Synthesis of B$_6$O powder and spark plasma sintering of B$_6$O and B$_6$O–B$_4$C ceramics

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Hard boron suboxide (B$_6$O) is a difficult-to-consolidate ceramic material that requires extreme processing conditions to achieve sintering activation and is only consolidated readily at high pressures above 4 GPa. In this contribution, for the first time, we report the consolidation of hard and tough laboratory-synthesized B$_6$O by the spark-plasma sintering (SPS) technique. The density of SPS-sintered specimens of above 98% is reported, and an optimal combination of 34 GPa hardness and 4 MPa·m$^{1/2}$ fracture toughness is achieved by controlling the amount of glassy phase boron oxide (B$_2$O$_3$) with an appropriate SPS set up. The effects of the type of protection used, i.e., graphite die lined only with graphite foil, BN coating, or tantalum foil, on the phase compositions and properties of bulk were studied. Finally, composites of boron suboxide and boron carbide, B$_6$O–xB$_4$C (x = 0, 3, 5, 10, 20, 40 wt %) were fabricated by SPS, and a significant improvement in the mechanical properties was achieved. Results showed that dense B$_6$O–10 wt % B$_4$C composite material with a hardness above 40 GPa and a fracture toughness of 4.8 MPa·m$^{1/2}$ were obtained.

Key-words : Boron suboxide, Spark plasma sintering, Ceramic, Composite, Hardness, Fracture toughness

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were measured. B$_2$O/TiB$_2$ composites with various compositions were produced by SPS at temperatures between 1850 and 1900°C. A fracture toughness of 2.6–5.0 MPa·m$^{1/2}$ and a hardness of 26–36 GPa (Hv,0.4) were recorded. Note, that samples with a good fracture toughness of 4–5 MPa·m$^{1/2}$ often showed a low hardness between 26–28 GPa. Thus, the decrease in hardness with increasing fracture toughness has been clearly observed in previous studies.

The existence of B$_2$O$_3$ on the surface of B$_6$O powder, which leads to the formation of B$_6$O$_3$ triple junctions, could be a possible reason for the low fracture toughness of bulk B$_6$O ceramic bodies consolidated by SPS[26,28] and hot pressing.[5,30] To overcome the problem of low fracture toughness while maintaining the high hardness of the B$_6$O material, two approaches were proposed in this study. In the first approach, B$_6$O–B$_4$C composites were fabricated to prevent the formation of B$_2$O$_3$–B$_4$C triple junctions and to simultaneously assist the formation of high-hardness B$_4$C$_3$ phases. In the second approach, tantalum foil was applied to protect the powder from carbon diffusion during sintering and to maintain the direct flow of current through the sample. As a result, we could take advantage of the beneficial features of SPS processing.

### 2. Experimental details

#### 2.1 Powder preparation

The starting materials for the synthesis of B$_6$O powder at ambient pressure were amorphous boron and B$_2$O$_3$ following the method reported in the literature. However, unlike in previous synthesis methods, amorphous boron (aB) (0.2–0.3 μm) and B$_2$O$_3$ were taken in a 14:1 mole ratio and mixed in distilled water. An excess amount of B$_2$O$_3$ for the stoichiometric mixing mole ratio of 14:1 was added to compensate for the evaporation of B$_2$O$_3$ during the heat treatment and to reduce the amount of unreacted aB. Taking into account the fact that very fine aB raw powder was used, B$_2$O$_3$ raw powder was dissolved in distilled water in order to enhance the reaction volume and thereby reduce the likelihood of the formation of large agglomerates. The prepared mixture was evaporated and dried at 70°C. The powder mixture was then heated in a vacuum furnace under Ar atmosphere at 1300°C for 2 h. The precursors reacted according to the following reactions:[31]

$$\begin{align*}
B_2O_3 + 3H_2O & \rightarrow 2H_2BO_3 \\
2H_2BO_3 & \rightarrow B_2O_3 + 3H_2O \\
16B + 2H_2BO_3 & \rightarrow 3B_6O + 3H_2O
\end{align*}$$

Possible traces of unreacted B$_2$O$_3$ in the reaction products were dissolved in hot ethanol (C$_2$H$_5$OH, 99.5% reagent-grade, Kanto Chemicals, Japan). In order to remove as much B$_2$O$_3$ as possible, the powder was washed three times. The prepared powder was dried at 170°C after ethanol evaporation.

The synthesized B$_6$O powder was mixed in distilled water with different amounts (0–40 wt%) of commercially available B$_4$C powder produced by Sinopharm Chemical Reagent Co. Ltd., China. The prepared dispersions were evaporated and dried at 170°C.

#### 2.2 Consolidation by SPS

The pure synthesized B$_6$O powder was loaded into the graphite die and punch unit for SPS processing. We used graphite dies with inner diameters of 10 mm. The outer surface of the die was wrapped with 5-mm-thick graphite felt to homogenize the temperature distribution and reduce heat loss by radiation. In the first case, only graphite foil was inserted between the powder and the die for easy release after SPS. In the second case, graphite foil coated with a BN suspension was used to prevent the interaction between the sample and the graphite. For similar reasons, additional tantalum foil (Sigma-Aldrich Chemie, Tantalum, foil, 0.025 mm thick, 99.9% + metals basis) was inserted between the powder and the graphite foil. After placing the die in the SPS apparatus (Dr. Sinter Model SPS-1050, SPS-Syntex, USA), the samples were subjected to SPS under 50 MPa (uniaxial pressure) at a temperature of 1800°C and a heating rate of 110°C/min, and the dwell time at this temperature was 1 min. Each specimen was gradually cooled to 600°C at a rate of 100°C/min and then naturally to room temperature with the furnace. The temperature was measured using an optical pyrometer.

The samples were named according to their preparation route. For example, 30B$_6$O.G denotes pure B$_6$O powder subjected to SPS at a uniaxial pressure of 30 MPa in the die lined only with graphite foil, 30B$_6$O.BN denotes pure B$_6$O powders subjected to SPS at uniaxial pressure of 30 MPa in the die lined by graphite foil coated with BN, and 30B$_6$O.Ta refers to the use of graphite foil together with Ta foil.

The B$_6$O–B$_4$C composites were then subjected to SPS under the same time-temperature sintering conditions as the first set of samples (Table 2). The maximum uniaxial pressure was 80 MPa during SPS processing, and additional Ta foil was used for all samples in the current experiment.

The samples ID were named according to their composition: for example, B$_6$O$_{40}$B$_4$C contains 40 wt% B$_4$C, B$_6$O$_{30}$B$_4$C–30 wt% B$_4$C.

The phase composition was determined by powder X-ray diffraction (XRD) analysis at room temperature (Rigaku Ultima IV, Japan, Cu K$_\alpha$ radiation). The intensity data were collected over the 2θ range of 15–85° in steps of 0.02° with a sampling time of 4 s at each step. The program used for the refinements was PDXL.[32]

The morphology and particle size of the powder were studied by scanning electron microscopy (SEM-EDX, Hitachi, Japan) and transmission electron microscopy (TEM 125K, SELMI, Japan).
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Table 2. Sintering conditions and properties of SPS B₆O–B₄C composites

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>B₄C amount, wt %</th>
<th>Temperature, °C</th>
<th>Time, min</th>
<th>Pressure, MPa</th>
<th>Remarks</th>
<th>Properties of samples</th>
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<tr>
<td></td>
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<td>Relative density, %</td>
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<td>Hardness, GPa</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Fracture toughness, MPa·m¹/²</td>
</tr>
<tr>
<td>B₆O₄₀B₄C</td>
<td>40</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>Tantalum foil</td>
<td>97.9</td>
</tr>
<tr>
<td>B₆O₂₀B₄C</td>
<td>20</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>Tantalum foil</td>
<td>98.2</td>
</tr>
<tr>
<td>B₆O₁₀B₄C</td>
<td>10</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>Tantalum foil</td>
<td>98.5</td>
</tr>
<tr>
<td>B₆O₅B₄C</td>
<td>5</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>Tantalum foil</td>
<td>98.6</td>
</tr>
<tr>
<td>B₆O₃B₄C</td>
<td>3</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>Tantalum foil</td>
<td>98.6</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern of B₆O powder synthesized at 1300°C for 2 h.

Fig. 2. (a) SEM general image of B₆O powder synthesized at ambient pressure and (b) TEM image showing details of the desired starlike structure of particles.

3. Results and discussion

3.1 Synthesis of B₆O powder

It has recently been shown that larger oxygen content can be achieved if the synthesis is performed at 1250°C. However, at relatively low temperatures, a longer dwell time is required. In addition, the presence of unreacted components (B₂O₃ and aB) in the powder is expected under the low-temperature synthesis condition. The X-ray powder diffraction pattern of the product is shown in Fig. 1 as no secondary phases were identified. Despite the fact that B₂O₃ was used in excess relative to the stoichiometry, the B₂O₃ phase was not detected by XRD analysis. In addition, a very small amount of residual aB was indicated. The present results were obtained with the use of (i) fine aB powder (0.2–0.3 μm) and (ii) the wet mixing technique to enhance the reactive value/homogeneity of precursors. Moreover, these two features of the synthesis process made it possible to reduce the time for synthesis to only 2 h at the relatively low temperature of 1300°C. We believe that such mild processing conditions can improve the stoichiometry of the B₆O material. Note that the synthesis temperature is slightly lower than that in the literature data (1380°C, 1420°C, and 1450°C) and the formation process is 3–6 times faster (2 h instead of 6 h and 12 h). TEM investigations (Fig. 2) show that the B₆O synthesized powders have a fine particle size (<1 μm) and consist of crystallites with a starlike structure. The starlike structure observed in the present study is a specific feature of B₆O crystals, as was previously reported.

3.2 Spark plasma sintering of pure B₆O powder

Pure B₆O powder was subjected to SPS under the same time-temperature conditions as above but with different options for sample protection. The sintering conditions and properties of the samples are given in Table 1. The pellets sintered using different types of protection (or without protection) have almost the same relative density. However, the samples sintered without protection (graphite die lined with only graphite foil) and with the BN coating have better fracture toughness than the sample sintered with Ta foil protection. According to the result of the XRD analysis (see Fig. 3), 30B₆O–G and 30B₆O–BN contain impurities such as B₂O₃, B₄C and B₄C, respectively, which are the result of phase transitions that took place owing to carbon diffusion. Nevertheless, the sample protected with Ta foil has a...
sufficiently high relative density (32.2 ± 0.8 GPa) than 30B6O.G and 30B6O.BN (31.7 ± 0.9 and 31.5 ± 0.7, respectively). This difference can be explained by the presence of impurities (see Fig. 3), that enhance fracture toughness and decrease hardness. Note that applying Ta foil prevents carbon diffusion into the samples. Besides, no Ti or Ta-related compounds were detected near the surface at 1800°C. Herrmann et al.22),27),28) used a BN coating applying Ta foil prevents carbon diffusion into the samples. Moreover, B6O and B4C have similar crystal structures (2H-Graphite), which are better represented as B13C2 with a C–B–C chain on the trigonal axis.5) According to reaction (7), B4C is a promising candidate for the elimination of B2O3 content on the one hand and for improving hardness on the other hand.11) It can be seen from Table 2 that the relative densities slightly decrease upon the addition of B4C for all compositions. However, the hardness does not change gradually but increases with the addition of B4C from 3 to 10 wt.% and then gradually decreases from 10 to 40 wt.%. This can be explained as follows: in the B4C concentration range of 3–10 wt.%, the improvement of hardness is just beginning to take effect; increasing the B4C content from 10 to 40 wt.% leads to a higher carbon concentration in the composite and a higher probability of reaction (6). As a result, the hardness decreases.

Fig. 3 XRD patterns of B6O materials fabricated via SPS at 1800°C for 1 min under uniaxial pressure of 30 MPa using different protective layers or without protection (graphite die lined only by graphite foil). Phases and ICSD files are indicated.

For the main diffraction line of B4C

$$2B_6O + 5C \rightarrow 3B_4C + 2CO.$$ (6)

The formed CO partial pressure is lower than the equilibrium pressure of reaction (5). Therefore, the reaction takes place only after the decomposition of B6O.30)

In addition, the reaction between B2O3 and B4C can occur:39)

$3B_4C + 1/2B_2O_3 \rightarrow B_{13}C_2 + CO + 1/4O_2.$ (7)

Moreover, B6O and B4C have similar crystal structures (α-rhombohedral boron type), which are better represented as B13C2 with a C–B–C chain on the trigonal axis.5) According to reaction (7), B4C is a promising candidate for the elimination of B2O3 content on the one hand and for improving hardness on the other hand.11) It can be seen from Table 2 that the relative densities slightly decrease upon the addition of B4C for all compositions. However, the hardness does not change gradually but increases with the addition of B4C from 3 to 10 wt.% and then gradually decreases from 10 to 40 wt.%. This can be explained as follows: in the B4C concentration range of 3–10 wt.%, the improvement of hardness is just beginning to take effect; increasing the B4C content from 10 to 40 wt.% leads to a higher carbon concentration in the composite and a higher probability of reaction (6). As a result, the hardness decreases.

Figure 4 shows the XRD patterns of the specimens after SPS treatment at 1800°C for 1 min under a uniaxial pressure of 80 MPa. Strong diffraction peaks for single-phase B6O can be observed without any addition of B4C. In the case of the samples with 3, 5, 10, 20, and 40 wt.% B4C, the diffraction lines for B4C are confirmed from their intensities, which increase with B4C content. The 2θ position of the main diffraction line of B4C (2θ ≈ 37.5°) slightly shifts to low angles. This can be attributed to the formation of the B13C2 phase, which has a slightly lower 2θ for the main diffraction line. It has been reported that no variation in lattice constants for B6O or B4C, and no formation of a solid solution or new compound under high pressure (3–5 GPa)11) and high temperature (1700–1900°C)25) conditions are observed, but they may have occurred during SPS processing. Moreover, no other diffraction lines were observed (Fig. 3). The sample B6O–10B4C, which contains 90 wt.% B6O and 10 wt.% B4C, showed the highest hardness of 40.8 ± 13 GPa with a relatively high fracture toughness of 4.8 ± 0.2 MPa m1/2. As was mentioned above, all measurements for hardness and fracture toughness were conducted under a load of 9.8 N. Itoh et al.11) prepared B6O-xB4C (x = 0–40 vol.%) composite materials under high-pressure conditions (3–5 GPa). They reported the maximum hardness of 46 GPa (load of 1.96 N) was applied for
the B$_6$O–30 vol% B$_4$C sintered composite. This hardness is the highest reported in the literature for B$_6$O-based composites. However, even when the load of 1.96 N was applied, the fracture toughness did not exceed 1 MPa·m$^{1/2}$. More recently, Herrmann et al.\textsuperscript{26,28,29} have fabricated dense B$_6$O samples doped with yttrium and alumina via SPS/field assisted sintering technology (FAST). With an indentation load of 4 N, the hardness and fracture toughness of the samples were 33 GPa and 4 MPa·m$^{1/2}$, respectively. Although the BN coating was used to inhibit the chemical reaction between the sample material and the graphite die, the current flow through the sample occurred with increasing temperature up to 1850°C. We believe that the achievement of a high fracture toughness with sufficient hardness can be attributed to the unique nature of the FAST/SPS technique, which explains the lower hardness and fracture toughness of same-composition materials consolidated by hot pressing.

In the current study, Ta foil was used to inhibit the chemical reaction between the sample material and the graphite die, the current flow through the sample occurred with increasing temperature up to 1850°C. We believe that the achievement of a high fracture toughness with sufficient hardness can be attributed to the unique nature of the FAST/SPS technique, which explains the lower hardness and fracture toughness of same-composition materials consolidated by hot pressing.

In the current study, Ta foil was used to inhibit the chemical reaction between the sample material and the die. As shown in Table 2, B$_6$O-based composites have the highest fracture toughness of 4.6–5.3 MPa·m$^{1/2}$ with a hardness of 35.4–40.8 GPa.

To the best of our knowledge, these are the highest hardness and fracture toughness reported for this system to date. As was concluded in our previous study\textsuperscript{30} the principle of a diluted composite with controlled grain boundaries and smaller particles is expected to be useful in controlling properties of different systems, targeting not only mechanical but also other properties. In the present work, we could draw similar conclusions. Additional studies of the effects of SPS processing and the nature of the grain boundary framework on the mechanical properties of B$_6$O-based composites are needed to gain better understanding.

4. Conclusions

Pure boron suboxide powder with fine particle size distribution was synthesized at ambient pressure and sintered by SPS under different die set conditions. The results showed that it is possible to produce a pure bulk B$_6$O material using protective Ta foil and to retain the very essence of SPS processing. In addition, the dense boron suboxide with a hardness (H$_1$) higher than 34 GPa and a fracture toughness of about 4 MPa·m$^{1/2}$ was produced.

B$_6$O–xB$_4$C (x = 0, 3, 5, 10, 20, 40 wt%) composites were subjected to SPS using the mixture of laboratory synthesized B$_6$O powder and commercially available B$_4$C powder as the starting powders. The phase composition evolution and mechanical properties of the sintered composites with increasing B$_4$C content were investigated. The composites with 10 to 20 wt% boron carbide exhibits the best hardness-to-toughness ratio among the compositions investigated and reported by other research teams (hot pressing or high-pressure consolidation).

The effect of direct current flow on the grain boundary framework of this new class of composites with a promising hardness-to-toughness ratio must be addressed in the future. Results of the present investigation are not limited only to the boron suboxide–boron carbide system and are expected to be applicable to other systems where carbon diffusion must be controlled and limited.

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