1. Introduction

Boron carbide B₄C has been widely used due to its excellent physical and, above all, mechanical characteristics. This material takes the third place in hardness, following diamond and cubic boron nitride. High hardness, elastic modulus, strength, wear resistance, and chemical stability in combination with low density and high thermal conductivity resulted in a widespread application of this material as a grinding powder, for protective and wear-resistant coatings, cutting tools and dies, and water-jet cutting nozzle (blasting nozzles).

By means of chemical reactions, B₄C is produced as powder, and for industrial applications, it is consolidated, mainly by hot pressing methods [1,2] and spark plasma sintering [3].

The hardness, tensile strength, elastic modulus, elastic wave velocity, and nonlinear mechanical properties of B₄C ceramics have been quite intensively studied with dynamic methods (shock-wave compression and Hugoniot’s analysis). This involves the use of this material as armor protection where such characteristics as toughness, ductility, and tensile strength are important. There is a lot of studies focused on the velocity of ultrasonic waves and associated elastic modulus [4-8]; theoretical analysis and calculation of the elastic constants held in [9].

There are a number of detailed reviews on the synthesis, sintering, physical properties, and applications of B₄C [10-12]. There have been recent work on the measurement of hardness and Young’s modulus of single crystals and films of B₄C by nanoindentation [13-15].

As stated, the mechanical and elastic B₄C ceramic properties depend on the composition and structure of the material, the structure and its uniformity are determined largely by the sintering parameters of the sample. So we were interested to study the local elastic properties (Young’s modulus and hardness) of B₄C ceramics, compared with the integral (averaged over the volume) ones. Local mechanical properties were studied by nanoindentation and scanning force microscopy methods, and the integral properties – by ultrasonic method for measuring the elastic modulus and microhardness measurements.

2. Experimental procedure

2.1. Materials and processing

Industrial boron carbide powder of a CB-16 brand was milled in a ball mill together with the sintering additives. The amount of additives did not exceed 3%. Milling had been carried out by grinding bodies of boron carbide in an isopropyl alcohol medium for 4 days. An average particle size of the milled boron carbide defined by Fischer apparatus was 1.6 μm. After the milling, the alcohol was evaporated at 80 °C. A plasticizer was added to the dried powder, a solution of rubber in gasoline for this purpose.

Consolidation of the powder for sintering was performed with uniaxial pressing in a steel mould at a pressure of 30 MPa.

Sintering was carried out under pressure in the graphite moulds. To remove the plasticizer, the preform was heated to 600 °C at a rate of 10°C/min and maintained under vacuum for 30 minutes. After that, we produced a rapid heating under the pressure of 150 MPa at 10°C/min to the maximum temperature of 1950°C. The exposure at a maximum temperature lasted 40 minutes.

The resulting products were treated mechanically with a diamond tool up to the predetermined geometrical shapes and sizes.

2.2. Experimental

For this study, we used five B₄C ceramic samples size 40×30×30 mm³, from a party of twenty four (24) pcs.

The density of the samples was measured using the KERN-770-60 electronic laboratory scales (Germany, class according to GOST 24104-88-1) with a Sartorius YDK 01 LP attachment for measuring the density. For different samples, the densities ranged from 2.51 to 2.55 (± 0.01) g/cm³.

Chemical composition in the ceramic sample as determined by Energy-dispersive X-ray spectroscopy (JSM-7600F scanning electron microscope) on the cleavage surface is represented in the table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>k Ratio</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Intensity</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Kα</td>
<td>0.00050</td>
<td>0.01900</td>
<td>0.016</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>Fe Kα</td>
<td>0.00273</td>
<td>0.01186</td>
<td>0.022</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>Si Kα</td>
<td>0.00373</td>
<td>0.00373</td>
<td>0.00373</td>
<td>0.00373</td>
<td>0.00373</td>
</tr>
<tr>
<td>Al Kα</td>
<td>0.01186</td>
<td>0.01186</td>
<td>0.01186</td>
<td>0.01186</td>
<td>0.01186</td>
</tr>
<tr>
<td>C Kα</td>
<td>0.01900</td>
<td>0.01900</td>
<td>0.01900</td>
<td>0.01900</td>
<td>0.01900</td>
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<tr>
<td>B Kα</td>
<td>0.65914</td>
<td>0.65914</td>
<td>0.65914</td>
<td>0.65914</td>
<td>0.65914</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The carbon concentration in the sample exceeds the upper limit of ~21.6 at.% for the B₄C phase, the formation of the small clusters of free carbon in the ceramic sample may be possible and the sample in this case sintered as a composite consisting from the B₄C and carbon phases (c-B₄C+C). Large error in the determination of the concentration of boron and carbon measurements due the measurements on the cleaved surface without its pretreatment.

XRD analysis was undertaken to identify the crystalline phases present after sintering. X-ray diffraction data obtained by a TETA ARL X’TRA powder diffractometer for structure investigation with a Peltier detector are plotted in Fig.1.
The elasticity map (Fig. 2b) clearly shows the light-spot bounded inclusions, which are more rigid, i.e. have greater value of elastic modulus (marked with blue dashed lines).

The quantitative measurements of elastic (Young's) modulus were carried out using force spectroscopy technique. This technique is based on recording the dependency of oscillating probe sensor resonant frequency shift versus indenter penetration depth into the sample surface during indentation. The elastic modulus value is proportional to the slope of the graph line in "frequency shift squared"-"penetration depth". Fig. 3 shown typical experimental dependencies of sensor frequency squared versus indenter penetration depth. Blue line correspond to more rigid areas on the surface (marked with dashed line on Fig. 2) and red line correspond to the surrounding binder material.

![Diagram](Image)

**Table 2. Ultrasonic and elastic properties of the B4C ceramics (average) at ambient state**

<table>
<thead>
<tr>
<th></th>
<th>V_L, km/s</th>
<th>V_S, km/s</th>
<th>C_L, GPa</th>
<th>C_S, GPa</th>
<th>E, GPa</th>
<th>K, GPa</th>
<th>σ, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.93</td>
<td>8.62</td>
<td>486</td>
<td>114</td>
<td>186</td>
<td>443</td>
<td>238</td>
<td>0.19</td>
</tr>
<tr>
<td>13.42</td>
<td>8.43</td>
<td>440</td>
<td>130</td>
<td>215</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.75</td>
<td>8.11</td>
<td>543</td>
<td>165</td>
<td>234</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.30</td>
<td>8.93</td>
<td>562</td>
<td>124</td>
<td>247</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.08</td>
<td>8.60</td>
<td>197</td>
<td>462</td>
<td>235</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The measured values of Young's modulus 530 ÷ 540 GPa. Kulikovsky et al., in the study of mechanical properties of the BCx films by nanoindentation [15,16] found that Young’s modulus were in the range from 250 to 402 GPa, and hardness exceed that of the bulk B4C single crystal, depending on the locations of measurement. In these studies indicated a large scatter in the measured hardness and Young's modulus as a function of the area at the surface, where the modules are measured.

**2. Results and discussion**

First, we note that the average value of the reduced elastic (Young’s) modulus for hard areas and the surrounding matrix 425 GPa, which is in good agreement with the integral (volume) value of Young's modulus determined by the acoustic method 443 GPa. There remains, however, the issue of abnormally high modulus value for the superhard inclusions. Measurements by means of nanoindentation on single crystal B4,3C, carried out in [14], gave values of Young's modulus 530 ÷ 540 GPa. Kulikovsky et al., in the study of mechanical properties of the B4C ceramics, found 78 GPa, and in the range of 90 ÷ 100 GPa, respectively.
4. Conclusion

B4C ceramic samples were prepared from the powder mixture with the 1.6 μm size boron carbide particles by hot pressing at a pressure of 150 MPa and a temperature of 1950 °C. The phases and elemental composition in the powders and sintered samples was analyzed by X-ray diffraction and Energy-dispersive X-ray spectroscopy, respectively. These studies have shown that the carbon concentration in the sample exceeds the upper limit of ~21.6 at.% for the B4C phase, the formation of the small clusters of free carbon in the ceramic sample may be possible and the sample in this case sintered as a composite consisting from the B4C and carbon phases (c-B4C+C).

Bulk elastic constants of B4C ceramic were calculated based on the measured values of the density and velocity of bulk acoustic wave (BAW) in the samples. Comparative analysis of the obtained values showed good agreement with the published data.

The local elastic modulus (the Young’s modulus) were determined from the dependence of detected change in the resonant frequency of the oscillating sensor mounted thereon indenter from indentation depth the surface of the sample. These measurements were performed on fresh chipped surface by scanning nano-indentation depth the surface of the sample. The samples were examined by scanning force microscopy.

We found a significant heterogeneity at the surface stiffness of the sample. Young's modulus of the surface areas with high stiffness values reached 760 GPa, while the Young's modulus with a small rigidity portions was 90 GPa. However, the average value of modules ~ 425 GPa is in good agreement with the value of the bulk Young's modulus determined by the acoustic method.

The heterogeneity of the mechanical properties of the surface of the sample is due to the composition of the ceramic B4C. Superhard areas probably consist of phases BCx and soft ones - phases of pure carbon, amorphous possible. The composite structure of the sample can significantly change the resulting modulus and hardness.

5. References