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Ceramics Made of Reaction-Bonded Boron Carbide. Effect of the Introduction of Carbon Nanotubes

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Abstract

Boron carbide powders were ground in a planetary ball mill, and the mixtures of various size fractions were compacted by uniaxial dry pressing. A green density of 75 % of the theoretical was achieved. Upon infiltrating B_4C framework with molten silicon, a non-porous composite is formed with a density of 2.45–2.55 g/cm^3 and hardness of 22–27 GPa. As a result of the introduction of 1–5 % MWCNTs (multi-walled carbon nanotubes), the green density of the compacts decreases, however, the strength of the infiltrated material increases significantly. The effect is due to the formation of platelike SiC crystals as a result of the interaction of nanotubes with silicon.

Keywords: carbon nanotubes, boron carbide, ceramics

INTRODUCTION

During recent years, ceramic armour has occupied a stable position on the market for use in individual protective equipment and for protection of land-based transport means, aircrafts, helicopters. The most promising material, especially for protection against microcalibre ammunition, is ceramics based on boron carbide (B_4C) due to a combination of low specific weight with high hardness, strength and specific rigidity [1–4]. However, a broad application of B_4C is held back by the difficulties of powder consolidation into dense material with high mechanical characteristics. Since boron carbide is a compound with strong covalent bonds, diffusion processes in its crystals are very slow in comparison with oxides, and sintering into dense material requires extremely high temperatures up to 2300 °C with simultaneous application of external pressure [5, 6].

One of the methods allowing substantial simplification of the production of armour ceramics of acceptable quality on the basis of B_4C is the infiltration of the porous matrix composed of boron carbide by fused silicon (Si) at a temperature of about 1600 °C, to obtain a material containing no pores. Thus formed composite of B_4C, SiC (silicon carbide) and Si is called reaction-bonded boron carbide. The lower is silicon content of the composite, the higher are mechanical properties of the product. The microstructure of the resulting material is composed of bound grains of boron and boron carbide, and silicon phase filling the space between them. The strength of the material usually varies within the range of 175–240 MPa, and its density is within 2.5–2.75 g/cm^3 [7, 8]. The bending strength up to 390 MPa with a density of 2.58 g/cm^3 was successfully achieved through optimization of Si content, B_4C particle size and the morphology of the formed SiC [9].

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Attempts are also made to achieve the further strengthening of the B_4C–Si composite by introducing multi-walled carbon nanotubes (MWCNTs). However, the bending strength of 506 MPa could be achieved by means of hot pressing at a temperature of 1860 °C and pressure 60 MPa for the material containing MWCNTs (1 mass %) and Si (8 mass %) [10], while the strength was only 149 MPa with the density of 2.79 g/cm^3 after infiltration of fused silicon into the boron carbide matrix containing nanotubes [11].

In the present work, several tasks have been put forward: to form a B_4C matrix with minimal porosity by grinding the powders of home-made boron carbide and mixing different size fractions, and to carry out its infiltration by silicon to obtain pore-free material; at the same time, to study the potential of introducing home-made MWCNTs into boron carbide matrix to obtain material infiltrated with silicon possessing acceptable strength characteristics.

EXPERIMENTAL

Boron carbide powders (LC OKB-BOR, Dzerzhinsk, Russia) with particle size 3–5 and 50–60 μm that are used at the LC NEVZ-Keramiks (Novosibirsk, Russia) in the production of armoured panels were used in the experiments. Powder grinding was carried out in an AGO-2M planetary mill (CC NOVITS, Russia) with an acceleration of 10*g* or 20*g* for 10–20 min using steel cylinders and balls 8–10 mm in diameter. The ratio of the mass of milling tools to the charge was 40 : 1. After grinding, the powders were washed from iron admixture using hydrochloric acid until the negative reaction to rhodanide ion was achieved. The powders with different fraction composition were mixed either in a mortar or in the AGO-2M mill at a minimal rotation frequency (acceleration 4*g*, duration 2 min).

Multi-walled carbon nanotubes (~20 nm in diameter) twisted in knots up to several ten micrometres in size were obtained at the Boreskov Institute of Catalysis SB RAS (BIC SB RAS, Novosibirsk) according to the procedure described in [12, 13]. Nanotubes were treated for several minutes with ultrasound in dimethylformamide (DMF) with a small amount of B_4C. The suspension was then either mixed with carbide in the mill or poured into a suspension of B_4C in DMF under intense mixing. The suspension was mixed for 1 h and then evaporated gradually under continued mixing for 4–5 h. The resulting viscous mixture was placed for 12 h into a drying box at a temperature of 40 °C and then used to mould the samples.

Moulding was performed by dry single-axis pressing at a pressure of 200 MPa. Infiltration of the pressed tablets 16 mm in diameter and 6 mm high, as well as bricks 8 × 8 × 60 mm, was carried out in an SNVE-1,7.3.1,7/20 vacuum furnace (LC Prizma, Russia, temperature 1450 °C, vacuum $<2 \cdot 10^{-5}$ Torr) using metallurgical silicon (Tekh. Grade, GOST 2169) containing Al, Fe, Ca as admixtures. The amount of silicon was calculated to fill the pores in the pressed samples completely, with a 20 % excess keeping in mind the high pressure of its vapour under experimental conditions.

The density of the moulded samples was determined geometrically (by measuring the mass the dimensions), and after infiltration, the density was determined by means of hydrostatic weighting according to GOST 20018–74. The samples

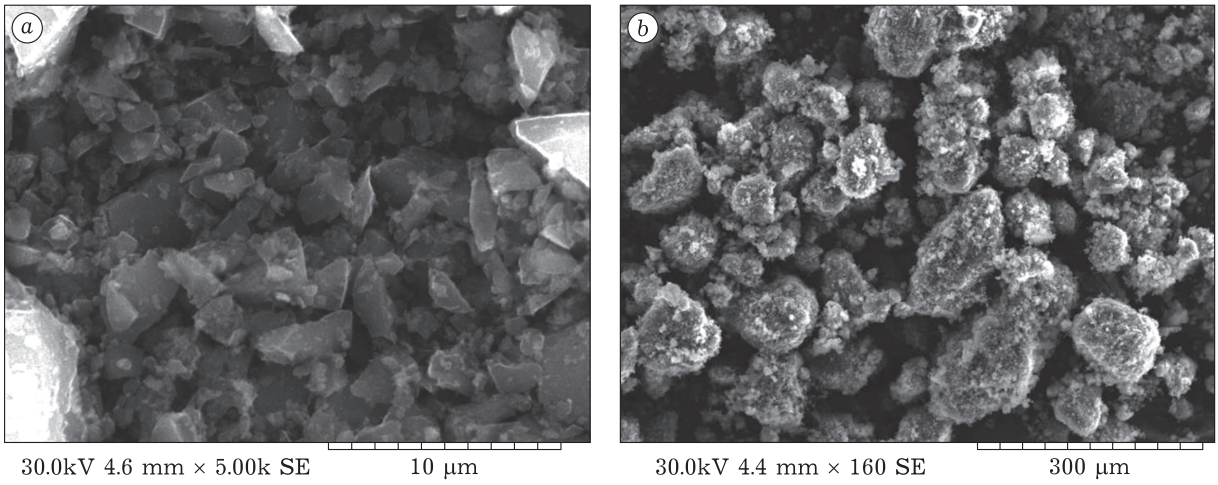

Fig. 1. SEM images of boron carbide powders: *a* – initial, *b* – ground with 10*g* for 20 min.

were preliminarily boiled in water for 30 min, and open porosity was calculated from an increase in their mass. Hardness was measured after surface polishing with the help of Metolab 502 hardness measuring instrument (PK Metolab, Russia), bending strength was determined using a three-point method with the help of an Instron 3366 testing machine (Instron, USA). The X-ray phase analysis of the powders was carried out using a D8 Advance diffractometer (Bruker, Germany) with a step of 0.02° over 2θ and accumulation time 0.2 s. Electron microscopic images and the data of X-ray fluorescence analysis were obtained with the help of a HITACHI SN 3400 electron microscope (Hitachi, Japan) and a JEM 2000FX2 transmission microscope (Jeol, Japan).

RESULTS AND DISCUSSION

Moulding and infiltration

Initial powders are the particles of irregular shapes with very sharp edges (Fig. 1, *a*). The powder with coarse (~60 μm) particles could not be pressed at any pressure, while the powder with the particles 3–5 μm in size is pressed into very frail tablets with the density of 1.63–1.65 g/cm^3. Grinding of fine powder leads to the formation of the aggregates of rounded shape (see Fig. 1, *b*) composed of the remains of particles 3–5 μm in size, and the fine fraction with particle size <0.5 μm. For this powder, the density of 72.5 % of theoretically possible value may be achieved under the accepted pressing conditions. The effect of using cold isostatic pressing is insignificant.

The data on pressing the mixtures of powders with different compositions are presented in Table 1. One can see that about 75 % of theoretically possible density (2.52 g/cm^3) of the raw blank may be achieved with a definite fraction composition.

Dense composites (2.45–2.55 g/cm^3) were obtained as a result of infiltration with silicon practically in all the cases. These density values agree with the calculated ones, obtained assuming that the composite is composed only of the boron carbide framework and silicon filling all the cavities. An exact coincidence with the calculated values should not be obtained because liquid silicon interacts partially with B_4C with the formation of SiC and a ternary phase in the B–C–Si system [14], which is confirmed by the presence of the reflections of silicon carbide in the X-ray diffraction patterns of the polished section.

The Vickers hardness of all infiltrated samples is within the range of 22–27 GPa and does not correlate with the density or with the composition of the powder mixture.

The effect of the introduction of nanotubes

The external surface of the pressed B_4C powder (particle size 5 μm) ground for 5 min at 20g together with MWCNTs (1 mass %) is shown in Fig. 2, *a*, and the same surface after infiltration with silicon is shown in Fig. 2, *b*. Nanotubes in the raw blank are distributed over the volume not uniformly but in agglomerations, or knots. After infiltration, only sole MWCNTs may be observed in the surface defects in which silicon had not entered but plate-like crystals appear in substantial amounts (see Fig. 2, *b*).

The diffraction patterns of the surface of the infiltrated sample (Fig. 3) point to the presence of boron carbide and metal silicon phases, as well as silicon carbide, which could be formed during the interaction of fused Si either with B_4C or with MWCNTs. It may be assumed that the plate-like crystals are the product of this interaction, the

TABLE 1

Data on the density of the pressed mixtures of boron carbide powders

Mixture composition (particle size)	Mixing method	Density, g/cm^3 (% of the theoretical value)
50 % (60 μm) + 50 % (5 μm)	Mortar	1.77 (70.2)
30 % (60 μm) + 70 % (5 μm)	>>	1.78 (70.6)
75 % (60 μm) + 25 % (5 μm)	Ball mill	1.87 (74.2)
66.6 % (60 μm) + 33.4 % (5 μm)	>>	1.86 (73.8)
50 % (60 μm) + 45 % (5 μm) + 5 % (20*g* 10 min)	>>	1.83 (72.6)
50 % (60 μm) + 20 % (5 μm) + 30 % (20*g* 10 min)	>>	1.91 (75.8)
50 % (60 μm) + 50 % (5 μm)	>>	1.84 (73.0)
30 % (60 μm) + 70 % (5 μm)	>>	1.86 (73.8)

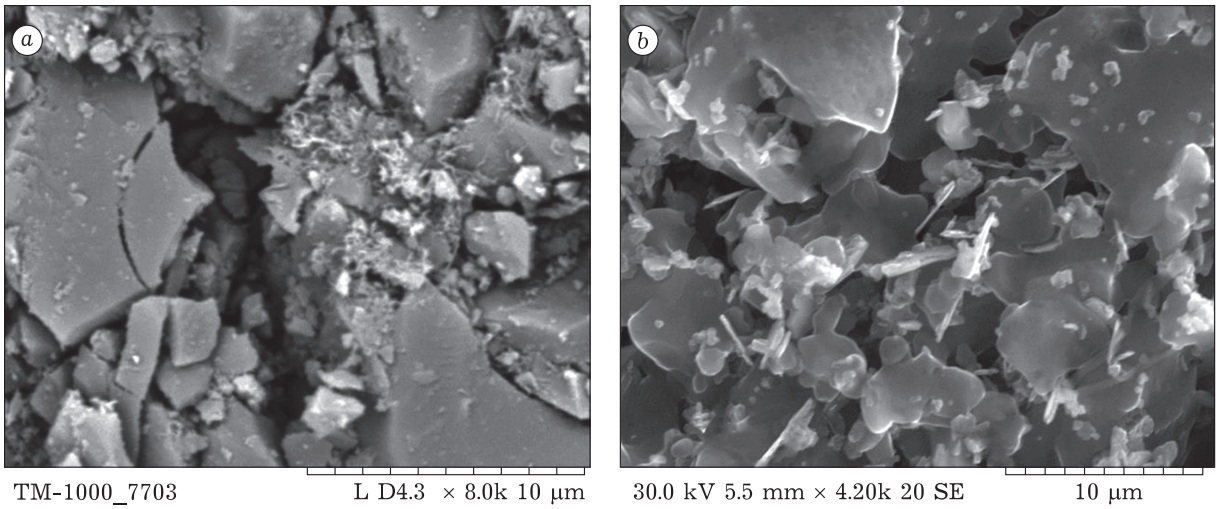

Fig. 2. SEM images of initial external surface of pressed powder with 1 mass % MWCNTs (*a*) and after infiltration with silicon (*b*).

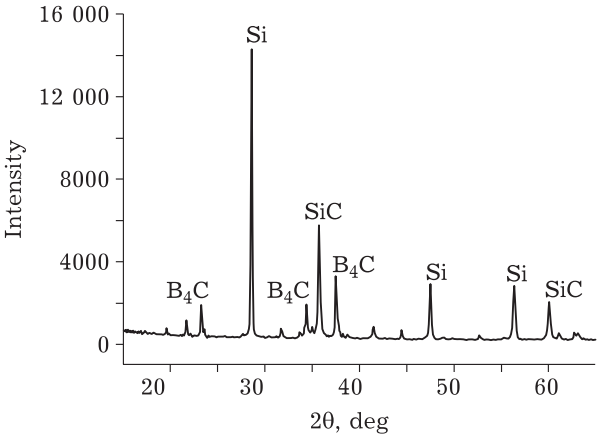

Fig. 3. Diffraction patterns of the surface of infiltrated sample with 1 mass % MWCNTs.

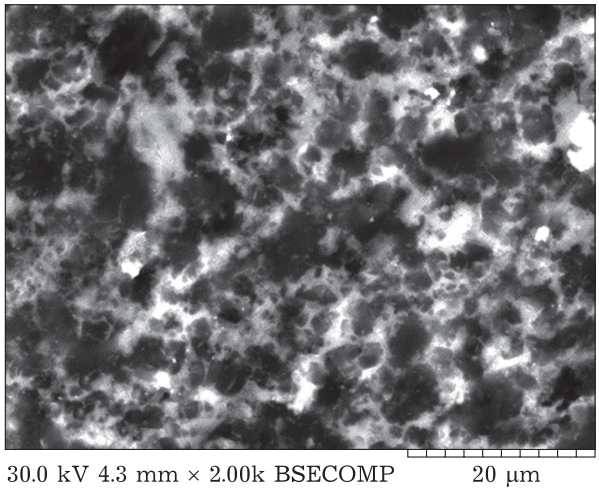

Fig. 4. SEM image of the polished cross section of the sample infiltrated with silicon, with 1 % MWCNTs.

more so as the ratio of the intensities of SiC reflections points to the prevalence of separate crystallographic planes, that is, to the non-isotropic shape of SiC particles. The resulting composite is almost free of pores (Fig. 4), therefore, the presence of nanotubes does not prevent infiltration. The density of the obtained composite is 2.56 g/cm^3, and open porosity does not exceed 0.5 % and may be due to non-ideal smoothness of the surface. Since the density of the pressed sample before infiltration was 1.73 g/cm^3 (68 %) in this case, one may calculate that the maximal density after all pores are filled with silicon should be equal to 2.46 g/cm^3. Evidently, the formation of silicon carbide having a higher density leads to a higher value than the calculated one.

If the amount of MWCNTa in B_4C powder is increased to 5 mass %, the density of the pressed framework of boron carbide decreases to approximately 63 %, that is, nanotubes draw carbide particles aside but do not occupy the positions in cavities between them, but the density of the composite after infiltration changes insignificantly.

Figure 5 shows the images of the cross fractured silicon-infiltrated bricks of the composite without (*a*) and with MWCNTs (5 mass %) (*b*). The X-ray fluorescence analysis confirms the data reported in [15] that dark particles are boron carbide, while the white network in the infiltrated sample is composed mainly of silicon. Grey fields surrounded by the white network are completely identical in Fig. 4 (the sample with 1 mass %

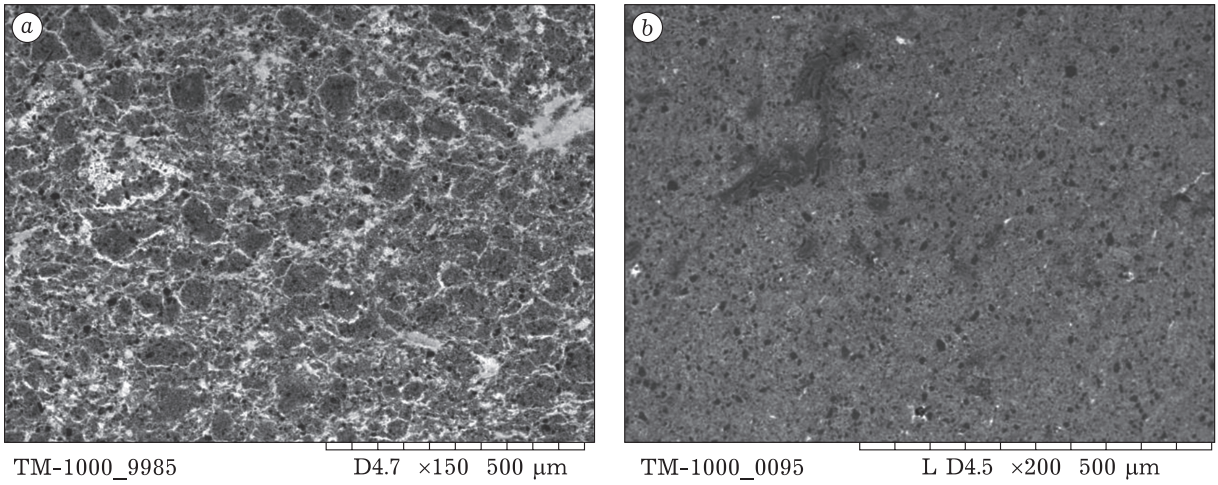

Fig. 5. SEM images of the polished cross sections of silicon-infiltrated composite brocks containing no MWCNTs (*a*) and containing 5 mass % MWCNTs (*b*).

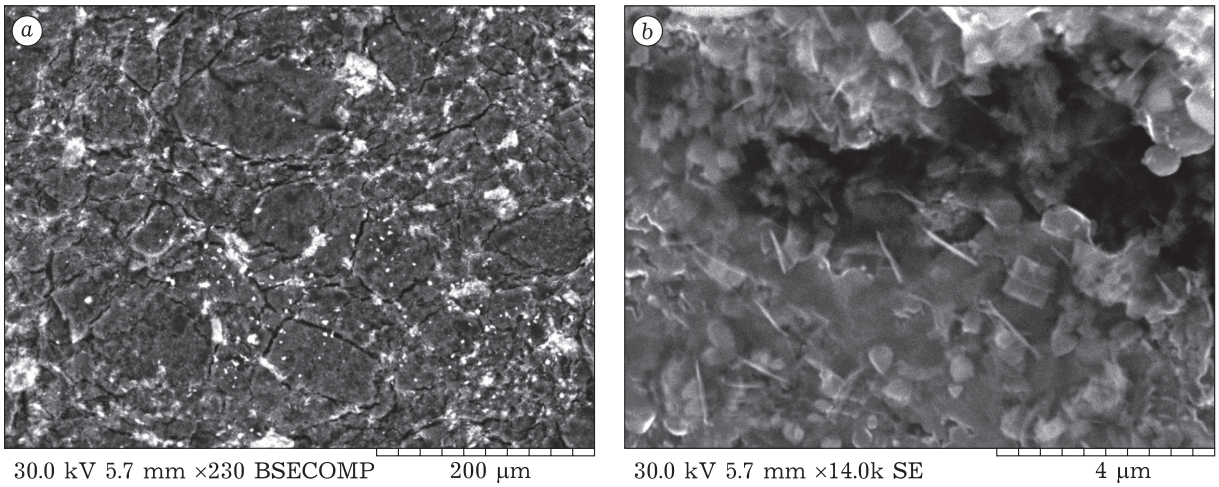

Fig. 6. SEM images of the polished cross section of silicon-infiltrated composite brick containing 5 mass % MWCNTs after leaching with NaOH solution, at different magnification.

MWCNTs) and in Fig. 5, *a* (sample without MWCNTs) and are boron carbide particles surrounded by silicon or a silicon-containing phase.

If silicon is leached with a NaOH solution, then the cavities are formed instead of the network. Around these cavities, we observe numerous plate-like particles (Fig. 6) similar to those shown in Fig. 2, *b*. So, under the accepted mixing conditions, MWCNTs are distributed over the matrix of boron carbide not uniformly but they form a spatial network. Infiltration involves the reaction Si + C → SiC with the formation of plate-like crystals.

To get sure that the plate-like particles are the result of the interaction of fused silicon with MWCNTs, a mixture composed of 5 mass % MWCNTs and Si was fused in an alundum crucible at 1450 °C for 30 min (that is, under the same conditions as those under which the infiltration of B_4C was carried out). Then the resulting piece of the alloy was leached by boiling in NaOH solution for several hours until it turned into the powder. According to the data of X-ray structural analysis, the powder is composed of silicon and its carbide. Therefore, the interaction of silicon with MWCNT under these conditions proceeds actively, and for SiC only the reflections from (102), (104) and (110) planes are present, which is the evidence of non-isotropic shape of the particles. In the electron microscopic image (Fig. 7), along with rounded particles ~0.2 μm in size, a spatial network composed of much larger anisotropic particles is observed (b), which look completely different from initial nanotubes (*a*). The MWCNTs are likely to react with silicon completely with the formation of SiC with scaly morphology.

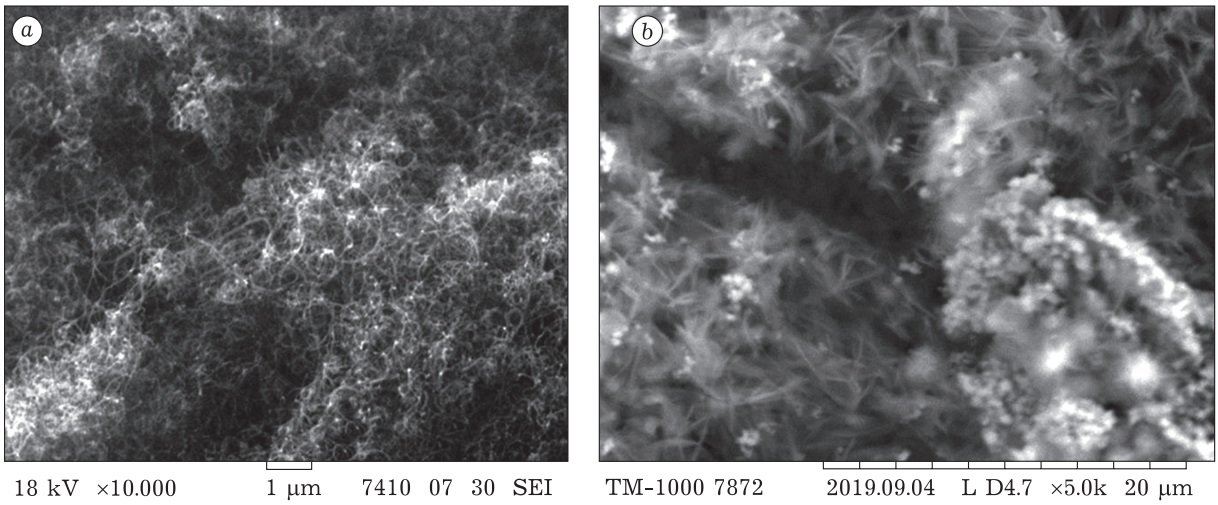

Fig. 7. SEM images: *a* – MWCNTs; *b* – results of leaching of the product of silicon interaction with MWCNTs.

It is known that the mechanical properties of the B_4C–Si–SiC composite are strongly dependent on the shape of SiC particles, and the presence of plate-like particles enhances the bending strength [9]. This is completely confirmed by the data shown in Table 2. One can see that the maximal density, similar to the case of the sample obtained by hot pressing at 1860 °C [10], is observed after the introduction of 1 mass % MWCNTs, however, in our case, this value is higher by at least 15 %. It should also be noted that the silicon-infiltrated samples obtained in [9] containing no nanotubes are characterized by the bending strength at a level of 400 MPa at the best.

CONCLUSION

Dry pressing of the mixtures of different fractions of boron carbide particles allows achieving the density of the pressed material ~75 % of the theoretically possible value. As a result of infiltration of thus obtained B_4C framework with fused silicon, a pore-free ceramic material with a density of 2.45–2.5 g/cm^3 and microhardness 22–28 GPa is formed.

TABLE 2

Bending strength of infiltrated samples

MWCNT content, mass %	Density, g/cm^3	Bending strength, MPa
0	2.57	375
1	2.58	585
5	2.59	435

The MWCNTs introduced into the pressed samples react during infiltration with fused silicon with the formation of plate-like crystals of silicon carbide, which may provide substantial strengthening of the composite. The resulting material possesses lower density and better mechanical characteristics in comparison with the ceramics made of α-Al_2O_3 and may be considered as a promising replacement for alumina ceramics as light armour protection.

Forthcoming investigations may allow us to combine the effect of the combination of different size fractions of B_4C powder with the effect of MWCNT introduction, which would improve the mechanical properties of the composite.

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