Preparation of Boron Suboxide Nanoparticles and Their Processing

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INTRODUCTION

Boron suboxide B2O is a promising chemically inert wear resistant material for manufacturing cutting tools and abrasives because its hardness is close to that of well known superhard materials – cubic boron nitride and diamonds [1, 2]. Commonly, synthesis of B2O includes continuous mechanical milling of mixture of boron and B2O3 with subsequent reducing of oxide by boron and formation of the product at 1400 °C at ambient or high pressure about 6 h. Boron suboxide formed at ambient pressure is poorly crystallized and the ratio of boron and oxygen is close to 7 [3]. Beside this B2O contains admixture of B2O3 [2]. High pressure during synthesis improves stoichiometry of boron suboxide and it increases crystallite size [1] but demands a complex technique. Bulk materials of B2O are produced by hot pressing at 1900 °C or at 1850 °C in presence of sintering additives (oxides, metals) at 50 MPa for 20 min [4 – 6].

The purpose of present work was intensification of B2O preparation and processing by modification of B2O synthesis from B2O3 mixture with different ratio of components at ambient pressure and densification of pure boron suboxide and its composites with TiN or Ni nanoparticles by using spark plasma sintering.

EXPERIMENTAL PROCEDURE

B2O particles were prepared by well known reaction of X-rays amorphous B (98.7) with B2O3 but mixture of the precursors was obtained by mixing boron with water solution of B2O3. The mixture was stirred, evaporated and dried at 70 °C – 80 °C in argon. The prepared precursors with specific surface area (SSA) of 20 m²/g and various ratio of B/B2O3 were calcinated at 1200 °C – 1400 °C in argon for one or two hours.

Composite powders of B2O were prepared by mechanical mixing of boron suboxide with 10 wt.% of TiN nanoparticles (SSA = 42 m²/g) and with 10 wt.% of Ni nanoparticles (SSA = 10.8 m²/g).

RESULTS AND DISCUSSION

According to XRD analysis of as-prepared samples formation of B2O particles starts at temperature above 1250 °C. Crystalline B2O is formed at 1400 °C during 1 h independently on B/B2O3 ratio in the range of 14 – 16 (Fig. 1). However, XRD patterns indicated to presence of small amount of H3BO3 admixture as the result of interaction of remaining B2O3 with water. Similar XRD patterns are obtained for B2O samples calcinated at 1400 °C for 2 h. It means that calcination of precursors at 1400 °C for one hour is quite enough for synthesis of crystalline B2O. The synthesis temperature corresponds well with literature data (1380 °C – 1420 °C) [2, 5] but the formation process is 3 times quicker, obviously, due to high homogeneity of the used precursors.
SEM images of B/B$_2$O$_3$ precursor and B$_6$O particles show that synthesis substantially changes the particle shape (Fig. 2). Unregular precursor particles with size in the range of 2 µm – 5 µm during synthesis turn into highly crystallized star-like plates with size in the range of 1.5 µm – 2 µm.

Despite to similar XRD patterns of the samples prepared at different ratio of B/B$_2$O$_3$ their SSA, crystallite size and the content of oxygen depend on the composition of precursors (Table 1).

Data shows that the powder produced at stoichiometric ratio of components is oxygen deficient due to partial evaporation of B$_2$O$_3$ during the synthesis. Application of the precursors with increased the content of B$_2$O$_3$ increases the content of oxygen in as-prepared powders. However, treatment of the samples by 1M HCl followed by washing in ethanol [5] reduces the content of oxygen. Only synthesis of precursor with molar ratio B/B$_2$O$_3$ = 14 ensures formation of B$_6$O with the content of oxygen close to stoichiometric.

Table 1. Characteristics of the B$_6$O prepared at 1400 ºC from precursors with several molar ratio of B/B$_2$O$_3$

<table>
<thead>
<tr>
<th>No</th>
<th>B/B$_2$O$_3$</th>
<th>SSA, m$^2$/g</th>
<th>Crystallite size, nm</th>
<th>Content of oxygen, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>15.1</td>
<td>40</td>
<td>15.2</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>16.0</td>
<td>36</td>
<td>18.4</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>17.2</td>
<td>32</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Presence of remaining B$_2$O$_3$ in the obtained powders increases SSA and decreases the crystallite size, possible by preventing growth of B$_6$O particles at high calcination temperature. The calculated crystalline size of B$_6$O differs strongly from particle size determined from SEM micrographs. It means that star-like particles are polycrystals.

The measurements of temperature, displacement of pistons and displacement rate (ds/dt) as a function of SPS process time indicate that densification of B$_6$O starts at 1540 ºC (Fig. 3). The further process includes 3 separate stages at 1580, 1700 and 1820 ºC with different densification rate. The maximal displacement of pistons and densification of pure B$_6$O is reached at 1900 ºC for 5 min. Increase of sintering time has little influence on densification.

Table 2. The density, open porosity and XRD analysis of spark plasma sintered B$_6$O

<table>
<thead>
<tr>
<th>Temperature, ºC</th>
<th>Density, g/cm$^3$</th>
<th>Relative density, %</th>
<th>Open porosity, %</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.06</td>
<td>80.5</td>
<td>9.4</td>
<td>B$_6$O</td>
</tr>
<tr>
<td>1800</td>
<td>2.28</td>
<td>89.0</td>
<td>6.6</td>
<td>B$_6$O</td>
</tr>
<tr>
<td>1900</td>
<td>2.50</td>
<td>98.0</td>
<td>0.95</td>
<td>B$_6$O</td>
</tr>
</tbody>
</table>

The density and XRD analysis of the sintered materials are given in Table 2. The optimal sintering temperature of the pure B$_6$O agrees with literature data for the hot pressed samples [4].
However, density reached by the spark plasma sintering is higher and sintering time is lower because the spark plasma sintering accelerates the densification process of B$_6$O. The SEM image confirms low porosity of the B$_6$O material sintered at 1900 °C. It shows that the B$_6$O material consists from relatively large plate-like grains (Fig. 4).

Fig. 4. SEM micrograph of fracture surface of B$_6$O sintered at 1900 °C; bar 50 µm

The Vickers hardness of sintered B$_6$O material is in the range of 31.2 GPa – 32.0 GPa using a load 1 kg. The hardness is comparable with the literature data – 30.2 GPa, 1 kg load for hot pressed B$_6$O [4] and 31 GPa – 33 GPa, 200 g load for the high pressure material [3].

Fig. 5. XRD patterns of sintered B$_6$O (1), B$_6$O/TiN (2), B$_6$O/Ni (3); ○ – B$_6$O; × – TiB$_2$; + – NiB; v – Ni$_6$Si$_2$B

The densification of boron suboxide composites with TiN or Ni nanoparticles starts at 1430 °C and 1500 °C respectively because presence of active nanoparticles and formation of additional phases intensified sintering. According to XRD analysis TiN and Ni nanoparticles interact intensively with B$_6$O and despite to short reaction time the manufactured bulk materials contain only B$_6$O and TiB$_2$ or mixture of Ni borides (Fig. 5).

CONCLUSIONS

1. Mixing of X-ray amorphous boron with water solution of B$_2$O$_3$ followed by evaporation and drying simplifies and intensifies the synthesis of B$_6$O at 1400 °C and ambient pressure, and it ensures high crystallinity of the particles with size in the range of 1.5 µm – 2 µm and crystallite size in the range of 32 nm – 40 nm.

2. Decrease of molar ratio B/B$_2$O$_3$ from 16 to 14 in the precursor mixture reduces nonstoichiometry of the prepared B$_6$O although simultaneously it increases admixture of B$_2$O$_3$.

3. The spark plasma sintering of dispersive B$_6$O particles at 1900 °C allows manufacturing the dense material (98 %) with high hardness during 5 min.

4. Additives of TiN or Ni nanoparticles reduce the spark plasma sintering temperature to 1700 °C and their promote formation of boride phases of Ti and Ni.

REFERENCES


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