OBTAINING OF BORON CARBIDE BASED TITANIUM-CONTAINING NANOCOMPOSITES (MINI-REVIEW)

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Abstract

A mini-review on obtaining methods of boron carbide based titanium-containing nanocomposite materials is presented. Due to their unique physical-mechanical properties, such materials have a wide field of technological applications.

Boron carbide-based ceramic materials are actively used in machine-building, nuclear power engineering, and ballistic armor production as well. This is due to the boron carbide unique physical-mechanical properties: high hardness, high melting point, and high modulus of elasticity, as well as high wear-, corrosion- and radiation-resistances, etc. In addition, boron carbide has the ability to absorb or transmit thermal neutrons depending on boron-isotopic composition since the capture cross sections of thermal neutrons by boron stable isotopes ^{10}B and ^{11}B differ from each other too significantly – by seven orders of magnitude. Among the currently used in technologies hard materials, boron carbide has the highest hardness-to-density ratio [1].

These properties make boron carbide attractive for the manufacture of abrasives and grinding materials, friction pairs in moving parts and machine units working in extreme environments and also nozzles for surface treatment with fluid abrasives, protective coatings (in particular, for the boronizing of steels and refractory metals), light ballistic armors, synthesis of nuclear industry materials (for example, manufacture of the nuclear reactors control rods), neutron detectors; etc.

Besides, there are developed various boron carbide-based thermoelectric converters, boron-carbide/graphite thermocouples, as well as nonlinear resistors. But, at the present time despite its attractive electronic properties boron carbide as a semiconductor material is used relatively rarely. The point is that the preparation of samples of sufficient for this purpose purity is associated with additional difficulties.

As for the superhard boron carbide based composite materials, they can be used for manufacturing indenters and tools for processing other solid materials, and the like.

However, the field of possible applications of boron carbide is significantly narrowed due to its brittleness and low stability against the cracks formation. Today, materials science

with these disadvantages is struggling with the creation of nanocrystalline structures of heteromodular, quasibinary, and multicomponent boron carbide based ceramic and/or metalceramic materials.

As is known, in general the creation of materials with nanostructure laid the foundation for the development of a new class of materials with unique complexes of properties. But, for boron carbide based materials in this direction significant results have not been achieved yet. Therefore, it is interesting to establish how physical-chemical and physical-mechanical properties, and also the performance characteristics of these materials are changed in the transition from crystalline state to nanocrystalline state by varying their morphological parameters.

Heteromodular ceramics successfully combine a high-modulus ceramic matrix with additional components in form of particles or fibers with a much lower modulus of elasticity. In other words, in these materials, the hardness and wear resistance of the ceramic matrix are combined with the impact strength and ductility of binder metal or alloy. It is known that brittle compounds such as carbides, nitrides, and part of borides are characterized by low thermal stability and impact strength and these characteristics can be improved by adding low-modular phases in matrix. In the seminal work **[2]**, on the basis of continuous medium and micromechanics theories it was shown how it is possible to significantly improve the properties of the high-temperature structures with low stability against thermal stresses by introducing the dispersed phases with low modulus of elasticity.

The high stability of heteromodular ceramics against to external influences is due to the peculiarity of easy absorption and / or transmission of energy released during the formation of cracks in their structure. In addition, they effectively dig up the front of the developing crack and / or divert it from the initial direction of propagation.

The creation of a boron carbide based heteromodular material is possible if:

– the starting material is finely dispersed, and
– the good adhesion of the metal binder to the boron carbide surface is combined with its low chemical reactivity.

So, to create effective boron carbide based nanocomposites, it is essential to know how to manipulate by the mechanically and thermally separating surfaces. If the assembling of the ceramic component (i.e. boron carbide) is carried out in the nanocrystalline state, the physical-mechanical properties of the material will be qualitatively improved. This is because the contribution of the surface layers will be decisive in the energy balance of the system. Under these conditions, the spectrum of atomic vibrations will change radically affecting diffusion and, in general, all the transport phenomena. Accordingly, the quality of adhesion relative to passive components will be also improved significantly.

An additional obstacle to the wider application of the boron carbide attractive properties is the complexity of the compacting of its powders. To this day, the main approach to the obtaining sufficiently dense samples of boron carbide based materials is their high-temperature (above 2000 °C) pressing. However, in this way it is possible to obtain only samples of small sizes and simple geometric shapes. At such temperatures the process of agglomeration of the boron carbide crystallites is rather intense. Accordingly, the preservation of the nanostructure in consolidated samples is complicated and the quality of the material is deteriorated. Proceeding from this, it seems expedient to search for such assembling processes of boron carbide based nanocomposites, which will be carried out at relatively moderate temperatures.

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Creation of boron carbide based quasibinary and multicomponent ceramic nanosystems will allow maintaining high hardness of this material simultaneously improving its toughness and maximizing the sintering temperature, which will ensure the creation of large-sized machine parts and units of complex shapes.

From number of boron carbide-based ceramic and metalceramic systems, the most promising, respectively, are titanium-containing metal alloys and boron carbide alloys with titanium diboride TiB_2: $B_4C–TiB_2$. This paper presents a mini-review of developments in technologies for their obtaining.

Methods for preparing eutectic alloys of boron carbide and titanium diboride $B_4C–TiB_2$ are widely known. An example of obtaining a eutectic $B_4C–TiB_2$ alloy was presented in **[3]**. This composite was also obtained *in situ* by consolidation directly from a mixture of powdered components **[4]**. In particular, the material containing 10 – 40 % of TiB_2 was obtained by reacting B_4C, TiO_2, and C (graphite) powders with the traditional sintering method at a temperature of > 2000 °C and a pressure of 35 MPa. In this case, the TiB_2 nanosized particles are located both within B_4C matrix grains and at their boundaries as well. Also the spark-plasma synthesis was used for hot pressing **[5]**. By the combination of pressing with reaction-synthesis, it is possible to reduce the consolidation temperature by 200 – 400 °C **[6]**. But, it still remains quite high. The $B_4C–TiB_2$ eutectic powder composite was prepared **[7]** by plasma treatment using a mixture of B_4C and TiB_2 powders for starting materials. This mixture was fed by argon flow in the plasma discharge region, where its components were fused. The powder passed through the plasma contains crystals both of B_4C and TiB_2 and additional phase of boron oxide B_2O_3. In relatively large-sized particles (above 10 μm), a plate-structured eutectic was observed, where the phases separation ranges from 100 to 650 nm. A common disadvantage of the above-mentioned technologies is that they are not able to provide product in a nanocrystalline structure.

In the literature, one can find extensive information on such boron carbide based materials, which contain different (usually metallic) additional elements, their oxides, borides and other compounds: Al **[8 – 11]**, Cr **[12 – 14]**, Fe **[15 – 19]**, Hf **[20]**, Mo **[21, 22]**, Nb **[22, 23]**, Ni **[14, 17, 24, 25]**, Sc **[12, 26]**, Si **[9, 21, 27 – 45]**, etc. Bearing in mind the main purpose of this review, below we consider only titanium compounds containing composites.

The $B_4C–TiB_2–TiO_2$ ceramics obtained by hot pressing of the $B_4C–TiO_2–C$ charge were studied in **[46]**. The addition of TiO_2 helps hot pressing to obtain a heterophase boron carbide-based material **[27]**. It activates the sintering process and allows the creation of ceramic materials of the $B_4C–TiB_2$ system.

The effect of the addition of B_4C, (Ti,Cr)C and P on the kinetics of oxidation in air under isothermal heating was studied by the thermogravimetric method **[14]**. The effect addition of aluminum together with titanium on kinetics of compaction, structure and properties of the materials of $B_4C–(Ti–Al)$ system was also studied **[47]**. In **[48]**, the reaction of boron carbide with titanium carbide was investigated under various conditions. Reactive sintering of the starting mixtures passing through the stage of lower boride formation gives the heterophase material $B_4C–TiB_2$. The concentration of the reaction product, adiabatic temperatures, and other thermal characteristics in the $Ti–B_4C$ system containing 99 wt. % B_4C were determined using thermodynamic analysis **[49]**.

For the production of alloys of titanium with its boride and carbide using self-propagating high-temperature synthesis, the composition of the appropriate mixture was

proposed. In isothermal and constant-rate heating, it was studied the sintering (without pressing) of boron carbide containing 0 – 25 vol. % TiB_2 together with a ceramic phase that was obtained by the chemical reaction between B_4C, TiO_2, and elemental carbon [**50**]. The study of crack formation in such ceramics shows [**51**] that both strength and crack-resistance depend on the volume fraction of TiB_2. The addition of TiO_2 significantly affects the B_4C sintering process [**52**]. These two powders react approximately at a temperature of 1500 °C according to the reaction: $B_4C + TiO_2 \rightarrow B_4C_{1-x} + TiB_2 + CO \uparrow$ (or $CO_2 \uparrow$). Above the temperature of 2000 °C, sintering of the resultant biphasic mixture B_4C_{1-x}–TiB_2 is faster and yields a compacted and fine-grained composite material consisting of substoichiometric B_4C_{1-x} and additives of TiB_2, TiO_2, and C. Reactive sintering of B_4C ceramics allows obtaining high-strength materials at a substantially lower temperature than it is possible with traditional sintering, when only C is added [**53**]. Using of the B_4C containing carbon-coated TiO_2 as a precursor material allows the production of high-quality TiB_2 powders that are suitable for forming composites consisting of submicron particles [**54**].

The method of chemical furnace is also suitable for the production of B_4C based materials [**55**]. In particular, in this way it is possible to heat the reagents for the independent formation and synthesis of the TiC–Al_2O_3 system as a precursor of the composite material obtained in the combustion process.

The effect of impurities and titanium boride additions on the SiC–B_4C ceramics structure and mechanical properties have been studied over a wide temperature range [**30**]. The W_2B–TiB_2–B_4C ceramics investigated in [**56**] were hot pressed from these powders during thermal synthesis by reduction together with boron carbide. Ceramic composites B_4C–(W,Ti)C with different content of the solid solution (W,Ti)C were obtained by hot pressing as well [**57**]. The chemical reaction leads to a B_4C–TiB_2–W_2B_5 composite with high density and improved mechanical properties.

The B_4C based composites with TiB_2 content of 20 mol.% were obtained by hot (at 2000 °C) pressing of submicron powders with nanometric additives of TiO_2 and C [**58**]. It seems that their extremely high strength is associated with the fine granular microstructure of B_4C and the uniform dispersion of the TiB_2 particles. The erosion rate of the B_4C–15%TiB_2 materials obtained by reactive hot pressing of B_4C–TiO_2–C powder mixtures was measured in [**59**].

Composites of boron-carbide–titanium-diboride were synthesized and consolidated by the spark-plasma synthesis method from mechanically ground powder mixtures of Ti–B–C elements [**60**]. It was reported [**8**] on the creation of ceramics from B_4C–TiB_2–Al_2O_3 powders obtained by self-propagating high-temperature synthesis using a phosphate binder. Directionally crystallized eutectic composite B_4C–TiB_2 was obtained by the method of floating zone (crucible-free) melting of compacted powders [**61**]. In the final product matrix, the fibers of diboride phase are distributed homogenously reducing its fragility.

A study of phase composition, structure, and erosion properties of B_4C–Al composite materials obtained by hot pulsed pressing showed [**62**] that the powder components interact actively, which causes the formation of some new phases, including TiB_2, during the pressing process since titanium served for substrate. The B_4C–TiB_2–SiC composite was also proposed [**44**]. Curves of polarization and Auger electron spectroscopy were used to study growth kinetics, formation mechanism, and the phase-composition of oxide layers growing on SiC–TiB_2–B_4C ceramics [**45**].

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The microstructure and mechanical properties of multiphase composites obtained from Nb–Ti–C–B systems have been studied in [23]. Composites contain (Nb,Ti)B boride and (Nb,Ti)C carbide phases. In the (Nb,Ti)B–(Nb,Ti)C hybrid, the united network microstructure is created. Boride and carbide phases effectively improve the strength and hardness of these composites. Also compounds with V [12, 63, 64], W [56, 57], and Zr [27, 30, 46, 65 – 67] were used in the boron carbide based composites.

The processes of accumulative recrystallization occurring in the grains of hot pressed boron powdered carbide during the subsequent vacuum annealing were studied in [68]. The morphology of a number of ceramic, graphite, and diamond-like, including boron carbide, powders was studied by a scanning electron microscope and their specific surface was determined by the BET-method [69]. Thermal treatment of some crushed hybrids at a temperature of 1500 °C in the argon atmosphere gives B_4C powders [70]. In them, the content of free C varies depending on the C/B ratio in the initial solutions.

The morphology and structure of B_4C nanocrystals in a thin film grown on a Si substrate by enhanced plasma deposition from vapor were studied before and after exposure to the synchrotron radiation [71]. It was found out that in nanocrystals and bulk samples the lattice parameters differ each from other. Ultra-fine-grained B_4C powders were successfully synthesized at temperature of 450 °C by the so-called self-reduction method [72]. The synthesis was carried out in an autoclave using BBr_3 and CCl_4 for reagent gases and metallic Na for co-reducer material. Typical of obtained B_4C crystals consisted of homogeneous spherical or whiskers-like particles. The formation of B_4C whiskers and plates was studied by carbothermal reduction of B_2O_3 [73]. In the absence of any additives of B_2O_3 and C, they were not formed. It was noted that $NiCl_2$ and K_2CO_3 also able to cause the growth of boron carbide whiskers and plates. Boron carbide nanoparticles were obtained by thermal decomposition in the reaction of boron with multi-walled carbon nanotubes at a temperature of 1150 °C in vacuum [74]. Sizes of formed nanoparticles were less than 100 nm. Evidently, each of them was a single crystal.

As is noted, the production of boron carbide requires high temperature, a deep vacuum and the use of toxic substances. To a certain extent, these problems were overcome in [75], where boron carbide in form of spherical particles was obtained under normal conditions by pulsed laser irradiation of boron particles introduced in an organic solvent (e.g. ethylacetide) served for a carbon source.

In general, the compacting of boron carbide during its sintering is achieved in a two-stage process: first by heating the powder to ~ 2000 °C in a vacuum and then by sintering at a temperature of 2190 °C in argon [76]. Sufficiently fine-grained starting powder allows reaching 95 % of the theoretical density. Often these stages are preceded by treatment of boron carbide powder at a temperature of 1900 °C in nitrogen (for example, infiltration of an Al-based melt into a boron carbide pressform), during which boron nitride is formed and the residual carbon settles in the form of graphite. Vacuum heat treatment in the first stage causes the decomposition of the material. In the second stage, boron is interacted with graphite and forms boron carbide, but in a much finer-grained structure.

Work [77] aimed at developing a low-cost low-temperature method for synthesizing boron carbide from polymer precursors. The polymer precursor was obtained in the reaction of boric acid with polyvinyl alcohol, which after pyrolysis at 400 and 800 °C gives boron carbide. The effect of the preliminary deformational processing – grinding in a spherical mill and the impact of shock waves – on boron carbide specimens of various sizes and compositions pressed

from powders, as well as on their structures and mechanical properties were investigated in **[78]**. The production of boron carbide nanoparticles in the reactor of a high-temperature furnace was also studied **[79]**. The reaction was carried out by heating a mixture of amorphous carbon and amorphous boron to a temperature of 1550 °C. The influence of selection of a liquid medium on the process of obtaining boron carbide was studied separately. A number of organic compounds were tested **[80]** and it turned out that the average particle size decreases inversely proportional to the permittivity of the solvent.

Finally, we list here the author's (L. Chkhartishvili) GTU (Georgian Technical University) and FTMMSI (Ferdinand Tavadze Metallurgy and Materials Science Institute) teams reports on the subject: **[81 – 104]**. The key stages of the technology suggested by them are:

– obtaining of biphasic B_4C–TiB_2 nanopowder (each particle of which consists of homogeneously distributed components) from a liquid charge at relatively moderate temperatures, and

– their consolidation by fast spark-plasma synthesis allowing to retain nanostructure in the solid state and, therefore, production of hard composite materials with significantly improved performance.

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References

[1] F. Thevenot. Boron carbide – A comprehensive review. J. Eur. Ceram. Soc., 1990, 6, 4, 205-225.

[2] D. P. H. Hasselman, P. F. Becher, K. S. Mazdiyasni. Analysis of the resistance of high-*E*, low-*E* brittle composites to failure by thermal shock. Z. Werkstofftech., 1980, 11, 82-92.

[3] I. Bogomol, P. Loboda, Y. Holovenko, O. Biliy. Preparation, structure and properties of sputtered powder of the eutectic B_4C–TiB_2 alloy. In: Proc. 5th Int. Conf. High Mat Tech, 2015, Kyiv, IPMS, 162-162.

[4] Y.-J. Wang, H.-X. Peng, F. Ye, Y. Zhou. Effect of TiB_2 content on microstructure and mechanical properties of *in-situ* fabricated TiB_2 / B_4C composites. Trans. Nonferrous Met. Soc. China, 2011, 21, S369-S373.

[5] M. V. Zamula, A. V. Derev'yanko, V. G. Kolesnichenko, O. B. Zgalat–Lozinskii, A. V. Samelyuk, A. V. Ragulya. Electric discharge sintering refractory composites systems TiN–AlN and B_4C–TiB_2. Mater. Sci. Nanostruct., 2009, 4, 69-76.

[6] M. V. Zamula, A. V. Derevyanko, V. G. Kolesnichenko, V. T. Varchenko, S. A. Umerova, O. B. Zgalat–Lozynskyy, A. V. Ragulya. Consolidation of refractory composites of TiB_2–B_4C by an electric current. In: Proc. 5th Int. Conf. High Mat Tech, 2015, Kyiv, IPMS, 168-168.

[7] R. M. White, J. M. Kunkle, Ch. Haines, E. C. Dickey. Plasma processing of B_4C–TiB_2 eutectic composite powders. J. Am. Ceram. Soc., 2013, 96, 7, 2050-2053.

 https://doi.org/10.52340/ns.2020.01

[8] O. Okrostsvaridze, G. Tavadze, D. Dzneladze, D. Gventsadze. Hetero-modulus composites: SHS powders–metalphosphates. In: Micro et Nano: Scientiæ Mare Magnum, 2 (Eds. S. Fiore, C. Belviso, M. L. Giannossi), 2009, Bari, SA Publ., 91-91.

[9] O. N. Grigor'ev, V. A. Kotenko, O. D. Shcherbina, N. D. Bega, T. V. Dubovik, V. I. Subbotin, T. V. Mosina, V. V. Lychko, I. L. Berezhinskii. Production and properties of impact-resistant composites based on boron carbide and aluminum nitride. Powd. Metall. Met. Ceram., 2010, 49, 3/4, 193-200.

[10] Yu. G. Tkachenko, V. F. Britun, D. Z. Yurchenko, M. S. Kovalchenko, I. I. Timofeeva, L. P. Isaeva. Structure and phase formation in boron carbide and aluminum powder mixtures during hot pressing. Powd. Metall. Met. Ceram., 2011, 50, 3/4, 202-211.

[11] A. A. Tofigh, M. O. Shabani. Efficient optimum solution for high strength Al alloys matrix composites. Ceram. Int., 2013, 39, 7, 7483-7490.

[12] V. B. Fedorus, G. N. Makarenko, S. P. Gordienko, E. V. Marek, I. I. Timofeeva. Interaction between boron carbide and chromium oxide. Powd. Metall. Met. Ceram., 1995, 34, 11/12, 637-639.

[13] V. A. Maslyuk, L. N. Tkachenko. Effect of P, B_4C, and (Ti,Cr)C additives on the kinetics of high-temperature oxidation of chromium carbide alloys at 1000 °C. Powd. Metall. Met. Ceram., 2002, 41, 5-6, 300-303.

[14] A. J. Pyzik, R. T. Nilsson. Boron-carbide–copper cermets and method for making same. US Patent, 1991, No. 5145504.

[15] Yu. V. Turov, B. M. Khusid, L. G. Voroshnin, B. B. Khina, I. L. Kozlovskii. Structure formation in sintering iron–boron carbide powder composite. Powd. Metall. Met. Ceram., 1991, 30, 6, 465-470.

[16] A. V. Byakova. Influence of texture on the strength and supporting capacity of boride coatings. Powd. Metall. Met. Ceram., 1993, 32, 4, 314-320.

[17] G. N. Makarenko, S. P. Gordienko, V. B. Fedorus, E. V. Marek, I. I. Timofeeva. Characteristic features of boron carbide synthesis for iron triad borides. Powd. Metall. Met. Ceram., 2004, 43, 3/4, 192-195.

[18] N. Frage, S. Hayun, S. Kalabukhov, M. P. Dariel. The effect of Fe addition on the densification of B_4C powder by spark plasma sintering. Powd. Metall. Met. Ceram., 2007, 46, 11/12, 533-538.

[19] G. A. Baglyuk, S. G. Napara–Volgina, V. I. Vol'fman, A. A. Mamonova, S. G. Pyatachuk. Thermal synthesis of Fe–B_4C powder master alloys. Powd. Metall. Met. Ceram., 2009, 48, 7/8, 381-383.

[20] P. Rogl, H. Bittermann. On the ternary system hafnium–boron–carbon. J. Solid State Chem., 2000, 154, 1, 257-262.

[21] H. Chen, M. Suzuki, S. Sodeoka, T. Inoue, K. Ueno. New approach to $MoSi_2$/SiC intermetallic-ceramic composite with B_4C. J. Mater. Sci., 2001, 36, 5773-5777.

[22] V. Paderno, Yu. Paderno, V. Filippov, A. Liashchenko. Directional crystallization of B_4C–NbB_2 and B_4C–MoB_2 eutectic compositions. J. Solid State Chem., 2004, 177, 2, 523-528.

[23] X. Zhang, X. He, C. Fan, Y. Li, G. Song, Y. Sun, J. Huang. Microstructural and mechanical characterization of multiphase Nb-based composites from Nb–Ti–C–B system. Int. J. Ref. Met. Hard Mater., 2013, 41, 11, 185-190.

[24] G. N. Makarenko, E. V. Marek, S. P. Gordienko, V. B. Fedorus, I. I. Timofeeva. Interaction of boron carbide with nickel oxide. Powd. Metall. Met. Ceram., 2001, 40, 11/12, 601-605.

[25] A. Kilicarslan, F. Toptan, I. Kerti. Modification of surface properties of boron carbide (B_4C) particles via electroless nickel coating technique. In: Proc. 4th Int. Boron Symp. (Eds. A. Konuk, H. Kurama, H. Ak, M. Iphar), 2009, Ankara, Osmangazi Univ. – TMMOB, 81-87.

[26] S. P. Gordienko, G. N. Makarenko, V. B. Fedorus, I. I. Timoveeva, K. F. Chernysheva, E. V. Marek. Interaction of boron carbide with scandium oxide. Powd. Metall. Met. Ceram., 1994, 33, 7/8, 406-407.

[27] O. N. Grigor'ev, V. V. Koval'chuk, V. V. Zametailo, R. G. Timchenko, D. A. Kotlyar, V. P. Yaroshenko. Structure, physicomechanical properties, and special features of failure of hot-pressed boron carbide base ceramics. Powd. Metall. Met. Ceram., 1990, 29, 7, 543-547.

[28] V. R. Maslennikova, A. A. Belkina, A. D. Panasyuk, L. I. Struk, V. P. Smirnov. Effect of high pressure on the structure and properties of materials based on boron carbide. Powd. Metall. Met. Ceram., 1995, 34, 9/10, 491-495.

[29] L. A. Shipilova, V. Ya. Petrovskii, S. I. Chugunova. Structure formation and electrophysical properties of a silicon carbide–boron carbide sintered composite. Powd. Metall. Met. Ceram., 1997, 36, 11/12, 652-656.

[30] O. N. Grigor'ev, G. A. Gogotsi, Yu. G. Gogotsi, V. I. Subbotin, and N. P. Brodnikovskii. Synthesis and properties of ceramics in the SiC–B_4C–MeB_2 system. Powd. Metall. Met. Ceram., 2000, 39, 5-6, 239-250.

[31] P. Larsson, N. Axen, S. Hogmark. Improvements of the microstructure and erosion resistance of boron carbide with additives. J. Mater. Sci., 2000, 35, 3433-3440.

[32] M. K. Aghajanian, B. N. Morgan, J. R. Singh, J. Mears, R. A. Wolffe. A new family of reaction bounded ceramics for armor applications. Ceram. Trans., 2001, 134, 529-539.

[33] G. Magnani, G. Beltrami, G. L. Minoccari, L. Pilotti. Pressureless sintering and properties of a-SiC–B_4C composite. J. Eur. Ceram. Soc., 2001, 21, 5, 633-638.

[34] L. A. Shipilova, V. Ya. Petrovskii. Structure formation, electrophysical and mechanical properties of an electrically conducting ceramic composite based on silicon and boron carbides. Powd. Metall. Met. Ceram., 2002, 41, 3/4, 147-149.

[35] S. Tariolle, C. Reynaud, F. Thevenot, T. Chartier, J. L. Besson. Preparation, microstructure and mechanical properties of SiC–SiC and B_4C–B_4C laminates. J. Solid State Chem., 2004, 177, 2, 487-492.

[36] R. Naslain, A. Guette, F. Rebillat, R. Pailler, F. Langlais, X. Bourrat. Boron-bearing species in ceramic matrix composites for long-term aerospace applications. J. Solid State Chem., 2004, 177, 2, 449-456.

[37] Yu. G. Tkachenko, V. F. Britun, D. Z. Yurchenko, L. F. Ochkas, G. A. Bovkun. Structure and certain properties of hot-pressed boron carbide-based ceramic with calcium–silicon additive. Powd. Metall. Met. Ceram., 2004, 43, 1/2, 99-104.

[38] Z. Abdel Hamid, F. Abdel Mouez, F. A. Morsy, N. A. Khalifa. Electrolysis Ni–Cr–B on diamond particles for fabricated copper / diamond composites as heat sink materials. Int. J. Eng. Prac. Res., 2013, 2, 3, 112-117.

[39] Yu. G. Tkachenko, V. F. Britun, E. V. Prilutskii, D. Z. Yurchenko, G. A. Bovkun. Structure and properties of B_4C–SiC composites. Powd. Metall. Met. Ceram., 2005, 44, 3/4, 196-201.

[40] S. Hayun, N. Frage, M. P. Dariel. The morphology of ceramic phases in B_xC–SiC–Si infiltered composites. J. Solid State Chem., 2006, 179, 9, 2875-2879.

[41] S. Hayun, D. Rittel, N. Frage, M. P. Dariel. Static and dynamic mechanical properties of infiltrated B_4C–Si composites. Mater. Sci. Eng. A, 2008, 487, 1/2, 405-409.

 https://doi.org/10.52340/ns.2020.01

[42] S. Hayun, A. Weizmann, H. Dilman, M. P. Dariel, N. Frage. Rim region growth and its composition in reaction bonded boron carbide composites with core–rim structure. J. Phys. Conf. Ser., 2009, 176, 012009, 1-7.

[43] S. Hayun, M. P. Dariel, N. Frage, E. Zaretsky. The high-strain-rate dynamic response of boron carbide-based composites: The effect of microstructure. Acta Mater., 2010, 58, 5, 1721-1731.

[44] D. Korablev, V. Rumyantsev, S. Ordanyan, V. Fischev. Wear-resistant materials based on B_4C–TiB_2–SiC system. In: Proc. 2nd Int. Conf. High Mat Tech, 2009, Kyiv, IPMS, 249-249.

[45] V. A. Shvets, V. A. Lavrenko, V. I. Subbotin, V. N. Talash, L. I. Kuznetsova. Anodic oxidation of SiC–TiB_2–B_4C composites in 3%NaCl solution. Powd. Metall. Met. Ceram., 2011, 49, 11/12, 702-706.

[46] M. S. Koval'chenko, Yu. G. Tkachenko, V. V. Koval'chuk, D. Z. Yurchenko, S. V. Satanin, A. I. Kharlamov. Structure and properties of hot-pressed boron carbide base ceramics. Powd. Metall. Met. Ceram., 1990, 29, 7, 523-526.

[47] V. R. Maslennikova, A. D. Panasyuk, L. I. Struk, A. A. Belkina. Compaction, structure formation, and properties of materials based on boron carbide. Powd. Metall. Met. Ceram., 1997, 36, 11/12, 570-574.

[48] A. I. Bykov, I. V. Gridneva, G. N. Makarenko, I. I. Timofeeva, V. B. Fedorus, S. I. Chugunova. Interactions of boron carbide with titanium and zirconium carbides under pressure. Powd. Metall. Met. Ceram., 1998, 37, 1/2, 45-47.

[49] S. P. Gordienko. Thermodynamic analysis of the reaction of titanium with boron carbide in a self-propagating high-temperature synthesis regime. Powd. Metall. Met. Ceram., 1999, 38, 3/4, 172-175.

[50] Vl. V. Skorokhod, V. D. Krstic. Processing, microstructure, and mechanical properties of B_4C–TiB_2 particulate sintered composites I. Pressureless sintering and microstructure evolution. Powd. Metall. Met. Ceram., 2000, 39, 7/8, 414-423.

[51] Vl. V. Skorokhod, V. D. Krstic. Processing, microstructure, and mechanical properties of B_4C–TiB_2 particulate sintered composites. II. Fracture and mechanical properties. Powd. Metall. Met. Ceram., 2000, 39, 9/10, 504-513.

[52] L. Levin, N. Frage, M. P. Dariel. Novel approach for the preparation of B_4C-based cermets. Int. J. Ref. Met. Hard Mater., 2000, 18, 2, 131-135.

[53] V. Skorokhod Jr., V. D. Krstic. High strength-high toughness B_4C–TiB_2 composites. J. Mater. Sci. Lett., 2000, 19, 237-239.

[54] R. Koc, D. B. Hodge. Production of TiB_2 from a precursor containing carbon coated TiO_2 and B_4C. J. Mater. Sci. Lett., 2000, 19, 667-669.

[55] J. H. Lee, C. W. Won, S. M. Joo, D. Y. Maeng, H. S. Kim. Preparation of B_4C powder from B_2O_3 oxide by SHS process. J. Mater. Sci. Lett., 2000, 19, 951-954.

[56] O. N. Grigor'ev, É. V. Prilutskii, E. G. Trunova, I. V. Kozak. Structure and properties of ceramics based on tungsten and titanium borides and boron carbide. Powd. Metall. Met. Ceram., 2002, 41, 3/4, 142-146.

[57] J. Deng, J. Zhou, Y. Feng, Z. Ding. Microstructure and mechanical properties of hot-pressed B_4C/(W,Ti)C ceramic composites. Ceram. Int., 2002, 28, 4, 425-430.

[58] S. Yamada, K. Hirao, Y. Yamauchi, S. Kanzaki. High strength B_4C–TiB_2 composites fabricated by reaction hot pressing. J. Eur. Ceram. Soc., 2003, 23, 7, 1123-1130.

[59] Yu. G. Tkachenko, V. F. Britun, G. O. Bovkun, D. Z. Yurchenko. Electroerosion behavior of a ceramic based on boron carbide: phase composition, structure, and properties of protective spark coatings. Powd. Metall. Met. Ceram., 2005, 44, 11/12, 537-544.

[60] D. V. Dudina, D. M. Hulbert, D. Jiang, C. Unuvar, Sh. J. Cytron, A. K. Mukherjee. In situ boron carbide–titanium diboride composites prepared by mechanical milling and subsequent spark plasma sintering. J. Mater. Sci., 2008, 43, 10, 3569-3576.

[61] I. Bogomol, T. Nishimura, O. Vasylkiv, Y. Sakka, P. Loboda. Microstructure and high-temperature strength of B_4C–TiB_2 composite prepared by a crucibleless zone melting method. J. Alloys Comp., 2009, 485, 1/2, 677-681.

[62] Yu. G. Tkachenko, M. S. Koval'chenko, V. F. Britun, G. A. Bovkun, D. Z. Yurchenko, A. V. Laptev, L. P. Isaeva. Production, properties, and erosion characteristics of B_4C–Al composite materials. Powd. Metall. Met. Ceram., 2009, 48, 1/2, 60-65.

[63] G. N. Makarenko, S. P. Gordienko, V. B. Fedorus, I. I. Timofeeva, É. V. Marek. Interaction of boron carbide with vanadium oxide. Powd. Metall. Met. Ceram., 1998, 37, 3/4, 229-231.

[64] O. N. Grigor'ev, V. V. Koval'chuk, O. I. Zaporozhets, N. D. Bega, B. A. Galanov, É. V. Prilutskii, V. A. Kotenko, T. N. Kutran', N. A. Dordienko. Synthesis and physico-mechanical properties of B_4C–VB_2 composites. Powd. Metall. Met. Ceram., 2006, 45, 1/2, 47-58.

[65] C. H. Liu, C. Huang. Structural changes of boron carbide induced by Zr incorporation. J. Mater. Sci., 2000, 35, 387-390.

[66] A. V. Kovalev, E. M. Dudnik, O. N. Grigor'ev, T. I. Shaposhnikova, I. S. Martsynyuk. Directionally solidified eutectic of the B_4C–ZrB_2 system. Powd. Metall. Met. Ceram., 2000, 39, 1/2, 63-66.

[67] S. Zhang, S. Wang, W. Li, Y. Zhu, Z. Chen. Mechanical properties of the low-temperature reactive melt infiltrated ZrB_2–ZrC based composites. Mater. Lett., 2012, 78, 7, 81-84.

[68] A. A. Korneev, I. T. Ostapenko, M. A. Dolzhek, A. G. Mironova, N. D. Rybal'chenko, I. A. Lyashenko, V. P. Podtykan. Effect of annealing on the structure and properties of hot-pressed boron carbide. Powd. Metall. Met. Ceram., 1992, 31, 1, 64-66.

[69] I. Dion, F. Rouais, Ch. Baquey, M. Lahaye, R. Salmon, L. Trut, J. P. Cazorla, P. V. Huong, J. R. Monties, P. Havlik. Physico-chemistry and cytotoxicity of ceramics. Part I. Characterization of ceramic powders. J. Mater. Sci. Mater. Med., 1997, 8, 325-332.

[70] I. Hasegawa, Y. Fujii, T. Takayama, K. Yamada. Phenolic resin–boron oxide hybrids as precursors for boron carbide. J. Mater. Sci. Lett., 1999, 18, 1629-1631.

[71] V. Ya. Shevchenko, G. S. Yur'ev. Morphology and structure of BN and B_4C nanocrystals. Inorg. Mater., 2001, 57, 9, 935-940.

[72] L. Shi, Y. Gu, L. Chen, Y. Qian, Z. Yang, J. Ma. A low temperature synthesis of crystalline B_4C ultrafine powders. Solid State Commun., 2003, 128, 1, 5-7.

[73] R. V. Krishnarao, J. Subrahmanyam. Studies on the formation of whiskers and platelets of B_4C and BN. J. Mater. Sci., 2004, 39, 6263-6269.

[74] S. Chen, D. Z. Wang, J. Y. Huang, Z. F. Ren. Synthesis and characterization of boron carbide nanoparticles. Appl. Phys. A, 2004, 79, 1757-1759.

[75] N. Koshizaki, Y. Ishikawa, T. Sasaki, K. Kawaguchi. Fabrication of boron carbide spherical particles by pulsed laser irradiation of boron in organic solution. In: Abs. 16th Int. Symp. Boron, Borides Rel. Mater., 2008, Matsue, Tokyo Univ., 87-87.

[76] N. Frage, L. Levin, M. P. Dariel. The effect of the sintering atmosphere on the densification of B_4C ceramics. J. Solid State Chem., 2004, 177, 2, 410-414.

[77] Sh. Mondal, A. K. Banthia. Low-temperature synthetic route for boron carbide. J. Eur. Chem. Soc., 2005, 25, 287-291.

[78] Yu. G. Tkachenko, V. I. Kovtun, V. F. Britun, D. Z. Yurchenko, G. A. Bovkun. Influence of shock wave treatment of boron carbide powders on the structure and properties of hot-

 https://doi.org/10.52340/ns.2020.01

pressed polycrystals based on such powders. Powd. Metall. Met. Ceram., 2005, 44, 7/8, 407-414.

[79] B. Chang, B. L. Gersten, S. T. Szewczyk, J. W. Adams. Characterization of boron carbide nanoparticles prepared by a solid state thermal reaction. Appl. Phys. Lett. A, 2007, 86, 83-87.

[80] Y. Ishikawa, N. Koshizaki, T. Sasaki, K. Kawaguchi. Fabrication of boron carbide spherical particles by pulsed laser irradiation of boron in organic solvent: Influence of liquid medium on particle formation. In: Abs. 16th Int. Symp. Boron, Borides Rel. Mater., 2008, Matsue, Tokyo Univ., 88-88.

[81] O. Tsagareishvili, D. Lezhava, M. Tushishvili, L. Gabunia, M. Antadze, L. Kekelidze, T. Dzigrashvili. Some physical properties of compacted specimens of high dispersed boron carbide and boron suboxide. J. Solid State Chem., 2004, 177, 2, 596-599.

[82] D. Gabunia, A. Gachechiladze, A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili. Obtaining opportunities of boron carbide powders based hetero-modulus ceramics. In: Micro et Nano: Sciantiæ Mare Magnum, 1 (Eds. S. Fiore, C. Belviso, M. L. Giannossi), 2009, Bari, SA Publ., 86-86.

[83] A. Gachechiladze, D. Gabunia, A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili. On technological process of synthesis of boron carbide nanodispersive powders. In: Proc. 4th Int. Boron Symp. (Eds. A. Konuk, H. Kurama, H. Ak, M. Iphar), 2009, Ankara, Osmangazi Univ. – TMMOB, 67-71.

[84] M. Antadze, R. Chedia, O. Tsagareishvili, A. Mikeladze, A. Gacheciladze, B. Margiev, D. Gabunia, T. Tsuladze, J. Khantadze. Metal-ceramics based on nanostructured boron carbide. Solid State Sci., 2012, 14, 11/12, 1725-1728.

[85] T. A. Batsikadze, D. L. Gabunia, V. M. Gabunia, T. G. Gigitashvili, O. A. Tsagareishvili, L. S. Chkhartishvili. Preparation of boron and boron carbide in arc – New approaches. In: Abs.18th Int. Symp. Boron, Borides Rel. Mater., 2014, Honolulu, Univ. Hawaii, 127-127.

[86] M. Antadze, A. Mikeladze, A. Gachechiladze, R. Chedia, B. Margiev, L. Chkhartishvili, O. Tsagareishvili. Fabrication of metal-ceramics composite based on B_4C–MeB_2. In: Abs.18th Int. Symp. Boron, Borides Rel. Mater., 2014, Honolulu, Univ. Hawaii, 144-144.

[87] T. A. Batsikadze, D. L. Gabunia, V. M. Gabunia, T. G. Gigitashvili, O. A. Tsagareishvili, L. S. Chkhartishvili. Obtaining of mixture of boron and boron carbide in electric arc. Proc. Georg. Natl. Acad. Sci. (Ser. Chem.), 2015, 41, 1/2, 160-163.

[88] A. Mikeladze, L. Chkhartishvili, R. Chedia, O. Tsagareishvili, M. Darchiashvili. B_4C–TiB_2 ceramic nanocrystalline composites: Synthesis, compacting, structure, and properties. In: Abs. 4th Int. Conf. “Nanotechnologies” (Eds. A. Gerasomov, L. Chkhartishvili), 2016, Tbilisi, Georg. Tech. Univ., 145-145.

[89] A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili, R. Chedia. Obtaining B_4C–TiB_2 ceramic nanostructured alloys. Proc. Georg. Natl. Acad. Sci. (Multi-Discip. Studies Ser.), 2017, 2, 37-44.

[90] A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili, M. Darchiashvili, R. Chedia, K. Sarajishvili. Synthesizing of nanostructured composite ceramics B_4C–TiB_2 and their properties. In: Abs. 19th Int. Symp. Boron, Borides Rel. Mater., 2017, Freiburg, Albert-Ludwigs Univ., 58-58.

[91] L. Chkhartishvili, A. Mikeladze, O. Tsagareishvili, A. Gachechiladze, A. Oakley, B. Margiev. Ch. 2: Boron-containing nanocrystalline ceramic and metal–ceramic materials. In: Handbook of Nanomaterials for Industrial Applications (Ed. Ch. M. Hussain), 2018, Amsterdam, Elsevier, 13-35.

[92] A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili, R. Chedia. Chemical method of obtaining of B_4C–TiB_2 ceramic composites. In: Proc. 26th Ann. Int. Conf. Compos. Nano Eng. (Ed. D. Hui), 2018, Paris, ICCE – AMAC – Guangzhou Univ., 1-2. https://www.dropbox.com/sh/jaxxr743yjif8f6/AABwXggdAHPYT4Xl9Nl0qzSLa?dl=0

[93] O. Tsagareishvili, A. Mikeladze, R. Chedia, L. Chkhartishvili. Method of obtaining boron carbide based hard nanocomposite materials. National Center for Intellectual Property of Georgia "GeoPatent" – Patent # GE P 2018 6709B, 2018 October 11.

[94] A. Mikeladze, L. Chkhartishvili, O. Tsagareishvili, R. Chedia, M. Darchiashvili. Ceramic composites B_4C–TiB_2 in nanocrystalline state: Production, structure, and mechanical properties. In: Book Abs. 3rd Int. Conf. "Inorg. Mater. Sci. Mod. Technol. Meth.", 2018, Tbilisi, Georg. Natl. Acad. Sci. Press, 62-65.

[95] A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili, R. Chedia, R. Tsiskarishvili. On production of hard nanocrystalline materials. In: Abs. 5th Int. Conf. "Nanotechnol." (Eds. A. Gerasimov, L. Chkhartishvili, G. Chikhladze), 2018, Tbilisi, Tech. Univ., 128-128.

[96] A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili, R. Chedia, R. Tsiskarishvili. Method for manufacturing nanocrystalline systems from liquid charge. Nano Studies, 2019, 19, 15-36.

[97] A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili, R. Chedia, M. Darchiashvili. Production of titanium-containing metal-ceramic composites based on boron carbide in the nanocrystalline state. Adv. Appl. Ceram., 2019, 118, 4, 196-208.

[98] L. Chkhartishvili, O. Tsagareishvili, A. Mikeladze. On commercialization of innovative studies in materials science. Economics and Finance, 2019, 1, 76-84.

[99] A. Mikeladze, O. Tsagareishvili, L. Chkhartishvili, R. Chedia. Obtaining of some boron-containing and related nanocrystalline systems from solutions and suspensions. In: Proc. Book Int. Symp. Boron, 2019, Nevsehir, Boren, 181-191.

[100] L. Chkhartishvili. On obtaining boron carbide based nanocomposites. In: Proc. Int. Conf. Mater. Sci. Mech. Automot. Eng. Technol. Cappadocia (Eds. B. Kurt, C. Carboga, Z. Bayer Ozturk, N. Kuckdeveci), 2019, Nevsehir, Bektas Veli Univ., 17-21.

[101] N. Barbakadze, K. Sarajishvili, R. Chedia, L. Chkhartishvili, O. Tsagareishvili, A. Mikeladze, M. Darchiashvili, V. Ugrekhelidze. Obtaining of ultrafine powder composites of tungsten, molybdenium, titanium and boron carbides using liquid precursors. In: Book Abs. 11th Japanese–Mediterranean Workshop Appl. Electromagn. Eng. Magn. Supercond. Multifunc. Nanomater., 2019, Batumi, Batumi State Univ., 114-115.

[102] L. Chkhartishvili, O. Tsagareishvili, A. Mikeladze, M. Darchiashvili, N. Barbakadze, K. Sarajishvili, R. Chedia, V. Ugrekhelidze. Production of B_4C–MeB_2 composite nanopowders from liquid charge. In: Abs. 20th Int. Symp. Boron, Borides Rel. Mater., 2019, Niigata, Nagaoka Univ. Technol., 103-103.

[103] N. Barbakadze, K. Sarajishvili, R. Chedia, L. Chkhartishvili, O. Tsagareishvili, A. Mikeladze, M. Darchiashvili, V. Ugrekhelidze. Obtaining of ultrafine powders of some boron carbide based nanocomposites using liquid precursors. Nanotechnology Perceptions, 2019, 15, 3, 1-14.

[104] L. Chkhartishvili, A. Mikeladze, R. Chedia, O. Tsagareishvili, N. Barbakadze, K. Sarajishvili, M. Darchiashvili, V. Ugrekhelidze, T. Korkia. Synthesizing fine-grained powders of complex compositions B_4C–TiB_2–WC–Co. Solid State Sci., 2020, 108, 106439, 1-8.

 https://doi.org/10.52340/ns.2020.01