

# DETERMINATION WITH INTEGRAL ULTRASONIC METHOD AND LOCAL FORCE MICROSCOPY METHOD OF ELASTIC PROPERTIES OF B<sub>4</sub>C CERAMICS PREPARED BY HOT PRESSING

Dr. Prokhorov V.<sup>1</sup>, dr. Perfilov S.<sup>1</sup>, dr. Useinov A.<sup>1</sup>, Veprincev K.<sup>2</sup>, Gnidash C.<sup>2</sup>, Kuftyrev R.<sup>2</sup>  
Technological Institute for Superhard and Novel Carbon Materials <sup>1</sup>, Russia  
Ltd "Technical Ceramics Plant"<sup>2</sup>, Russia

**Abstract:** B<sub>4</sub>C ceramic samples were prepared from the powder mixture with the 1.6 mkm size boron carbide particles by hot pressing at a pressure of 150 MPa and a temperature of 1950 °C. Exposure time at a maximum temperature was 40 minutes.

The phases and elemental composition in the powders and sintered samples was analyzed. Bulk densities of samples were measured by the Archimedes method. The hardness were measured using a Vickers indenter. The elastic constants of B<sub>4</sub>C ceramic were calculated based on the measured values of the density and velocity of bulk acoustic wave (BAW) in the samples. Measure the velocities of BAW were made by pulse-echo method using a laser opto-acoustic excitation of ultrasonic pulses.

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. We investigated the surface of fresh cleavage. A comparative analysis and discussion of the results are made.

**KEYWORDS:** PETROL-ETHANOL BLENDS, SPARK IGNITION ENGINES, OCTANE NUMBER, HEATING VALUE

## 1. Introduction

Boron carbide B<sub>4</sub>C 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, B<sub>4</sub>C 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 B<sub>4</sub>C 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 B<sub>4</sub>C [10-12].

There have been recent work on the measurement of hardness and Young's modulus of single crystals and films of B<sub>4</sub>C by nanoindentation [13-15].

As stated, the mechanical and elastic B<sub>4</sub>C 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 B<sub>4</sub>C 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 100 °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 B<sub>4</sub>C ceramic samples size 40×30×30 mm<sup>3</sup>, 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/cm<sup>3</sup>.

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 1. Chemical composition of the B<sub>4</sub>C ceramic sample

| Element | k Ratio | Weight% | Weight%<br>Sigma | Intensity<br>Corn. | Atomic% |
|---------|---------|---------|------------------|--------------------|---------|
| Ni Kα   | 0.00050 | 0.051   | 0.070            | 0.7566             | 0.010   |
| Fe Kα   | 0.00273 | 0.276   | 0.043            | 0.7603             | 0.055   |
| Si Kα   | 0.00373 | 0.324   | 0.022            | 0.8834             | 0.129   |
| Al Kα   | 0.01186 | 0.451   | 0.016            | 1.0677             | 0.187   |
| C Kα    | 0.01900 | 26.674  | 0.562            | 0.0547             | 24.854  |
| B Kα    | 0.65914 | 72.224  | 0.558            | 0.7008             | 74.765  |
| Totals  |         | 100.000 |                  |                    |         |

The carbon concentration in the sample exceeds the upper limit of ~21.6 at.% for the B<sub>4</sub>C 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 B<sub>4</sub>C and carbon phases (c-B<sub>4</sub>C+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.

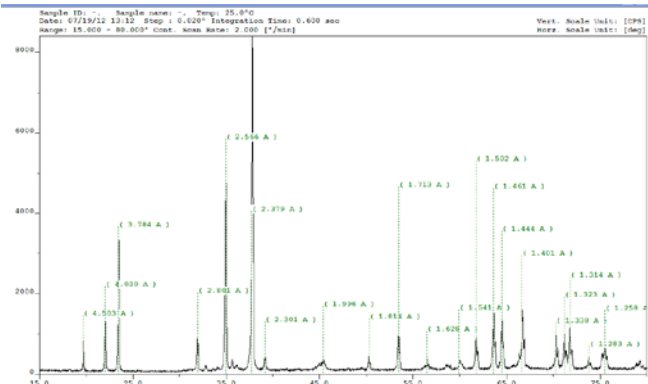


Fig. 1. XRD pattern of a  $B_4C$  ceramic sintered at pressure 150 MPa and maximum temperature 1950 °C.

The hardness were measured using a Vickers indenter (hardness tester DuraScan 10/20) with a 10 N load for 15 seconds. Average hardness value was 34 GPa.

The elastic constants of  $B_4C$  were calculated based on the measured values of the density and velocity of bulk acoustic wave (BAW) in the samples. The BAW velocities were measured with a pulse-echo method using a laser opto-acoustic excitation of ultrasonic pulses [16]. The velocities of longitudinal  $V_L$  and shear  $V_T$  BAWs defined with high precision allowed, in the approximation of an isotropic solid, to compute elastic constants  $C_{ij}$ , Young's modulus  $E$ , bulk modulus  $K$ , and Poisson's ratio  $\sigma$  in the samples.

Numerical values of these modules are presented in Table 2

Table 2. Ultrasonic and elastic properties of the  $B_4C$  ceramics (average) at ambient state

| $V_L$ ,<br>km/s      | $V_S$ ,<br>km/s     | $C_{11}$<br>GPa    | $C_{12}$<br>GPa    | $C_{44}=G$<br>GPa  | $E$<br>GPa         | $K$<br>GPa          | $\sigma$            |
|----------------------|---------------------|--------------------|--------------------|--------------------|--------------------|---------------------|---------------------|
| 13.93 <sup>a</sup>   | 8.62 <sup>a</sup>   | 486 <sup>a</sup>   | 114 <sup>a</sup>   | 186 <sup>a</sup>   | 443 <sup>a</sup>   | 238 <sup>a</sup>    | 0.19 <sup>a</sup>   |
| 13.42 <sup>[4]</sup> | 8.43 <sup>[4]</sup> |                    |                    | 179 <sup>[4]</sup> | 420 <sup>[4]</sup> | 215 <sup>[4]</sup>  | 0.17 <sup>[4]</sup> |
| 13.78 <sup>[6]</sup> | 8.11 <sup>[8]</sup> | 543 <sup>[8]</sup> | 130 <sup>[8]</sup> | 165 <sup>[8]</sup> | 448 <sup>[7]</sup> | 234 <sup>[10]</sup> | 0.21 <sup>[7]</sup> |
| 14.3 <sup>[5]</sup>  | 8.93 <sup>[5]</sup> | 562 <sup>[6]</sup> | 124 <sup>[7]</sup> | 200 <sup>[5]</sup> | 472 <sup>[5]</sup> | 247 <sup>[5]</sup>  | 0.18 <sup>[5]</sup> |
| 14.08 <sup>[9]</sup> | 8.86 <sup>[9]</sup> |                    |                    | 197 <sup>[9]</sup> | 462 <sup>[9]</sup> | 235 <sup>[9]</sup>  | 0.17 <sup>[9]</sup> |

<sup>a</sup> – present work

Local mechanical properties were measured with scanning nano-hardness tester «NanoScan-3D» (FSBI TISNCM, Russia) [18-20]. This instrument is designed for investigation of topography and mechanical properties of materials surface with high spatial resolution. The design of the probe sensor allows both obtaining the topography profile simultaneously with elastic modulus mapping in scanning probe microscopy (SPM) mode and doing dynamic or static nanoindentation tests for quantitative measurements of hardness and elastic modulus. The diamond pyramid of Berkovich type is used as a tip for both topography imaging and indentation.

Local elastic properties of  $B_4C$  samples were performed on a surface of fresh cleavage without any additional surface treatment. Typical images of surface topography and elastic modulus map obtained in SPM mode are shown on Fig. 2.

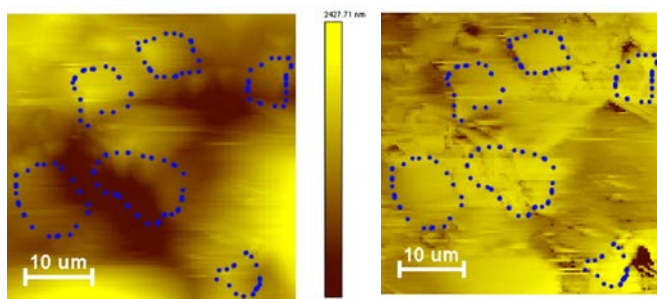


Fig. 2. Surface topography (a) and elastic modulus map (b) of sample surface.

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.

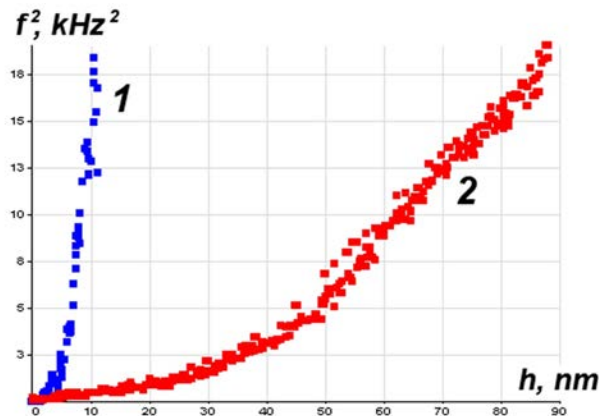


Fig. 3. Experimental dependencies of sensor frequency squared versus indenter penetration depth for rigid (blue line) and soft (red line) areas on the sample surface.

According to the curves in Figure 3 the calculated value of reduced elastic (Young's) modulus of the rigid areas is  $760 \pm 60$  GPa and for the surrounding binder material is  $90 \pm 30$  GPa.

## 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  $B_4C$ , carried out in [14], gave values of Young's modulus  $530 \div 540$  GPa. Kulikovskiy et al., in the study of mechanical properties of the  $B_4C$  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  $B_4C$  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.

Based on the analysis of our study and literature data, it can be assumed that such behavior of mechanical properties may be caused by inhomogeneous of the microstructure, namely, by a composite structure due to some segregation of locally excessive carbon.

The excess of carbon can lead to the synthesis of new cubic  $BC_x$  phases such as detected and examined in the study by Richter et al. [21], where new phase was obtained by thermobaric treatment in diamond anvil cells. The measured by multicyclic nanoindentation hardness and modulus of new superhard cubic  $BC_x$  phase, were 78 GPa, and in the range of 900 to 1000 GPa, respectively.

#### 4. Conclusion

B<sub>4</sub>C ceramic samples were prepared from the powder mixture with the 1.6 mkm 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 B<sub>4</sub>C 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 B<sub>4</sub>C and carbon phases (c-B<sub>4</sub>C+C).

Bulk elastic constants of B<sub>4</sub>C 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-hardness tester «NanoScan-3D», operating on the principle of 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 B<sub>4</sub>C. Superhard areas probably consist of phases BC<sub>x</sub> 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

- [1] Kim H-W., Y-H. Koh, H-E. Kim. Reaction sintering and mechanical properties of B<sub>4</sub>C with addition of ZrO<sub>2</sub>. *J. Mater. Res.*, **15**, 2000, 2431–2436.
- [2] Deng J., J. Zhou, Y. Feng, Z. Ding. Microstructure and mechanical properties of hot-pressed B<sub>4</sub>C/(W, Ti)C ceramic composites. *Ceramics International*, **28**, 2002, 425–430.
- [3] Kim K. H., et al. Sintering behavior and mechanical properties of B<sub>4</sub>C ceramics fabricated by spark plasma sintering. *J. of Ceramic Processing Research*, **10**, 2009, 716–720.
- [4] Zhang Y., et al. Shock compression behaviors of boron carbide (B<sub>4</sub>C). *J. Appl. Phys.*, **100**, 2006, 113536-5.
- [5] Gieske J. H., T. L. Aselageand, D. Emin. "Elastic Properties of Boron Carbides"; pp.376–9 in *Boron-Rich Solids*. AIP Conf. Proc., Vol.231, Edited by D. Emin, T. Aselage, C. L. Beckel, A. C. Switendick, and B. Morosin. American Institute of Physics, NewYork, 1991.
- [6] Добролюбов А. Ю., К. М. Воскобойников. Скорость звука в ударно-сжатых корунде, карбиде бора и карбиде кремния. *Ж. Тех. Физ.*, **63**, 1993, 203–208.
- [7] Murthy S. R. Elastic Properties of Boron Carbide. *J. Mater. Sci. Lett.*, **4**, 1985, 603–5.
- [8] McClellan K. J., F. Chu, J. M. Roper, and I. Shindo. Room Temperature Single Crystal Elastic Constants of Boron Carbide. *J. Mater. Sci.*, **36**, 2001, 3403–7.
- [9] Manghnani M.H., Y. Wang, F. Li, et al. Elastic and Vibrational Properties of B<sub>4</sub>C to 21 GPa. pp. 945-948. in *Science and Technology of High Pressure*, Edited by M. H. Manghnani, W. J. Nellis, and M. F. Nicol. Universities Press, Hyderabad, India, 2000.
- [10] Lee S. B., D. M. Bylander, and L. Kleinman. Elastic Moduli of B-12 and its Compounds. *Phys. Rev.*, **B45**, 1992, 3245–7.
- [11] Sury A. R., C. Subramanian, J. K. Sonber and T. S. R. Ch. Murthy. Synthesis and consolidation of boron carbide: a review. *Int. Mater. Rev.*, **55**, 2010, 4–40.
- [12] Thévenot F. Boron carbide - a comprehensive review. *J. Eur. Ceram. Soc.*, **6**, 1990, 205–225.
- [13] Domnich V., S. Reynaud, R. A. Haber, and M. Chhowalla. Boron Carbide: Structure, Properties, and Stability under Stress. *J. Am. Ceram. Soc.*, **94**, 2011, 3605-3628.
- [14] Domnich V., Y. Gogotsi, M. Trenary and T. Tanaka. Nanoindentation and Raman spectroscopy studies of boron carbide single crystals. *Appl. Phys. Lett.*, **81**, 2002, 3783–3786.
- [15] Kulikovskiy V., V. Vorliceck, P. Bohac et. al. Mechanical properties and structure of amorphous and crystalline B<sub>4</sub>C films. *Diam. and Related Mater.*, **18**, 2009, 27–33.
- [16] Куликовский В. Ю., В. І. Иващенко, М. І. Даниленко и др. Структурні та механічні властивості аморфних і полікристалічних плівок B<sub>4</sub>C. *Наноструктурное материаловедение (Украина)*, №2, 2009, 83–92.
- [17] Гусев В. Э., А. А. Карабутов. *Лазерная оптоакустика*. М.; Наука. 1991. 304 с.
- [18] Усеинов А. С. Измерение модуля Юнга сверхтвердых материалов с помощью сканирующего зондового микроскопа «НаноСкан». *Приборы и техника эксперимента*, №1, 134–136. 2004.
- [19] Useinov A., K. Gogolinskiy, V. Reshetov. Mutual consistency of hardness testing at micro- and nanometer scales. *Int. J. Mater. Res.*, No. 7, 2009, 968–972.
- [20] Useinov A. S., S. S. Useinov. Scratch hardness evaluation with in-situ pile-up effect estimation. *Phil. Magazine*, **92**, 2012, 3188–3198.
- [21] Richter A., Ch. P. Daghljanb, R. Riesc, V. L. Solozhenko. Investigation of novel superhard materials by multi-cycling nanoindentation. *Diam. and Related Mater.*, **15**, 2006, 2019–2023.