terms of the molar fraction of end members: B\(_2\)O\(_3\), TiO\(_2\), and H\(_2\)O. To make the composition #1 of the starting material, in which an H\(_2\)O-oversaturated condition is necessary, additional water was stoichiometrically added by a microsyringe.

**High-Pressure Processing.** All the experiments were performed in a high-pressure toroidal-type chamber, and a detailed description of this high-pressure method is given elsewhere.\(^5\)\(^6\) The temperature was controlled to ± 3 °C and was measured with a Chromel-Alumel type K thermocouple encapsulated in an Al\(_2\)O\(_3\) sleeve. The pressure cells consisted of a graphite heater (height of 9.2 mm, diameter of 7.0 mm, and wall thickness of 1.5 mm), and two small disks of fired pyrophyllite (diameter of 4.0 mm, and height of 1.5 mm). A capsule with the sample was placed between these two disks. All experiments up to 800 °C were conducted in a hBN capsule (3.0 mm internal diameter). For experiments at higher temp-

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temperatures, graphite capsules (2.0 mm internal diameter) were used, placed inside a hBN ring of 3.0 mm internal diameter. The hBN acts as a nearly hydrostatic pressure-transmitting medium and, at lower temperature experiments (up to 800 °C), it behaves as an inert material.

In a typical experiment, pressure was initially applied to the sample cell to a particular value at room temperature. After pressure stabilization, the sample was heated to the final temperature. Quenching was performed by turning off the heating power, and, after 5 to 10 min, the pressure was released. The pressure calibration was performed by the "fixed points" technique, using Bi and Yb, which allowed the calibration of the pressure in the following three fixed points: Bi with temperatures, graphite capsules (2.0 mm internal diameter) were used, placed inside a hBN ring of 3.0 mm internal diameter. The hBN acts as a nearly hydrostatic pressure-transmitting medium and, at lower temperature experiments (up to 800 °C), it behaves as an inert material.

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The experimental results are summarized in Table 2. All the phases were identified by X-ray diffraction and confirmed by micro-Raman spectroscopy.

**Table 2. Summary of the Experimental Results**

<table>
<thead>
<tr>
<th>sample</th>
<th>starting material</th>
<th>temp (°C)</th>
<th>time (min)</th>
<th>phases observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTO-1</td>
<td>#1</td>
<td>RT</td>
<td>90</td>
<td>R + A + HBO3</td>
</tr>
<tr>
<td>BTO-2</td>
<td>#1</td>
<td>250</td>
<td>90</td>
<td>R + A + HBO3</td>
</tr>
<tr>
<td>BTO-3</td>
<td>#1</td>
<td>350</td>
<td>90</td>
<td>TiO2-II + HBO3</td>
</tr>
<tr>
<td>BTO-4</td>
<td>#1</td>
<td>450</td>
<td>90</td>
<td>TiO2-II + HBO3 + Gl</td>
</tr>
<tr>
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<td>#1</td>
<td>600</td>
<td>60</td>
<td>TiO2-II + HBO3 + Gl</td>
</tr>
<tr>
<td>BTO-6</td>
<td>#1</td>
<td>750</td>
<td>60</td>
<td>TiO2-II + HBO2 + Gl</td>
</tr>
<tr>
<td>BTO-7</td>
<td>#1</td>
<td>850</td>
<td>60</td>
<td>R + HBO2 + Gl</td>
</tr>
<tr>
<td>BTO-8</td>
<td>#1</td>
<td>900</td>
<td>60</td>
<td>R + Gl</td>
</tr>
<tr>
<td>BTO-12</td>
<td>#2</td>
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<td>60</td>
<td>TiO2-II + HBO2 + Gl</td>
</tr>
<tr>
<td>BTO-13</td>
<td>#2</td>
<td>750</td>
<td>60</td>
<td>TiO2-II + HBO2 + Gl</td>
</tr>
<tr>
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<td>60</td>
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<td>60</td>
<td>TiO2-II + HBO2 + Gl</td>
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<tr>
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<td>#3</td>
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<td>60</td>
<td>R + HBO2 + Gl</td>
</tr>
<tr>
<td>BTO-22</td>
<td>#3</td>
<td>950</td>
<td>60</td>
<td>R + Gl</td>
</tr>
<tr>
<td>BTO-23</td>
<td>#4</td>
<td>800</td>
<td>100</td>
<td>R + HBO2 + Gl</td>
</tr>
<tr>
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<td>#4</td>
<td>900</td>
<td>100</td>
<td>R + HBO2 + Gl</td>
</tr>
<tr>
<td>BTO-25</td>
<td>#4</td>
<td>1000</td>
<td>100</td>
<td>R + B2O3 (?) + Gl</td>
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<td>BTO-26</td>
<td>#4</td>
<td>1200</td>
<td>100</td>
<td>R + Gl</td>
</tr>
</tbody>
</table>

a R, titanium dioxide, rutile form; b A, titanium dioxide, anatase form; c Gl, glass phase.

The experimental results are summarized in Table 2. All the phases were identified by X-ray diffraction and confirmed by micro-Raman spectroscopy.

**Experimental Results**

The experimental results are summarized in Table 2. All the phases were identified by X-ray diffraction and confirmed by micro-Raman spectroscopy.

The composition #1 corresponds to H$_3$BO$_3$ + TiO$_2$ (I-I), in which 10 mol% of water was added. Raman spectrum of this sample, after the experiment at 7.7 GPa and at room temperature, is displayed in Figure 2, and indicates the presence of boric acid, anatase, and rutile. H$_3$BO$_3$ is characterized by the peak at 880 cm$^{-1}$, that corresponds to the v$_{13}$ BO$_3$ breathing mode. In the starting material, anatase is characterized by sharp peaks at 393, 515, and 631 cm$^{-1}$, while rutile is characterized by peaks at 447 and 612 cm$^{-1}$. However, after processing at room temperature, 7.7 GPa, for 40 min, anatase peaks became broader. The rutile peak at 447 cm$^{-1}$ became broader, and the peak at 612 cm$^{-1}$ shifted to 609 cm$^{-1}$. Similar results are reported by Mammone et al., who suggest that the band at 447 cm$^{-1}$ is actually an envelope containing bands from TiO$_2$-II, a high-pressure polymorph of TiO$_2$ with the α-PbO$_2$ structure. The Raman spectra remained practically the same for processing at temperatures up to 350 °C, except for the appearance of a sharp peak at 362 cm$^{-1}$. From this temperature up to 800 °C, TiO$_2$-II is the stable TiO$_2$ phase, and it is characterized by the Raman peaks at 356, 426, 442, 531, 572, 608, and 820 cm$^{-1}$. The peak at 880 cm$^{-1}$ characteristic of the H$_3$BO$_3$ decreases up to 600 °C, and at higher temperatures, it is replaced by a sharp peak around 780 cm$^{-1}$, characteristic of the HBO$_2$-II. This peak remains up to 880 °C, when it finally disappears. Experiments conducted above 800 °C, showed...
that TiO$_2$-II is replaced by rutile, that is present up to very high temperatures (around 1600 °C). Moreover, above 400 °C, Raman analysis indicated the presence of a very fluorescent material, not observed at lower temperatures. The amount of this material increases at higher temperatures. X-ray diffraction for these samples did not show any other phases besides the ones already identified by micro-Raman analyses, which indicates that this phase could be amorphous. Besides, the texture observed by light optical microscopy and SEM show crystalline grains involved by this phase. We believe that this material corresponds to a quenched liquid, which is denoted as glass in Table 2, produced by the partial melting of the bulk sample. Although we could not analyze precisely the composition of this amorphous phase, EDS analyses show that it is composed of Ti, B, and O, and the proportion of these elements changes with the temperature.

The compositions #2 and #3 correspond to H$_3$BO$_3$ + TiO$_2$ (1:1), and HBO$_2$ + TiO$_2$ (1:1), respectively. Experiments in both compositions were made at temperatures higher than 600 °C, and the results are similar as shown in Table 2. The Raman spectra in Figure 3 showed peaks characteristic of TiO$_2$-II at low temperatures, that were replaced by peaks of rutile at 800 °C for both compositions. At low temperatures, HBO$_2$-II is the stable phase; however, it disappears at temperatures around 850 °C, for composition #2, and around 900 °C, for composition #3.

The composition #4 corresponds to B$_2$O$_3$ + TiO$_2$ (1:1), in which 10 mol % of water was added with a microsyringe. This composition is assumed to be lower than that necessary to transform all B$_2$O$_3$ in H$_3$BO$_3$. Because of the previous heating at 1000 °C, all TiO$_2$ is present as rutile in the starting material. The Raman spectra of the samples processed at temperatures from 800 to 1000 °C are displayed in Figure 4, showing rutile phases a very sharp peak at 783 cm$^{-1}$, with a shoulder at 770 cm$^{-1}$, which is characteristic of HBO$_2$-II. At temperatures higher than 1000 °C, the characteristic peaks of HBO$_2$-II decrease, and a peak at 725 cm$^{-1}$ appears. We believe that this indicates the onset of B$_2$O$_3$ crystallization.

In all experiments with compositions #1, #2, #3, and #4, the amorphous material interpreted as glass was present. Rutile is always the stable phase above 800 °C; however, it differs from the starting material by the shift of the peak from 612 to 607 cm$^{-1}$. These results are in agreement with Mammone et al. that suggested an irreversible transformation of anatase and rutile to TiO$_2$-II around 7.0 GPa. Moreover, our experiments indicate that TiO$_2$-II transforms to rutile at high-pressure (7.7 GPa) above 800 °C.

Discussion

In the P-T range considered in this work, B$_2$O$_3$ is probably far below its critical point, and this conclusion comes from its observed boiling point at 1 atm, around 2400 °C. This observation and the data from this work enable the summarization of the experimental results in Table 2. The phases recognized as primary phases are rutile, anatase, and TiO$_2$-II, as TiO$_2$ phases; boric acid (sassolite) and orthorhombic metaboric acid, representing the hydrous boric oxide phases; B$_2$O$_3$ crystal, representing the anhydrous boric oxide phase; and the glass phase, representing the quenched liquid phase (L).

These results suggest the following reactions and piercing points:

\[
\begin{align*}
B_2O_3 + TiO_2 + L_4 &\rightarrow HBO_2 + TiO_2 + L_2 \text{ at around } 1100 \, ^\circ C, (1) \\
HBO_2 + TiO_2 + L_3 &\rightarrow H_2BO_3 + TiO_2 + L_4 \text{ at around } 600 \, ^\circ C, (2)
\end{align*}
\]

where \( L_1, L_2, L_3, \) and \( L_4 \) are liquid with different Ti/B ratios. TiO_2 can occur as anatase and rutile, at low temperature, as TiO_2-I, up to 800 °C, and as rutile above 800 °C. Its behavior is not represented in the reactions depicted above.

Following these assumptions, a polythermal, isobaric diagram is suggested in Figure 5. However, the position of the cotectic lines and piercing points in the diagram are only schematic due to lack of analysis of the melt composition (glass phase). The elaboration of this schematic ternary phase diagram obeyed the following premises:

(a) All cotectic lines must be on the left side of the line that connects all the compositions of the starting materials (denoted by the numbers 1, 2, 3, and 4), due to the characteristics of the system as, for example, the solubility and the melting point of the phases.

(b) The cotectic piercing point (A) defined by the reaction 1 must be placed between the projection of the tie line of the composition 4 and 3, on the cotectic lines, according to the experimental results.

(c) The cotectic piercing point (B) defined by the reaction 2 must be placed beyond the projection of the tie line of the composition 1 on the cotectic lines.

At pressures of 5 and 10 GPa, \( H_2O \) melts at 230 and 315 °C, respectively, and all compositions used to build this diagram are out of the solid \( H_2O \) stability field. This feature suggests that the vapor field and the vapor–liquid boundary are reduced in the conditions of these experiments, and that \( B_2O_3 \) with \( H_2O \) are soluble in the liquid. EDS analyses in the quenched liquid emphasize this assumption. Optical microscope observation and electron microscopic images do not suggest liquid–liquid immiscibility in any composition studied to build this diagram at 7.7 GPa.

Vitreous \( B_2O_3 (\sim B_2O_3) \) consists of boroxol groups (\( B_2O_6 \)), which is a three-membered ring of \( BO_3 \) triangles, constrained to be planar by delocalized \( \pi \) bonding. The breathing mode of this boroxol group is Raman active and characterized by a sharp peak at 808 cm\(^{-1}\). High-pressure monitoring of this peak has shown that with increasing pressure, the peak shifts up to 810 cm\(^{-1}\), up to 16 GPa, when it disappears. With the pressure release, this peak reappears, but with lower intensity. With addition of alkalis (M_2O, M = K or Na) up to \( R = 0.5 (R = [\text{mol} \% M_2O]/[\text{mol} \% B_2O_3]) \), the boroxol groups are progressively replaced by structural units with tetrahedral coordination of B atoms (tetraborate, six-membered borate rings with one and maybe two BO_4 tetrahedrons, diborate groups). To obtain some information about the glass phase produced in this study, all compositions were processed to temperatures higher than the cotectic temperatures. This procedure increases the amount of glass in the capsule. Raman analysis of the glass phase was performed on all samples, and no peaks were observed. From these data, it is not possible to ascertain that \( B \) is arranged in boroxol groups. The EDS analysis shows only that Ti, B, and O are present in this liquid. Microscopic investigation does not show immiscibility of phases. This information suggests that any liquid composed of oxygen-bearing phases decreases the eutectic point. This phenomenon can produce a melt phase that could act as a medium for material transporting, contributing to the grain growth and decrease of hardness and density of ceramics composed of TiB_2.

**Conclusions**

The system TiO_2–H_2O–B_2O_3 was studied at high-pressure (7.7 GPa) and high temperatures, and a phase diagram was schematically proposed. The eutectic point was identified to be at around 400 °C. Two piercing points where identified at around 600 and 1100 °C, with the stabilization of HBO_2 rather than H_2BO_3, and the stabilization of B_2O_3 rather than HBO_2, respectively. Besides its fundamental scientific interest, this study can be directly applied to help understanding of the sintering of borides such as TiB_2, in which the presence of oxygen-bearing phases decreases the eutectic point of the system. This phenomenon can produce a melt phase that could act as a medium for material transport and produce grain growth influencing the sintering and tribological properties of the ceramic.

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