Effect of carbon nanotubes on ballistic armour performance of ceramics from boron carbide

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Abstract. The structure, phase composition and properties of hot-pressed mixtures based on boron carbide (B₄C) and carbon nanotubes (CNT) were studied. Used boron carbide powder was produced by LLC PIChT and CNTs were made in Russia and Korea. Sintering was carried out in vacuum at 2100 ºC and under the pressure of 30 MPa. The samples of ceramics have been obtained with the ballistic armour performance, which is ~ 26% higher than that of ceramic samples without additives.

1. Introduction

One of the global trends in armor-plating of ground and aircraft equipment is the use of ceramic armor, which is lighter than steel and not inferior to it in terms of strength. Elements of ceramic armor find wide application in production of personal protective equipment, military automobiles, airplanes and helicopters. Boron carbide (B₄C) appears to be a promising ceramic material used for such armor. B₄C has extremely high hardness (38 GPa) and low specific gravity (compared with armored steel and aluminum oxide), and the Young modulus (460 GPa), which is close to the corresponding values for diamond [1].

The disadvantage of ceramics based on B₄C is a low value of crack resistance. One of the effective ways to increase the fracture toughness of ceramics is the formation of various heterogeneous structures that contribute to the deviation of the crack trajectory, its branching and lead to an increase in energy dissipation during fracturing. Therefore, the initial ceramic matrix is reinforced either with fibers or with dispersed solid particles. As a result of a dissimilar substances combination, we can obtain the materials that combine the initial strength of the ceramic matrix and increased crack resistance owing to reinforcing components.

One of the most promising approaches to improving the mechanical properties of B₄C-based ceramics is the introduction of reinforcing elements, i.e. particles and fibers into its matrix, which can significantly improve its strength characteristics such as the elastic modulus, crack resistance, strength, hardness, and increase of resistance to wear. For these purposes, the use of carbon nanotubes (CNTs) is the most promising, due to the uniqueness of their properties: high tensile strength (up to 1500 GPa), high Young’s modulus (~1 TPa), high thermal and corrosion resistance, high thermal...
conductivity (> 3000 W·m⁻¹·K⁻¹), high electrical conductivity (> 105 S·m⁻¹) and low density (1.4 g·cm⁻³) [2].

In [3], data are presented on the study of composite ceramics based on B₄C multi-wall CNTs (MWCNTs) fabricated by hot pressing. The isothermal exposure time was 60 min, pressing was carried out at 1950 °C, and pressure reached 60MPa. Modification of boron carbide MWCNTs (0.5…10 vol. %, diameter ~ 150 nm) results in high values of bending strength (~ 400 MPa), hardness (11 GPa), crack resistance (4.2 MPa·m⁻¹²) and change in the density of the obtained material. According to [4], MWCNTs (d ~ 150 nm) introduction into a boron carbide matrix leads to an increase in crack resistance (up to 7.9 MPa·m⁻¹²) of B₄C ceramics obtained by the method of spark plasma sintering. The increase of following parameters is also noted by the authors: resistance to bending (710 MPa) and microhardness (36 GPa). According to [5], modification of boron carbide with carbon nanotubes (average diameter 15 nm) tends to improve the mechanical properties of the fabricated composite compared to the initial material, in particular, the ultimate tensile strength.

The research was conducted on a single carbon nanotube coated with boron carbide. An abnormally high value of the flexural strength was observed (~ 25000 MPa), which is several orders of magnitude higher than in unmodified B₄C ceramics. The experimental data [6] also indicate a significant improvement in strength characteristics of carbon modified B₄C ceramics. Ceramic samples were obtained by hot pressing method (the duration of isothermal exposure was 120 minutes, temperature 2025 °C, pressure 200 MPa). It is shown in this study that crack resistance reaches a high value (4.2 MPa·m⁻¹²). The density of the resulting composite is 2.51 g·cm⁻³, which is close to the maximum theoretical density of boron carbide [1]. The flexural strength of modified ceramics also increases and amounts to 564 MPa. The results obtained in [7] indicate the improvement of physical and mechanical characteristics of the ceramics obtained by hot pressing (duration of isothermal exposure 60 min, temperature 1850 °C, pressure 60 MPa) when a MWCNT (diameter of 40…60 nm) and a silicon activating additive (8 wt. %) are introduced into the boron carbide matrix. The data analysis shows that B₄C–Si–MWCNTs composites are characterized by high values of bending strength (506 MPa) and fracture toughness 5.7 MPa·m⁻¹².

The objective of this research is to study the effect of carbon nanotube additives on the ballistic efficiency of boron carbide ceramics.

2. Materials and experimental procedure

During the experiments, boron carbide powder fabricated by Polygon of Innovative Chemical Technologies (PICHt), LLC and carbon nanotubes (CNTs) manufactured by OCSiAl (Russia) and Kumho Petrochemical Co., Ltd. (Korea) were used as feedstock material. The average particle size of boron carbide powder was 3.55 μm.

Its elemental composition was (wt. %): B 72.29, C 25.51, O 1.16, Al 0.06, Si 0.55, Fe 0.19 and Cu 0.24. To remove oxygen impurities (in the form of boron oxide) during hot pressing, an additional isothermal exposure was carried out at 1300 °C in vacuum for two hours. B₂O₃ evaporates at this temperature, and thereby the starting material is purified. The distinctive characteristics of OCSiAl CNTs are: 89 ± 2 wt. % carbon content (the rest is metal impurities); one layer; length ≈ 5 μm; average diameter 1.5 ± 0.4 nm; specific surface is ~ 510 m²·g⁻¹. TEM image of a carbon nanotube manufactured by OCSiAl is shown in Figure 1.

Modified boron carbide ceramics were manufactured by the following techniques. A calculated sample of a CNTs aqueous suspension was added to an aqueous solution of organic binders and the resulting mixture was subjected to ultrasonic treatment for 10 minutes. Then, the dispersed CNTs solution was sputtered onto the initial powder in a XLB-5 dryer to obtain a granular boron carbide powder. Next, 59.5×59.5×7 mm plates and 59.5×7×7 mm standard samples were pressed from the granular powder, the binders were removed, the plates and standard samples were placed in a graphite mold, and hot pressing was performed on an FCT HP W-400 System at 2100 °C and under the pressure of 30 MPa. The obtained sintered samples were studied by X-ray phase analysis (XRD) and scanning electron microscopy (SEM) method. Density, porosity, bending and compression strength
were measured on the standard samples. Additionally, micro-hardness was determined by indentation with the Vickers diamond pyramid. Ballistic testing of the elements was carried out with 7.62 mm caliber bullets fired out of the SVD rifle on flat samples being up to 9 mm thick.

Figure 1. TEM image of CNTs manufactured by OCSiAl.

3. Results and discussion
When the samples were fabricated, the content of CNTs in ceramics was equal to (wt. %): 0.1, 0.3, 0.5, 3 and 5. In case the CNTs content amounted to 0.1, 0.3, 3 and 5 wt. %, low values of wet density were determined for pressed samples, and hot-pressed samples were characterized by low density and reduced strength. Consequently, in that case the optimal content of CNTs is 0.5 wt. %. X-ray analysis shows that the following phases are present in the sintered samples: B₄C, FeB and graphite. The presence of the latter could be explained by the reaction conditions:

$$4\text{Fe} + \text{B}_4\text{C} = 4\text{FeB} + \text{C}$$

The presence of iron could be attributed to grinding of the grinding media (steel balls). With regard to the laws of thermodynamics such a reaction is quite possible. To avoid this undesirable reaction, it is advisable to use the ceramic grinding media. Figure 2 shows the micrographs of the sintered samples after electrochemical etching. It can be seen that boron carbide-based ceramics are a homogeneous materials without introduction of CNTs. However, ceramics appear to be composite materials with the addition of CNTs fabricated by OCSiAl. Similar results were obtained with the use of carbon nanotubes (CNTs) manufactured by Kumho Petrochemical Co., Ltd. (Korea).

Figure 2. Micrographs of microstructures: (a) the sample of boron carbide; (b) the sample of boron carbide with the addition of CNTs (0.5 wt. %).

The indentations made with a diamond indenter on the samples are shown in Figure 3. The micrographs show the significant difference between fracture and crack growth patterns in the samples. With the addition of CNTs, a branched fracture pattern appears in the sample by means of the
diamond pyramid. However, the indentation left with the diamond pyramid is clearly defined in the sample without introduction of CNTs, and it has clear boundaries in the form of a rhombus, from whose vertices straight cracks propagate along the sample. The fracture pattern in the sample with the addition of CNTs is more preferable from the point of view of the armor-defeating performance since the kinetic energy of the bullet will be more efficiently dissipated.

Figure 3. The indentations: (a) on the surface of the boron carbide sample; (b) on the surface of boron carbide sample with the addition of CNTs (0.5 wt. %).

Samples of $59.5\times59.5\times7$ mm armored plates were made for ballistic tests without and with the addition of CNTs (0.5 wt. %). Armor-piercing bullets of 7.62 mm caliber were fired out of the SVD rifle on the armored plates at a distance of 10 meters, the speed of the bullet was 801 m/s. The ballistic armor performance was calculated based on the test results by the DoP method. The test results are given in table 1.

| Parameter                                      | Armoured ceramics based on $\text{Al}_2\text{O}_3$ | Armoured ceramics based on $\text{B}_4\text{C}$ | Modified armored ceramics based on $\text{B}_4\text{C}$ |
|------------------------------------------------|---------------------------------------------------|---------------------------------------------------|--------------------------------------------------|
| Density ($\text{g} \cdot \text{cm}^{-3}$)      | 3.90                                              | 2.51                                              | 2.51                                             |
| Porosity (%)                                    | 0.0049                                            | 0.0031                                            | 0.0032                                           |
| Hardness (GPa)                                  | 16.8                                              | 31.0                                              | 31.1                                             |
| Bending strength (MPa)                          | 354                                               | 481                                               | 458                                              |
| Compressive strength (MPa)                      | 2300                                              | 2562                                              | 2577                                             |
| The speed of sound propagation in ceramics, m/s  | 11348                                             | 15548                                             | 14526                                            |
| Ballistic armor performance, (BAP)              | 5.13                                              | 6.93                                              | 8.55                                             |

With consideration for the data presented in the table, it is assumed that the ballistic armor performance (BAP) of the samples with the addition of 0.5 wt.% CNTs is 1.23 and 1.27 times higher for Korean and Russian CNTs, respectively, compared to BAP of boron carbide sintered without CNTs additives. It is related to the fact that fracturing of boron carbide modified with CNTs results in a branched fracture formation which is responsible for the efficient kinetic energy dissipation of the armor-piercing bullet.
4. Conclusion
A composite material based on boron carbide with the addition of 0.5 wt. % CNTs was fabricated. The material exhibits high ballistic armour performance compared to boron carbide without CNTs addition. BAP growth accounts for 26%. It was found that fracturing of boron carbide modified with CNTs leads to a branched fracture pattern which is a cause of efficient kinetic energy dissipation of the armour-piercing bullet.

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