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Spark Plasma Sintering of Boron Carbide Powder

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Abstract

The results presented in this article demonstrate that boron carbide ceramics of a perfect microstructure, of a high density (up to 99.8%) and microhardness (36.1 GPa) can be made from the industrial micron fraction powder thanks to spark plasma sintering, that opens prospects for wide SPS application in economical production of high-quality boron carbide ceramic products.

Optimal ceramics production mode is based on B4C (technical powder), which makes the best combination of physical and mechanical properties and uniform microstructure. The experimentally set mode of spark-plasma sintering of high-density B4C ceramics allows to lower the sintering temperature by 300 °C and to shorten the process time by 20 minutes relative to the corresponding values when traditional hot pressing.

Keywords: spark - plasma sintering, boron carbide, density.

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1. INTRODUCTION

Boron carbide is interesting for its number of beneficial physical and chemical properties. It has a relatively low density, is the third hardest substance (after diamond and cubic boron nitride), has high chemical resistance in various corrosive mediums, has a high neutron capture cross section, is a semiconductor. The main fields of boron carbide application are production of abrasive and cutting materials, nuclear power sector (the material of reactor rods) and production of light armor. Also, boron carbide is used as a thermo- and electrically insulating material and material for microelectronics devices [1, 2].

However, the relatively high cost of raw materials and also difficulty of obtaining densely-sintered boron carbide products largely limits its wide application. Creation of high-density boron carbide products of a controlled structure is associated with certain difficulties, of which the most significant one is low diffusion mobility at temperatures provided for sintering in industrial conditions [3].

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Boron carbide possesses unique physic-mechanical properties due to its strong covalent bonds. On the other hand, covalent nature causes poor compaction of ceramics based on B4C. This origin prevents from sintering without pressure.

According to [4], the initial boron carbide powder compacting begins at a temperature of 1800 °C. The practical temperature of ceramic material creation is above 2200 °C. Additional additives during sintering can improve the compacting process, as well as significantly lower the consolidation temperature. However, a large number of additives worsen properties of the resulting products [5].

Another solution to the problem is alternative powder sintering method usage when pressure is applied. The most popular method is hot pressing, which features a wide range of applied pressures from 20 to 100 MPa. This procedure helps to obtain B4C samples with a relative density higher than 95%. But the processing temperature still exceeds 2150 °C [6].

Method of spark-plasma sintering (SPS) of powders (sintering in a spark discharge plasma) with high consolidation process kinetics has been actively developing in last decade, that makes it possible to lower grain growth and to obtain high-density ceramic materials.

SPS is the most modern method of pressure sintering and has been used by most researchers since 2000. The principle is a joint effect on powder material by pulsed direct current and mechanical pressure. The material in the zone of effect is heated to very high temperatures up to the plasma condition and the mechanical pressure in the zone of effect creates the required properties of the resulting products. Technical SPS implementation has become possible via direct powder heating by passing the DC pulse sequences.

High-density boron carbide was made by SPS-sintering at relatively low pressures of 35 [7] or 120 MPa [8] at temperatures of 2050 to 2100 and 1800 °C, respectively. It's remarkable that not only lower temperature were used, but also the processing time for SPS (5-10 min) was shorter in comparison with other sintering methods. Spark plasma sintering is a powerful alternative to the high-quality boron carbide production.

2. MATERIALS AND METHODS

All the experiments were based on industrial powder B4C. You can see the obtained powder particle size measurement results, SEM images (fig.1-2).

The first milestone is B_4C powder sintering in the Labox-625 machine. The principle is that pulsed direct current and mechanical pressure jointly effect on the powder

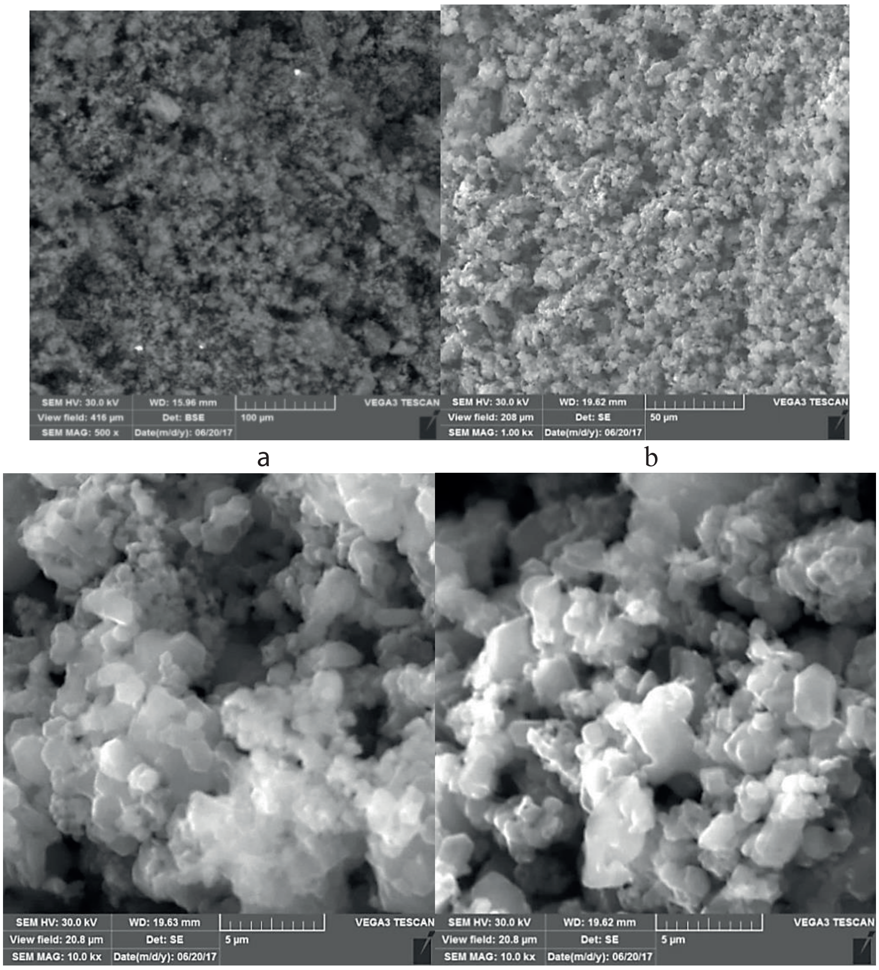

Figure 1: REM powder image. a - magnification 100 μm; b - magnification 50 μm; c - magnification 5 μm; d - magnification 5 μm;

material. TESCAN REM (model VEGA3) photographed structure and size of the sintered tablet grains. The microhardness of the sintered samples was measured by the Vickers method. FM-800 (Future-Tech) microhardnesser was used for that purpose: a diamond tip was automatically loaded with a square tetrahedral pyramid base was used, providing a geometric and mechanical similarity to prints with the deepening of the indenter under the load.

3. RESULTS AND DISCUSSION

Sintering was carried out at four different temperatures and compaction pressures, the processing time was 15 min and did not change in each mode. That was done in order to find out optimal modes for high-density boron carbide ceramics production. Heating and cooling speeds in all the experimental sets did not change and amounted: heating

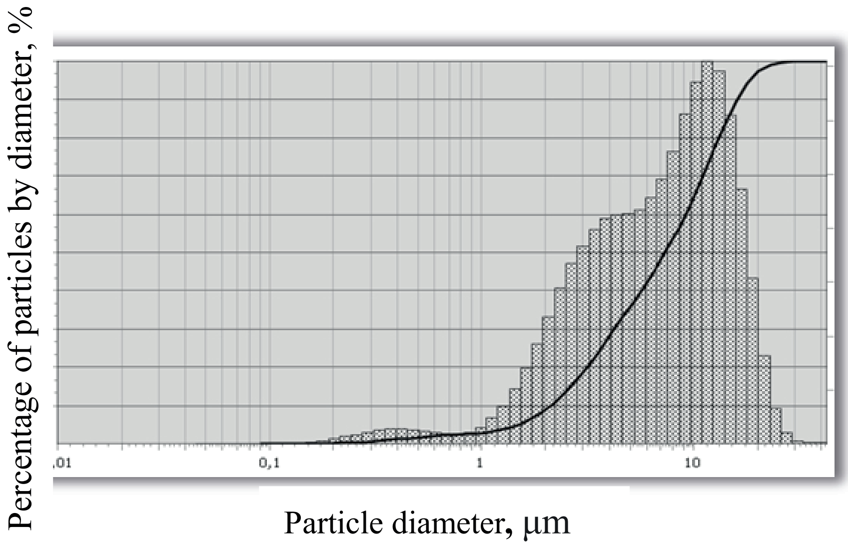

Figure 2: The results of particle size measurements via laser analyzer.

- 300 °C / min, cooling - 200 °C / min. The technological modes of SPS-sintering are given in Table 1.

Table 1: Technological modes of boron carbide ceramics sintering.

Sintering temperature °C / sintering time, min	Compaction pressure, MPa			
1950/15	30	45	60	75
1900/15	30	45	60	75
1850/15	30	45	60	75
1800/15	30	45	60	75

The density ρ of the obtained ceramics samples was determined by measuring the linear dimensions, then the relative density ρ ratio (%) was calculated.

Figure 3 presents graphs of the sintered sample density dependence on the applied pressure in the sintering process at different temperatures, obtained by experimental compaction data processing.

The graphs show that at the highest research temperature 1950 °C, the density dependence on the applied compaction pressure is practically absent, that is, the compaction pressure P does not effect much on the density of the B_4C samples sintered by the SPS method at 1950 °C, and this temperature makes the highest density already at the minimum preload pressures (from 30 MPa). The low applied preload pressure has a significant effect on the density of the boron carbide material at low sintering temperatures, but for these temperatures an increase in pressure from 45 to 75 MPa

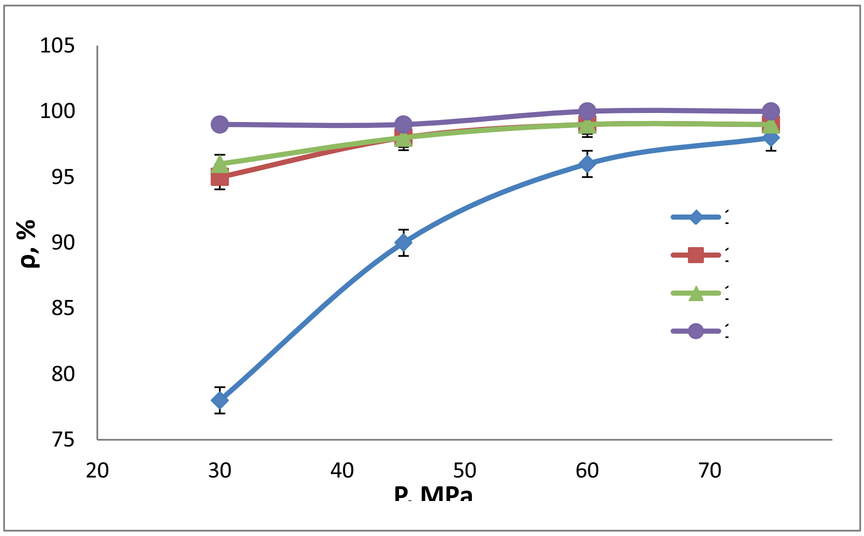

Figure 3: Sintered sample density dependences on the compaction pressure at different SPS temperatures.

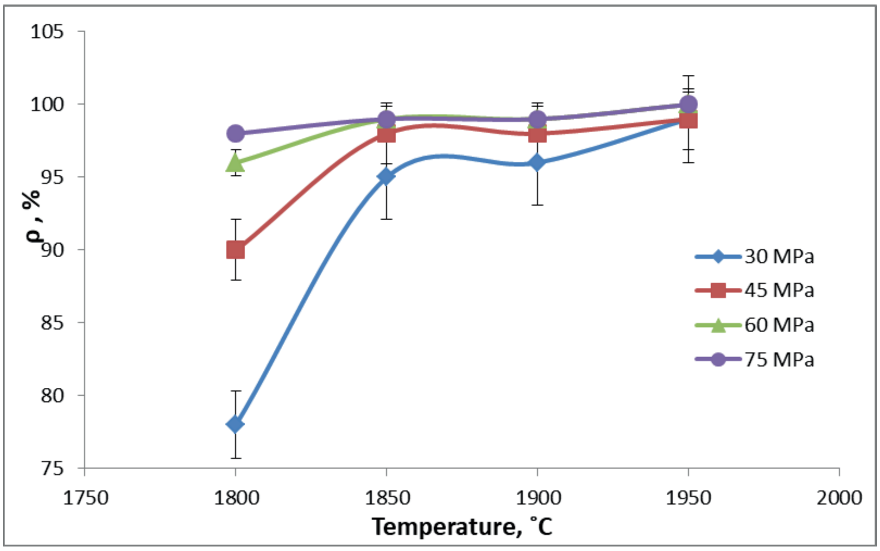

Figure 4: Sintered sample density dependences on the sintering temperatures at different preload pressures.

does not increase the sample density beyond the confidence interval. The determining factor for the test material density increase (when SPS is carried out) is the sintering temperature (Fig. 4)

The different effect is discovered when analyzing other characteristics of ceramics. Figure 5 shows the sintered B_4C sample microhardness dependences on the preload pressure P at the same sintering temperature.

Figure 6 describes the microhardness dependences on temperature at the same preload pressure. A significant preload pressure influence on the achieved level of

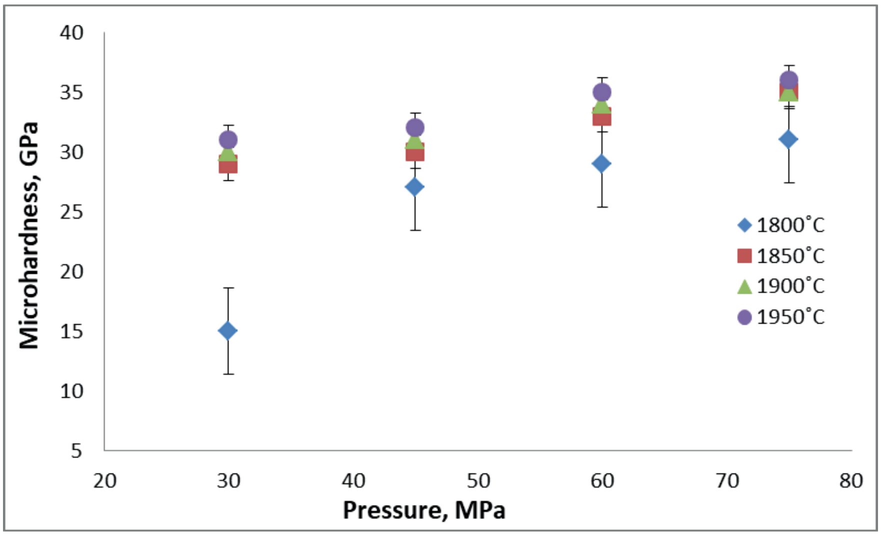

Figure 5: Sintered B_4C sample microhardness dependences on the preload pressure.

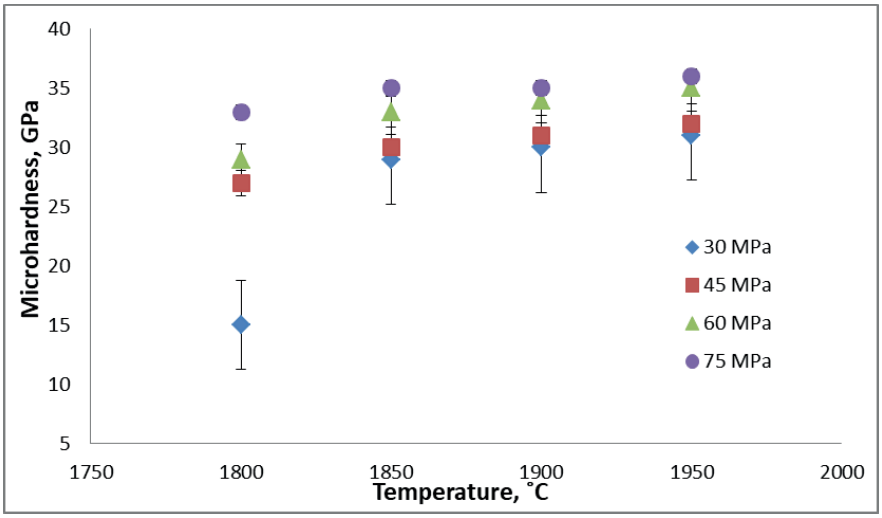

Figure 6: Sintered B_4C sample microhardness dependences on the sintering temperature.

microhardness is traced at any sintering temperature. The sintering temperature influence is expressed to lesser extent, and its increase from 1900 to 1950 °C does not make a significant microhardness growth.

The key factor for the perfect B_4C structure is the density depending significantly on the temperature. Analyze the obtained samples: 1800 °C / 30 MPa mode does not provide durable B4C tablet production, as the density of such ceramics does not exceed 78% (Fig. 3).

The maximum microhardness value can be discovered on a sample obtained at 1850 °C / 75 MPa (Fig.5-6).

In overall, the influence made by the sintering temperature and the preload pressure on the obtained properties of ceramics is consistent with the classical sintering theory, and the general trend is confirmed by other scientific teams' research in boron carbide powder sintering via SPS method [9-12]. Reported in the experiments deviations of microhardness linear dependences on temperature can be explained by the high-temperature test material deformation features, when the stress fluctuation occurred during its consolidation continues to function after sintering as the remainders and increases resistance during indentation. Thus, in spite of the fact that the maximum values of the ceramics density can be achieved already at the minimum preload pressure values, it is reasonable to maintain a relatively high level of pressure along with an increased sintering temperature in order to achieve high microhardness values.

Analysis of the microstructure of the obtained ceramics samples (Fig.7) confirms that temperature of 1800 °C provides the start of grain sintering and interparticle bond (intergranular boundaries) formation. Contacts between the powder particles are imperfect in nature, the cleavage passes along the intergrain boundaries, which indicates their weak connection. The grain growth during sintering is practically absent: the average grain size corresponds to the size of the initial powder particle - 6 μm. The ceramics grain size is comparable to the pore size in the entire volume.

Figure 7 b describes a structure formed under more intense sintering conditions. The grain interparticle contact is more perfect (has a larger area). The average grain size does not exceed 6 μm, but there are local sintered grain formations up to 10 μm in size. The content of consolidated grains is higher than in structure obtained at 1800 °C, but intergranular bond durability is still low and does not let consider such ceramics as a structural material.

Thus, boron carbide micron powder compaction begins at almost 1300 °C. The intensive SPS process starts at a temperature above 1800 °C. The quality consolidated structure formation should be expected at temperatures above 1850 °C. At the same time, the porosity changes from open to closed. Meanwhile, a relatively short sintering time (2 minutes - heating at 300 °C - from 1850 to 1950 °C and holding for 15 minutes) limits the grain growth: from 5 to 10 μm. The number of pores and their size intensively lowers while the temperature increases, and already it is less than 2% of the volume of the ceramic with a size of not more than 1 μm at 1900 °C.

4. CONCLUSIONS

This complex of experimental studies on ceramics spark-plasma sintering (SPS) was based on industrial B_4C powder and determination of its physical-mechanical properties (density, microhardness, durability), its structure and elemental composition and now it's time to make conclusions:

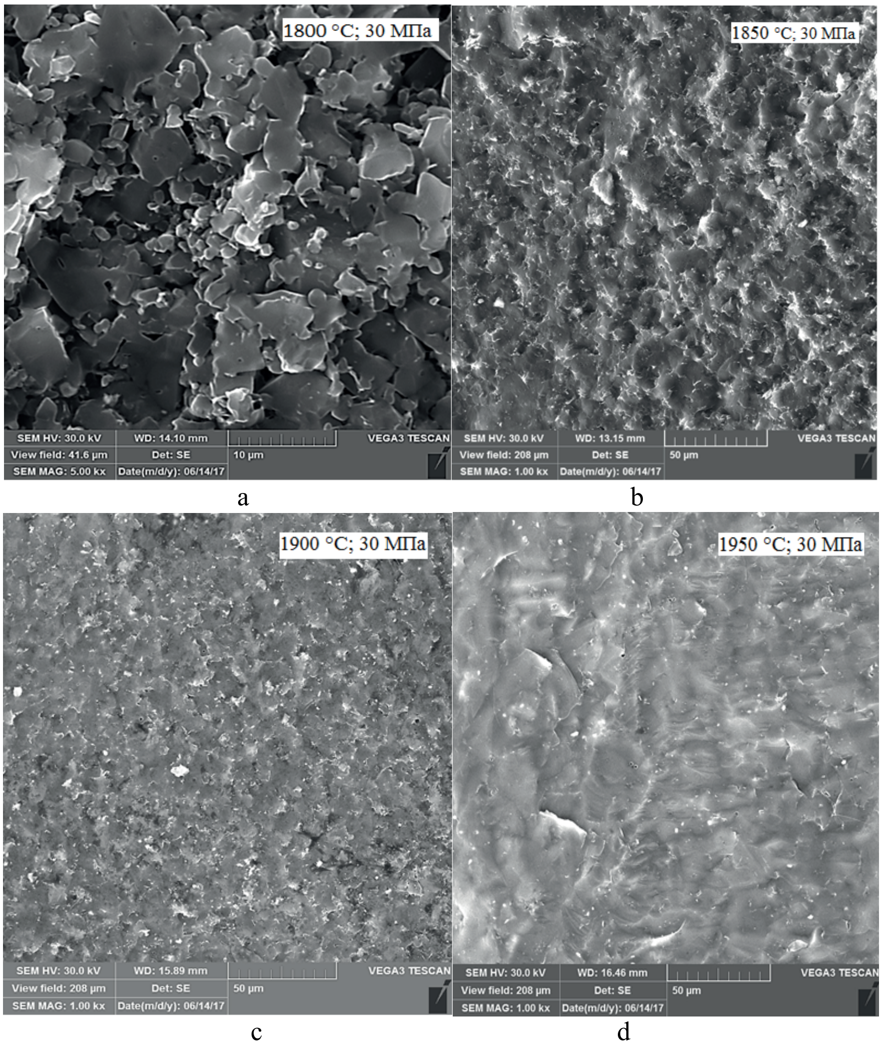

Figure 7: Sintered ceramics grain structure evolution when sintering temperature increases: a – magnification 100 μm; b - magnification 50 μm; c - magnification 5 μm; d - magnification 5 μm .

1. The possibility of obtaining of structural ceramics based on high density boron carbide, a uniform microstructure, with a microhardness of 35.1 GPa for a shorter processing time in comparison with traditional hot pressing methods has been revealed. SPS time reduction is achieved by the sintered product heating and cooling speed increases.

2. The optimal mode for production of ceramics based on B4C from a technical powder is recommended, as it makes the best combination of physical and mechanical properties and a uniform microstructure:

   - Sintering temperature: 1850 °C;
   - Preload pressure: 75 MPa;
   - Sintering (holding) time: 15 min;
   - Heating speed is 300 °C / min, cooling speed is 200 °C / min.

3. It has been discovered that sintering by the SPS method makes it possible to make technically pure products with a minimum amount of impurities.

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