

Synthesis of Boron Carbide from Boric Acid and Carbon-Containing Precursors

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The paper compares low-temperature techniques for boron carbide synthesis. Boron carbide was synthesized via reaction between boric acid and various carbon precursors, e.g. phenol-formaldehyde resin, sucrose, carbon black, and potato starch. Initial compositions and carbon precursor preparation techniques were selected for synthesis. The resulting products were characterized by IR spectrometry, X-ray diffraction (XRD) and scanning electron microscopy. Possible boron carbide yields up to 95 % of the theoretical yield as calculated from initial boron contents at temperatures of 1550 °C were demonstrated. XRD confirmed that the synthesized boron carbide (B_4C) has a rhombohedral crystalline structure. Final product morphology may be tailored, ranging from isometric to needle-like crystallite morphology. Nanopowders as processed via high-energy milling may be further used as sintering additive for processing of boron carbide ceramics.

Keywords: Boron carbide, Powder, Synthesis, Phenol-formaldehyde resin, Sucrose, Starch, Pre ceramic polymer

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1. INTRODUCTION

Boron carbide (B_4C) has a special place among ultrahard high-melting nonmetals, featuring a unique combination of properties, e.g. excellent hardness (30-40 GPa, Hv10), low density (2.52×10^3 kg/m³), good Young's modulus (450-470 GPa), resistance to corrosion, and neutron absorption. Due to this combination of properties, boron carbide is one of the most promising materials for nuclear applications, wear parts and efficient armor systems.

Due to the highly covalent bonding nature in B_4C crystals, the major ceramic sintering mechanisms, such as grain-boundary and volume diffusion are retarded in boron carbide. This led to extensive research effort in identifying the new consolidation techniques, as well as alternative raw materials and processing methods in order to facilitate sintering processes. One of the most promising approaches in this field may be processing of submicron and nanosized boron carbide powders, as well as special particle morphologies that may subsequently be used for ceramics sintering and processing of materials with improved performance.

Boron carbide is commercially produced by the classical process of carbothermal reduction of the boron oxides at high temperatures. An interesting possible alternative to the high-temperature powder techniques may be found in solution chemical methods that use intermediate preceramic polymer products. The results of earlier research in sol-gel processing of boron carbide powders showed that gel synthesizing the intermediate organic/inorganic hybrids before the synthesis leads to the tailored distribution of carbon at molecular level [1-5]. Our paper used similar approach to synthesize boron carbide powder. Our research was aimed at esti-

imating the yield of the targeted product at lower synthesis temperatures, as well as characterization of the product for its composition and morphology.

2. MATERIALS AND METHODS

Boric acid H_3BO_3 (as per GOST 9656-75) was used as a starting material. Four different types of carbon precursors were selected: 1) sucrose; 2) potato starch (food grade); 3) phenol-formaldehyde resin (PFR), grade SF-010 (as per GOST 18694-80); 4) carbon black (PRINTEX V grade, as per GOST 7885-86). The mixture of boric acid with carbon black was used as a reference. Optimal premix compositions for each carbon precursor type were identified based on a series of preliminary tests, with optimal ratio corresponding to that with excess boric acid, as compared to stoichiometric (30 to 100 % excess). This corresponds to the earlier published findings [5-7].

The process included the premix-processing stage that was implemented by using various techniques, e.g. mechanical mixing; solution mixing with subsequent evaporation and milling; and melting + milling. The compositions and processing techniques for premix processing are given in Table 1. The as-processed premixes were placed into heat-treatment system UTO-1PS. First heat-treatment phase in Ar at $T=800$ °C served for carbonization of the carbon-rich component and H_3BO_3 dehydration. Second stage of heat-treatment was used for actual boron carbide synthesis. The carefully weighed quantity of the premix, preprocessed at 800 °C, was placed into a 5-litre graphite crucible, coated with pyrocarbon. Heating ramp up to the preset final temperature was 300 °C/hour. Synthesis was carried out in Ar at temperatures of 1300 to

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1550 °C, and at 1900 °C, with dwell time of 1 to 3 hours.

The processed samples were characterized by X-ray diffraction (XRD) using the DRON-4 XRD system. Microstructural characterization was carried out in the JSM 6460 scanning electron microscope. The intermediate products, as obtained at the premix processing stage, were also characterized by infrared spectrometry (using FSM 1201 IR-spectrometer).

The product yield (based on boron) was calculated as per technique detailed in GOST 5744-85.

Samples featuring maximum yield were additionally milled in the high-energy planetary lab mill (Aktivator 2SL).

3. RESULTS AND DISCUSSION

The IR spectrometry results for all intermediate products showed the presence of B-O-C bond (absorption peak at 1050 cm^{-1}), which confirms the reaction between the boric acid and the polymer carbon precursor. This reaction and the nature of the synthesized preceramic polymer have an effect on the boron carbide yield. Precursors with similar boron and carbon con-

tents after the calcination at 800 °C in Ar atmosphere showed different yields (as based on boron), namely: 80 to 95 %, depending on the initial composition and processing route (see Table 1).

Mixture of boric acid with carbon black yielded negligible amounts of boron carbide when treated under similar conditions. This fact may be attributed to the better synthesis conditions in the porous system that is obtained after the carbonization of the polymer precursors. Still, this process and its possible optimization require further research.

The onset of boron carbide synthesis was confirmed by XRD technique in the samples heat-treated at 1350 °C, with main components of the mixture being amorphous carbon and boron anhydride. Rising heat-treatment temperature to 1450 °C led to much higher boron carbide contents. In samples based on optimal initial compositions, heat-treated at 1550 °C, boron carbide crystallites had rhombohedral structure and was the main reaction product (see Fig. 1a,b,c). When premixes with no excess boron were used, reaction products contained disordered carbon as the main component (see Fig. 1d).

Table 1 – Characterization of the initial premixes and boron carbide powder samples as synthesized at 1550 °C

Sample description	Processing details	Initial components	Boric acid excess, relative to stoichiometric contents, %	Product yield (based on boron), %	Phase analysis
SEB	Component mixing Isothermal dwell of premix at T=175 °C	sucrose; boric acid; ethylene glycol	100	80	Boron carbide, carbon
SB	Melting of components on Si bath at T=165 °C; milling	sucrose; boric acid;	30	95	Boron carbide, carbon
KKB	Evaporation of the water-based solution of boric acid and starch until gelation.	potato starch; boric acid	30	88	Boron carbide, carbon
FB2	evaporation of the ethanol-based solution of the boric acid and PFR; milling	PFR; boric acid	100	90	Boron carbide, carbon
FB1	evaporation of the ethanol-based solution of the boric acid and PFR; milling	PFR; boric acid	0	negligible	Boron carbide (negligible), disordered carbon
TUB	Mechanical mixing of the components in ethanol (12 hours); drying; milling	carbon (tech grade); boric acid	0	negligible	Boron carbide (negligible), disordered carbon

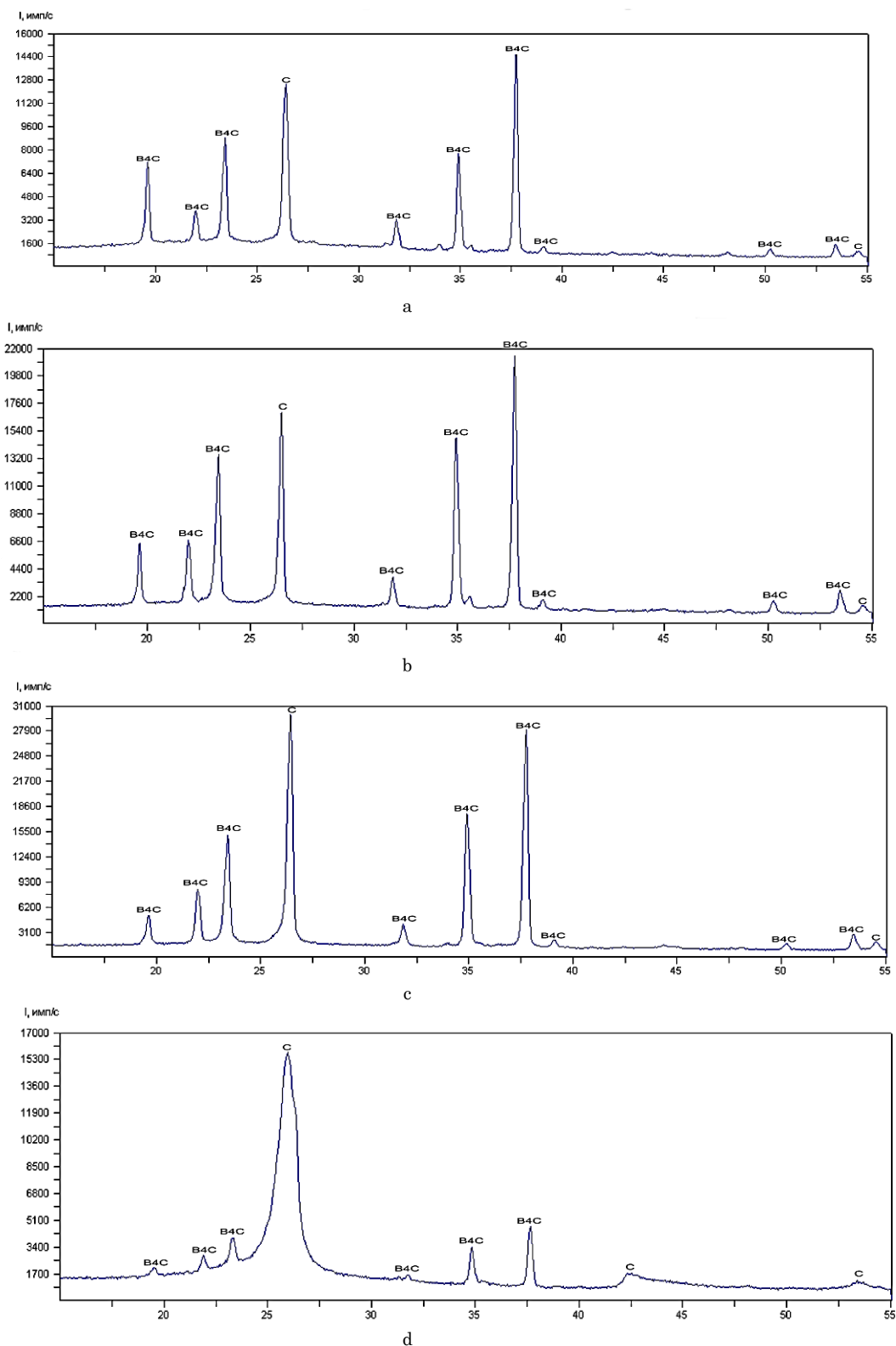


Fig. 1 – X-ray diffraction patterns of the different boron carbide powder samples: SEB (a), SB (b), FB2 (c), FB1 (d)

When sucrose was used for boron carbide synthesis (SEB sample) with significant boric acid excess, the B_4C product predominantly consisted of coarse needle-shaped crystals (see Fig. 2a). When boric acid content in the premix was reduced, and the premix was melt-processed (SB sample) the product yield was maximized, while boron carbide was obtained as single iso-

metric crystals (see Fig. 2b).

Product morphology also depends on the component type and ratio in the initial premix. When PFR was used as carbon source, the boron carbide was obtained as coarse well-faceted crystals coalesced into agglomerates (see Fig. 2c). At lower B : C ratios the crystals are growing on the carbon component residue (see Fig. 2d).

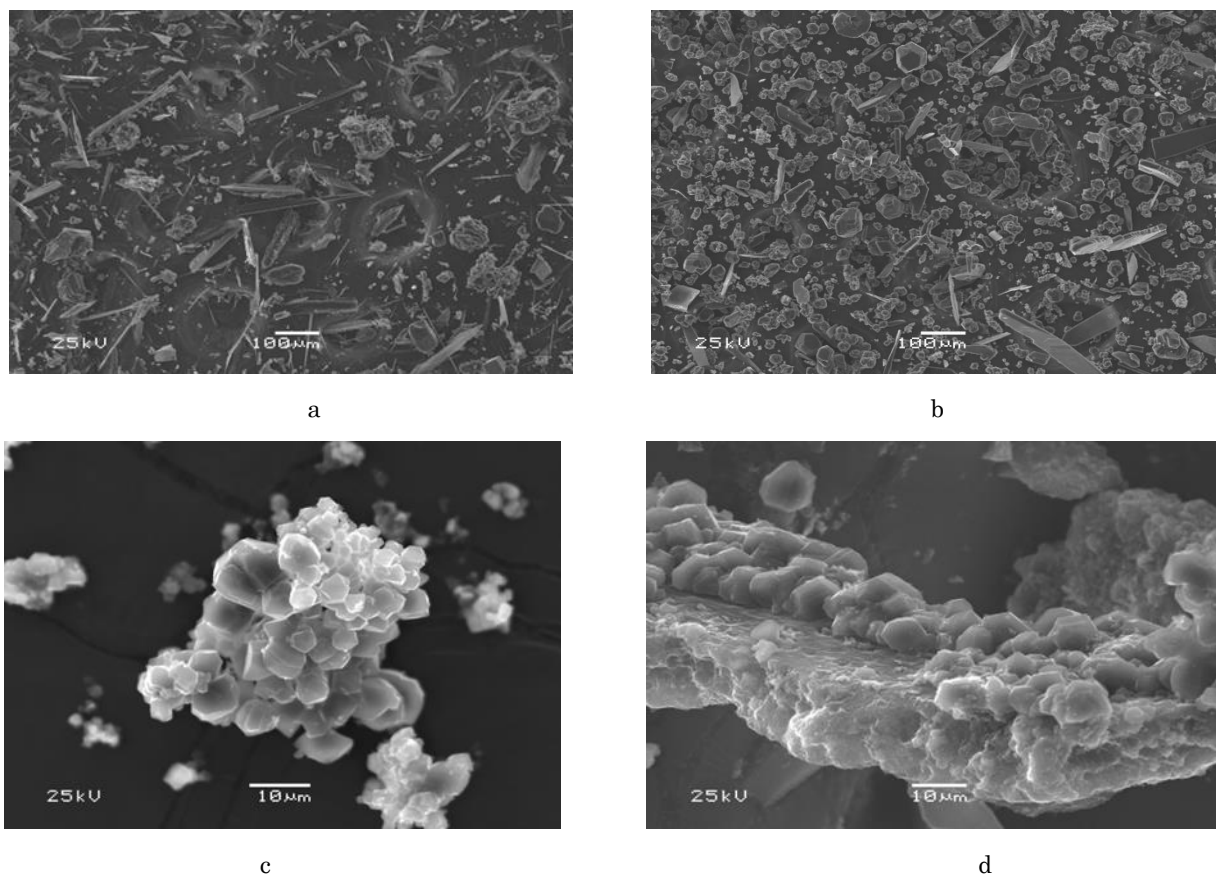


Fig. 2 – Scanning electron micrographs of the different boron carbide powder samples: SEB (a), SB (b), FB2 (c), FB1 (d)

4. CONCLUSIONS

The results of experiments showed that the low-temperature synthesis process using preceramic polymer-containing premixes, as obtained through reaction of the boric acid with organic polymers, it is possible to achieve boron carbide yields of up to 95 % of the initial boron contents.

Boron carbide (B_4C), as processed by the developed technique, shows rhombohedral crystalline structure. Morphology of the final product may be tailored, ranging from isometric to needle-shaped crystallites.

High-energy milling of the synthesized product was an efficient way to obtain boron carbide powder with particles sized of 10 to 150 nm.

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