Boron carbide nanopowder synthesized using electrical discharge plasma

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Abstract. In this paper we present the possibility to realize the direct plasmadynamic synthesis of dispersed crystalline boron carbide in the supersonic jet of boron-carbon electrical discharge plasma flowing into the chamber filled with argon at ambient pressure and temperature. The phase composition was determined using X-Ray diffraction method. The predominance of boron carbide crystalline phase with average particle size of 50 nm was determined. Particles morphology was shown using transmission electron microscopy. The obtained nanosized powder was used to produce the bulk ceramic material using Spark Plasma Sintering method. The hardness and crack resistance values were measured and equal to 35 GPa and 6.5 MPa*m¹/², respectively.

1. Introduction
Boron carbide is one of the superhard materials and attracts an interest due to its high hardness, refractory properties, chemical and wear resistance and low density. Therefore it is used as reinforcing additives in ceramic materials, in cutting tools, nozzles of jet adhesive machining and also as neutron absorber material [1, 2]. In the temperature range above 1000 °C the hardness of this material is higher than the hardness of cubic boron nitride and even diamond [2]. Due to low density and low weight it can be used for low-weight armour ceramic [3].

Synthesis of boron carbide can be realised by different methods, such as carbothermic reduction [1, 2], mechanoynthesis [3], sol-gel method [4] or gas-phase laser synthesis [5]. These methods have a number of well-known disadvantages such as the duration of process, the necessity of implementing high temperature and as a result high energy consumptions. Plasmadynamic synthesis method is one of the alternative ways to solve these problems. This synthesis method is realized in the system based on a pulse high current coaxial magnetoplasma accelerator (CMPA).

This paper shows the experimental results on possibility of plasmadynamic synthesis of nanosized boron carbide in the supersonic electrical discharge plasma jet, generated by CMPA, which is powered from the pulse capacitive energy storage.

2. Experimental
The synthesis was realized with the use of a high current (~100 kA) pulse (~500 μs) CMPA, which generates the supersonic (~2 km/s) electrical discharge plasma jet, flowing into the chamber, filled with argon at ambient pressure and room temperature. The initial powder mix of amorphous boron and carbon black in ratio 4:1 with mass of 1.0 g was put into the plasma formation zone electrodes gap and
slightly pressed. Capacitive energy storage with values of capacity 6.0 mF and charging voltage 3.0 kV was used to supply the system connected to electrodes. The voltage and current waveforms registered during the experiment and calculated curves of power and released energy are shown in figure 1. The opening and collecting of obtained powder product were done after one hour after the experiment. The weight of the collected powder was 0.6 g when 1.0 g of initial precursor mix was loaded.

The synthesized product was investigated using XRD (Shimadzu XRD 7000S, 0.15406 nm), TEM (Philips CM12) and sintered to bulk ceramic material with Dr. Sinter SPS system.

The XRD pattern shown in the figure 2 presents that product is highly crystalline and heterophase. The phase analysis shows that product mainly consists of boron carbide B$_4$C and has some impurities such as graphite, silicon carbide and boron oxide. The calculated lattice parameters $a$ and $c$ for synthesized boron carbide are 0.5601 nm and 0.1209 nm, respectively. It is in a good accordance with the data of ICDD card [01-075-0424 PDF4]. The presence of small amount of impurities can be caused by several reasons. Graphite, eroded from the accelerating channel surface under plasma influence, reacts not only with boron but with silicon, the presence of which can be explained by the electro erosion of the electrodes gap insulator. Boron oxide is a residue from initial amorphous boron powder precursor. But it worth noting the level of impurities does not exceed 5 %. Average value of the boron carbide particle’s CSA is about 45 nm.

3. Results and discussions

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![Figure 1. Voltage, current, power and released energy waveforms of the synthesis process](image1)

![Figure 2. XRD pattern of the synthesized product](image2)
Particles have rounded plate shape and according to TEM data (figure 3) their sizes are in the range of 30 nm up to 200 nm.

**Figure 3.** TEM picture of the synthesized product

Bulk ceramic material was sintered using SPS system with following conditions: temperature 1950 °C, pressure 60 MPa, graphite die diameter 15 mm, rate of temperature rise 100 °C/min, holding time at maximum temperature 5 min. After sintering the ceramic tablet (figure 4) was obtained and polished to measure the density and investigate its phase composition.

**Figure 4.** Bulk ceramic material of the synthesized boron carbide base
The relative density of sintered ceramic was measured by geometric and hydrostatic methods. Both methods show that density value is similar and close to 98% from theoretical density of the boron carbide monocrystall. The XRD pattern of polished boron carbide ceramic sample is shown in the figure 5.

![XRD Pattern](image)

The XRD analysis shows that the lattice parameters of boron carbide ceramic $a$ and $c$ became 0.5606 nm and 0.12084 nm, respectively. Average value of CSA became about 85 nm that indicates on low level of recrystallization of grains during sintering using SPS method. The hardness and crack resistance were measured for the synthesized boron carbide ceramic using Vickers indentation with diamond pyramid. Average values of hardness and crack resistance were 35 GPa and 6.5 MPa*m$^{1/2}$, respectively, that evidence on the increasing of crack resistance in comparison with ceramic produced from micron particle sizes powder with silicon carbide additives intended for improving of the poor crack resistance of pure boron carbide ceramic [6].

5. Conclusions
The possibility of the synthesis of nanosized boron carbide with low amount of impurities using a high current pulse CMPA is shown. The improving of mechanical properties of the boron carbide ceramic produced by SPS method using nanosized powder confirms the suitability of method for producing boron carbide powder.

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