

Preparation of Boron Suboxide Nanoparticles and Their Processing

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Crystalline boron suboxide B_6O particles with size in the range of $1.5\ \mu\text{m}$ – $2\ \mu\text{m}$ and crystallite size in the range of $32\ \text{nm}$ – $40\ \text{nm}$ were prepared by calcination at $1400\ ^\circ\text{C}$ for one or two hours of precursors obtained by mixing X-ray amorphous boron with water solution of B_2O_3 followed by evaporation and drying. Decrease of molar ratio B/B_2O_3 from 16 to 14 in the precursor mixture reduced nonstoichiometry of prepared B_6O although simultaneously it increased admixture of B_2O_3 . Particulate composites of B_6O with TiN or Ni nanoparticles were prepared by mechanical mixing. The spark plasma sintering process intensified the densification of prepared boron suboxide nanoparticles at $1900\ ^\circ\text{C}$ and allowed manufacturing of fully dense bodies (98 %) during five minutes. Additives of TiN or Ni nanoparticles reduced sintering temperature to $1700\ ^\circ\text{C}$ and their promoted formation of Ti or Ni borides.

Keywords: boron suboxide; spark plasma sintering; synthesis.

INTRODUCTION

Boron suboxide B_6O 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 B_6O includes continuous mechanical milling of mixture of boron and B_2O_3 with subsequent reducing of oxide by boron and formation of the product at $1400\ ^\circ\text{C}$ 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 B_6O contains admixture of B_2O_3 [2]. High pressure during synthesis improves stoichiometry of boron suboxide and it increases crystallite size [1] but demands a complex technique. Bulk materials of B_6O are produced by hot pressing at $1900\ ^\circ\text{C}$ or at $1850\ ^\circ\text{C}$ in presence of sintering additives (oxides, metals) at 50 MPa for 20 min [4–6].

The aim of present work was intensification of B_6O preparation and processing by modification of B_6O synthesis from B/B_2O_3 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

B_6O particles were prepared by well known reaction of X-rays amorphous B (98.7) with B_2O_3 but mixture of the precursors was obtained by mixing boron with water solution of B_2O_3 . The mixture was stirred, evaporated and dried at $70\ ^\circ\text{C}$ – $80\ ^\circ\text{C}$ in argon. The prepared precursors with specific surface area (SSA) of $20\ \text{m}^2/\text{g}$ and various ratio of B/B_2O_3 were calcinated at $1200\ ^\circ\text{C}$ – $1400\ ^\circ\text{C}$ in argon for one or two hours.

Composite powders of B_6O were prepared by mechanical mixing of boron suboxide with 10 wt.% of TiN

nanoparticles (SSA = $42\ \text{m}^2/\text{g}$) and with 10 wt.% of Ni nanoparticles (SSA = $10.8\ \text{m}^2/\text{g}$).

The prepared samples were pressed into graphite dies with diameter of 20 mm and densified in vacuum at $1600\ ^\circ\text{C}$ – $1900\ ^\circ\text{C}$ and a pressure of 30 MPa using the spark plasma sintering technique (SPS-825.CE, SPS Syntex Inc.). After sintering the bulk material was ground to remove reaction products with graphite from surface.

Phase composition of powders and bulk materials was determined by XRD analysis (8Advance, Bruker AXS). Crystallite size was calculated from broadening diffraction maxima using the Scherer formula.

The content of oxygen was controlled by X-ray photoelectron spectroscopy (XPS, Pioneer, Bruker AXS) and by ELTRA ON900 (ELTRA GmbH). SSA of powders was determined by the argon absorption-desorption method. Particle size and shape, microstructure of the bulk material were examined by SEM. Presence of B_2O_3 admixture was controlled by treatment of samples in hot water followed by detecting H_3BO_3 maxima in XRD patterns. Density of samples was determined by using the Archimede's method. The Vickers hardness (H_v) was found by the indentation technique under the pressure of 1 kg.

RESULTS AND DISCUSSION

According to XRD analysis of as-prepared samples formation of B_6O particles starts at temperature above $1250\ ^\circ\text{C}$. Crystalline B_6O is formed at $1400\ ^\circ\text{C}$ during 1 h independently on B/B_2O_3 ratio in the range of 14–16 (Fig. 1). However, XRD patterns indicated to presence of small amount of H_3BO_3 admixture as the result of interaction of remaining B_2O_3 with water. Similar XRD patterns are obtained for B_6O samples calcinated at $1400\ ^\circ\text{C}$ for 2 h. It means that calcination of precursors at $1400\ ^\circ\text{C}$ for one hour is quite enough for synthesis of crystalline B_6O . The synthesis temperature corresponds well with literature data ($1380\ ^\circ\text{C}$ – $1420\ ^\circ\text{C}$) [2, 5] but the formation process is 3 times quicker, obviously, due to high homogeneity of the used precursors.

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SEM images of B/B₂O₃ precursor and B₆O 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.

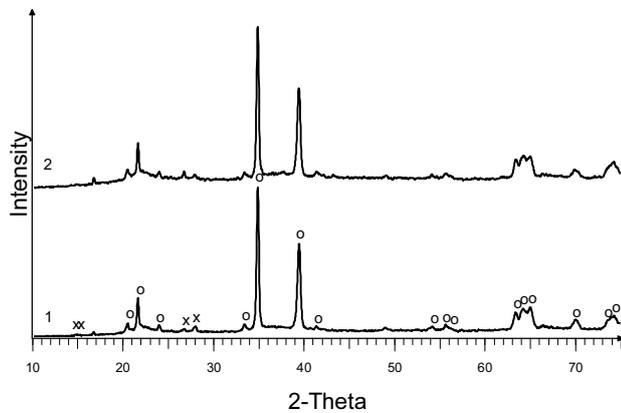


Fig. 1. XRD patterns of the prepared samples at 1400 °C for 1 h at ratio B/B₂O₃ = 16 (1) and 15 (2); o – B₆O; x – H₃BO₃

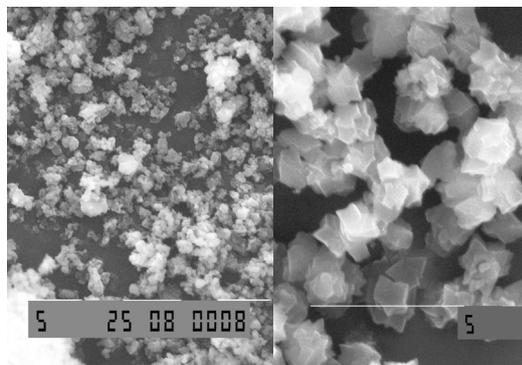


Fig. 2. SEM images of precursor (left) and B₆O particles prepared at 1400 °C (right); bar 5 μm

Despite to similar XRD patterns of the samples prepared at different ratio of B/B₂O₃ 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 B₂O₃ during the synthesis. Application of the precursors with increased the content of B₂O₃ 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/B₂O₃ = 14 ensures formation of B₆O with the content of oxygen close to stoichiometric.

Table 1. Characteristics of the B₆O prepared at 1400 °C from precursors with several molar ratio of B/B₂O₃

No	B/B ₂ O ₃	SSA, m ² /g	Crystallite size, nm	Content of oxygen, wt%	
				as-prepared	treated
1	16	15.1	40	15.2	15.1
2	15	16.0	36	18.4	18.4
3	14	17.2	32	21.6	19.1

Presence of remaining B₂O₃ in the obtained powders increases SSA and decreases the crystallite size, possible by preventing growth of B₆O particles at high calcination temperature. The calculated crystalline size of B₆O 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 B₆O starts at 1540 °C (Fig. 3). The further process includes 3 separate stages at 1580, 1700 and 1820 °C with different densification rate. The maximal displacement of pistons and densification of pure B₆O is reached at 1900 °C 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 B₆O

Temperature, °C	Density, g/cm ³	Relative density, %	Open porosity, %	XRD
100	2.06	80.5	9.4	B ₆ O
1800	2.28	89.0	6.6	B ₆ O
1900	2.50	98.0	0.95	B ₆ O

The density and XRD analysis of the sintered materials are given in Table 2. The optimal sintering temperature of the pure B₆O agrees with literature data for the hot pressed samples [4].

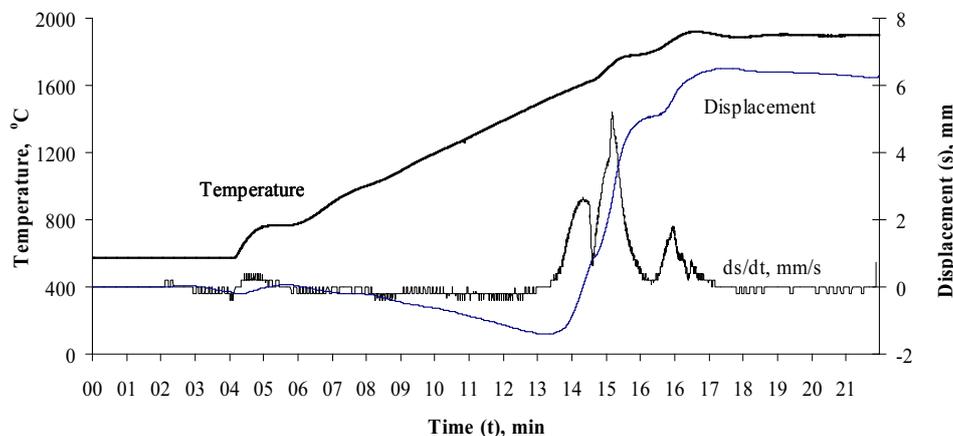


Fig. 3. Temperature, displacement of pistons and displacement rate (ds/dt) as a function of time for spark plasma sintering of the B₆O

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_6O . The SEM image confirms low porosity of the B_6O material sintered at $1900^\circ C$. It shows that the B_6O material consists from relatively large plate-like grains (Fig. 4).

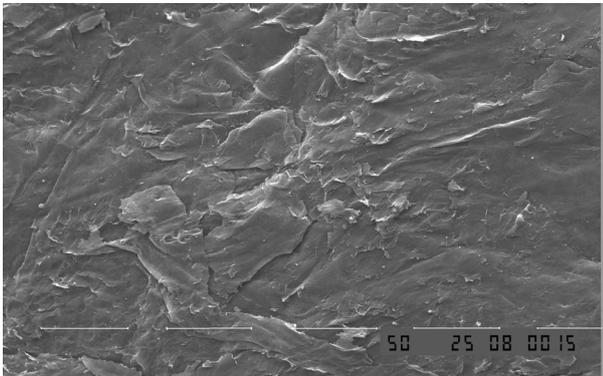


Fig. 4. SEM micrograph of fracture surface of B_6O sintered at $1900^\circ C$; bar $50\ \mu m$

The Vickers hardness of sintered B_6O 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_6O [4] and $31\ GPa - 33\ GPa$, $200\ g$ load for the high pressure material [3].

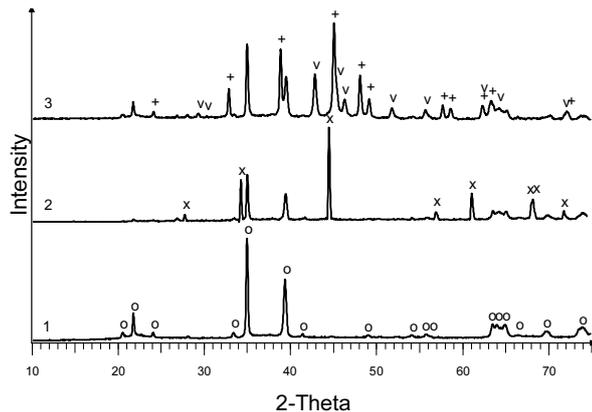


Fig. 5. XRD patterns of sintered B_6O (1), B_6O/TiN (2), B_6O/Ni (3); o – B_6O ; x – TiB_2 ; + – NiB ; v – Ni_6Si_2B

The densification of boron suboxide composites with TiN or Ni nanoparticles starts at $1430^\circ C$ and $1500^\circ C$ 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_6O and despite to short reaction time the manufactured bulk materials contain only B_6O and TiB_2 or mixture of Ni borides (Fig. 5).

CONCLUSIONS

1. Mixing of X-ray amorphous boron with water solution of B_2O_3 followed by evaporation and drying simplifies and intensifies the synthesis of B_6O at $1400^\circ C$ and ambient pressure, and it ensures high crystallinity of the particles with size in the range of $1.5\ \mu m - 2\ \mu m$ and crystallite size in the range of $32\ nm - 40\ nm$.

2. Decrease of molar ratio B/B_2O_3 from 16 to 14 in the precursor mixture reduces nonstoichiometry of the prepared B_6O although simultaneously it increases admixture of B_2O_3 .

3. The spark plasma sintering of dispersive B_6O particles at $1900^\circ C$ 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 $1700^\circ C$ and their promote formation of boride phases of Ti and Ni .

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