

Synthesis and Characteristics of B₄C–TiB₂ Composite

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Abstract

B₄C–TiB₂ composites, containing B₄C 10–50 % wt. were obtained from the elemental powders by the method of SHS-pressing. Thermodynamic calculations and X-ray analysis showed that the equilibrium synthesis products are refractory compounds TiB₂ and B₄C, forming a dispersed phase and a ceramic binder in the ceramic composite. The influence of the composition of the reaction mixture on the formation of the microstructure and phase composition of ceramic composites was studied. It was found that the formation of the microstructure of SHS-composites was greatly affected by B₄C content. It was shown that the minimum residual porosity is achieved when the B₄C content in the composite is 20–40 % wt. and the ratio of a green sample and a chemical oven is 1:4. When the content of B₄C is less than 20 % wt., a homogeneous ceramic composite with a particle size of TiB₂ up to 10–12 μm is formed. Increase in the content of B₄C up to 50 % wt. reduces the TiB₂ particle size to 0.5 μm and leads to the formation of a composite with inhomogeneous microstructure. An increase in B₄C content results in a decrease in the residual porosity of composites to 3.0–3.8 %, wherein the ceramic composites have bending strength of 140–210 MPa and microhardness of 37.1–44.8 GPa.

Keywords

Ceramic composite; pressing; SHS.

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Introduction

The development of ceramic composites remaining functional at high temperatures is an important task of innovation development of modern mechanical engineering, metal processing, metallurgy, power engineering, aircraft engineering. Ceramic composites based on refractory metals borides of IV–VI groups of the Mendeleev Periodic System can be widely used. The unique combination of physical and mechanical properties makes it possible to produce materials with new properties.

Promising materials are ceramic composites based on B₄C–TiB₂ system with high hardness, strength and low density [1–3]. They are used for manufacturing lightweight ceramic armor, cutting tools for machining of hardened steels and hard materials, wear-resistant parts working in aggressive environments at high temperatures.

Titanium diboride (TiB₂) has a unique set of properties: high melting temperature of 3490 K, low density of 4.52 g/cm³, high microhardness of 34 GPa,

high thermal and electrical conductivity [4–7], high resistance to wear and corrosion resistance. These are appealing properties for using it as cutting tools, wear parts, remaining functional at high temperatures [8, 9].

Boron carbide (B₄C) is widely used for various structural applications because of its extremely high hardness and wear resistance, low specific gravity, high thermal stability and chemical stability [6–8]. However, the use of boron carbide as the material of construction is limited by its low fracture toughness. Adding TiB₂ and B₄C particles improves the mechanical characteristics of the composite. It was found [10] that the addition of 30.5 % wt TiB₂ increases the B₄C viscous fracture coefficient up to 6 MPa·m^{1/2}. A similar result was obtained in [11], where it was shown that the boron carbide particles containing TiB₂ had a strength of 621 MPa and a fracture toughness of 6.1 MPa·m^{1/2}.

In powder metallurgy the B₄C–TiB₂ composite is obtained by sintering [12] or hot pressing [13] the mixed powders of refractory compounds at a temperature close to the melting temperature

Table 1

Compositions of the reaction mixtures and SHS-products

Composition <i>x</i>	Content of reactants*, % wt.			Composition of final product, % wt.		Theoretical density, g/cm ³ –
	Ti	B	C	TiB ₂	B ₄ C	
0	68.9	31.1	0	100	0	4.53
0.1	63.3	34.9	1.8	90	10	4.33
0.2	57.5	38.9	3.6	80	20	4.13
0.3	51.4	43.1	5.5	70	30	3.93
0.4	45.1	47.4	7.5	60	40	3.73
0.5	38.4	52.0	9.6	50	50	3.53

* In the paper, the content of reactants and composite are given as weight percentage.

of boron carbide. Electric current-assisted sintering under pressure makes it possible to vary the temperature and the rate of heating to effect the consolidation of the composite [14, 15]. However, despite good physical and mechanical properties of the composites obtained by conventional methods, their main disadvantage is a small size of resulting products.

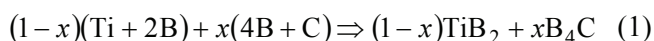
The preparation of these materials by conventional methods of powder metallurgy is complicated by high-energy costs, the complexity of the process equipment and low productivity. A promising method of producing ceramic composites is SHS-compaction [16]. It differs from hot-pressing known in powder metallurgy so that the ceramic composite is heated by the heat generated during the heat-producing synthesis of refractory compounds. The advantages of this method include the simplicity of equipment, lack of electricity costs and the possibility of making large-sized products from ceramic composites.

The formation of the microstructure of the B₄C–TiB₂ composite obtained under pressure by the SHS-method was studied in [17]. The formation of homogeneous composite microstructure depends on the B₄C content, which is 20 % wt.

In this paper, submicron powders of carbon black and boron were used as starting reactants. The purpose of the research is to investigate the influence of the B₄C mass fraction on the formation of the composite microstructure and its physical and mechanical properties.

Experimental Procedure

Heat-producing composite synthesis reactions were carried out according to the scheme



The final product was calculated as the formation of the product with different content of refractory compounds. The reaction mixtures for the synthesis of SHS-composites were prepared from the powders of titanium (PTM), boron (amorphous black) and carbon (P804), and the chemical oven was made from the powders of titanium (PTM), boron (amorphous black). The starting powders were pre-dried at a temperature of 373–393 K and mixed in a two-liter ball mill of the “tumbling barrel” type. The compositions of the reaction mixtures are shown in Table 1.

Self-propagating high-temperature synthesis and compaction of hot products were carried out in the reaction mold, a diagram of which is shown in Fig. 1, *a*. The green samples 30 mm in diameter, a height of 16 mm and a relative density of 0.6 were placed in a reaction mold equipped with a system initiating the heat-producing synthesis reaction. The free space in the mold was filled with silicon dioxide with dispersion of 300–500 μm used as dispersion medium. The photos of equipment for SHS-compaction are shown in Fig. 2.

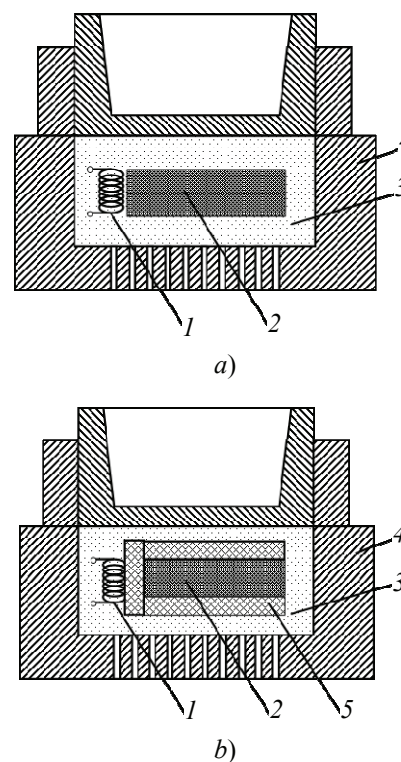


Fig. 1. Block-diagrams of the reaction molds for preparation of ceramic composites by SHS-pressing without a chemical oven (*a*) and with a chemical oven (*b*): 1 – tungsten spiral; 2 – green samples; 3 – disperse heat insulator (SiO₂); 4 – mold; 5 – chemical oven

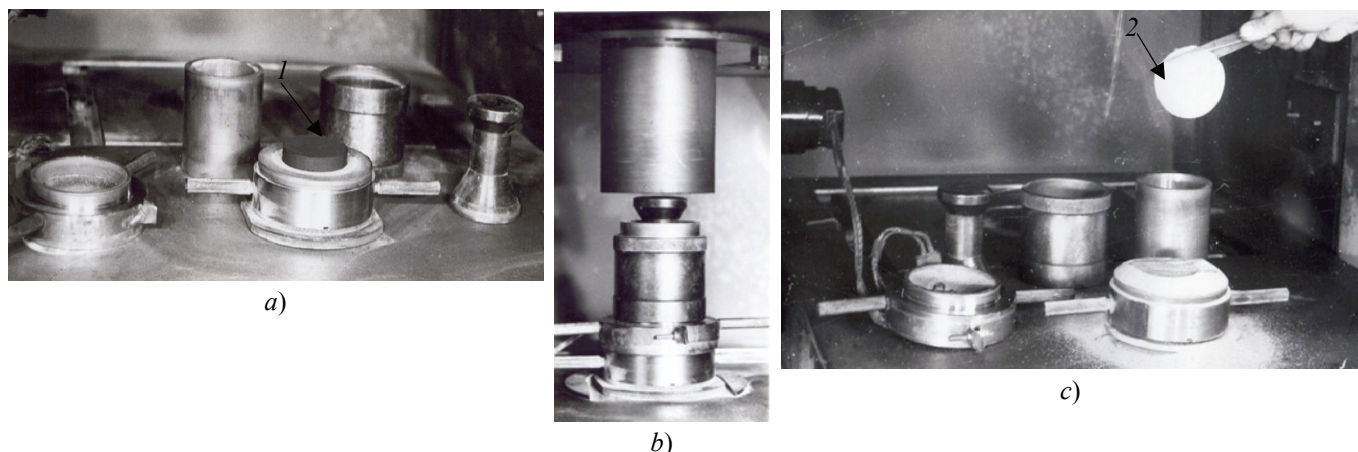


Fig. 2. The process equipment for the implementation of SHS compaction:

a – green samples (1) and mold parts; *b* – assembled mold on the worktable of a hydraulic press; *c* – the resulting hot SHS product (2)

The combustion reaction was assisted with the electric current sintering of tungsten spiral. The heat-producing synthesis was carried out under the pressure of 10 MPa, while the compaction of the target product was made at a pressure of 100 MPa.

Low pressure in the first stage was caused by the need to remove the impurity gas released during combustion and prevents densification of the final product. The obtained sample was removed from the mold and placed in the quartz sand for cooling. The duration of the first stage corresponded to the burning time of the heterogeneous mixture, the second stage corresponded to the time of hot compacting of the ceramic composite. The duration of this stage depends on the cooling time, during which the synthesized product manifested the ability to deform.

To improve the efficiency of compaction of synthesis products a chemical oven was used. The block diagram of the reaction mold with a chemical oven is shown in Fig. 1, *b*. Green samples were placed between layers of the chemical oven, which was isolated with the layers of graphite foil (see Fig. 1, *b*). Tablets pressed from a stoichiometric mixture of titanium and boron powders were used as a chemical oven; the heat-producing chemical reaction in the oven was carried out by the scheme



The ratio of the green sample and chemical oven mass was 1:4. The adiabatic combustion temperature of the chemical oven was 3500 K. The pressing time (holding pressure) was 3–60 s.

The microstructure of the composites was studied by scanning electron microscopy using Zeiss Ultra

plus – a field emission scanning electron microscope with ultra-high resolution. The phase composition of the SHS-composites was studied with “DRON-3” diffractometer using monochromatic Cu-K α radiation, the computer program “Crystallographica Search Match” and base of diffraction data “Power Diffraction File” (PDF-2, ICDD, USA, Release 2011). To study the microstructure and phase composition of the samples their surfaces were ground and polished. The Vickers hardness test was conducted using PMT-3 device under a load of 100 g in accordance with GOST 3450–76. The ceramic density of the samples was determined by hydrostatic weighing in accordance with GOST 25281–82.

Experimental Results

The results of the thermodynamic analysis of the system $(1-x)(\text{Ti}+2\text{B})+x(4\text{B}+\text{C})$ obtained by Thermo program are shown in Fig. 3.

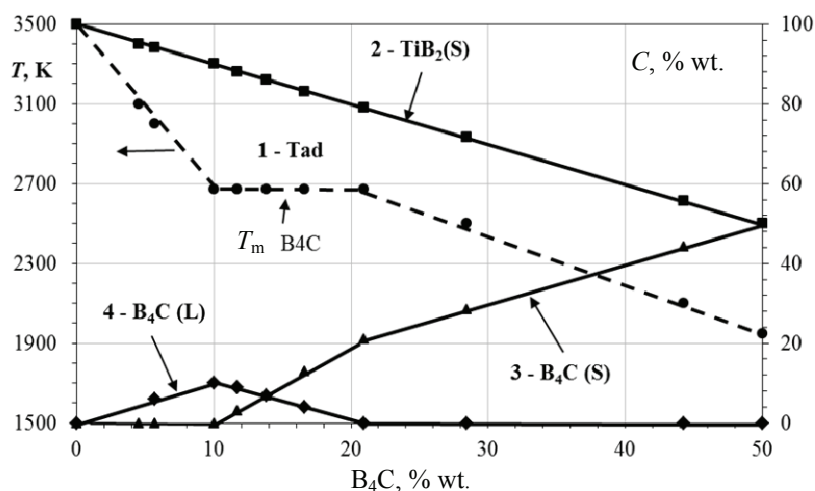


Fig. 3. Dependences of adiabatic combustion temperature (*T*) and composition of final product equilibrium on B₄C content:
2 – TiB₂ (S); 3 – B₄C (S); 4 – B₄C (L)

We see that the equilibrium product contains TiB_2 and B_4C , and their weight ratio is determined by the composition of the reaction mixture. With increasing content of B_4C in the final product to 50 % wt., the adiabatic combustion temperature (T_{ad}) decreases from 3500 to 2000 K. If you change the content of B_4C from 10 to 21 % wt., T_{ad} remains constant, equal to the melting point of boron carbide. The maximum proportion of the molten boron carbide in the final product is 10 % wt.

The results of thermodynamic calculations agree well with the data of X-ray diffraction of SHS-composites. Diffraction patterns in Fig. 4 show that the final product formed during the combustion of mixtures 1–5 contains TiB_2 and B_4C . The coincidence of compositions of the synthesized composite with the calculated data indicates the formation of the equilibrium SHS-products.

The efficacy of compacting SHS-products depends on its content of the liquid phase. With an increase in the content of the liquid phase the porosity of the final product decreases [18]. As shown above, the maximum proportion of the molten boron carbide is 10 % wt. It was assumed that at 10 % wt. B_4C a SHS-composite with minimal residual porosity can be obtained. However, the minimum porosity of the SHS-composite prepared without a chemical oven was 6 % (Fig. 5, curve 1). This is due to the fact that high thermal conductivity causes a rapid cooling of the synthesized product. This reduces the amount of liquid phase and its lifetime during which the resulting product manifests plastic properties.

In order to reduce the residual porosity the SHS-composites were synthesized using a chemical oven. Figure 5 (curve 2) shows the dependence of the

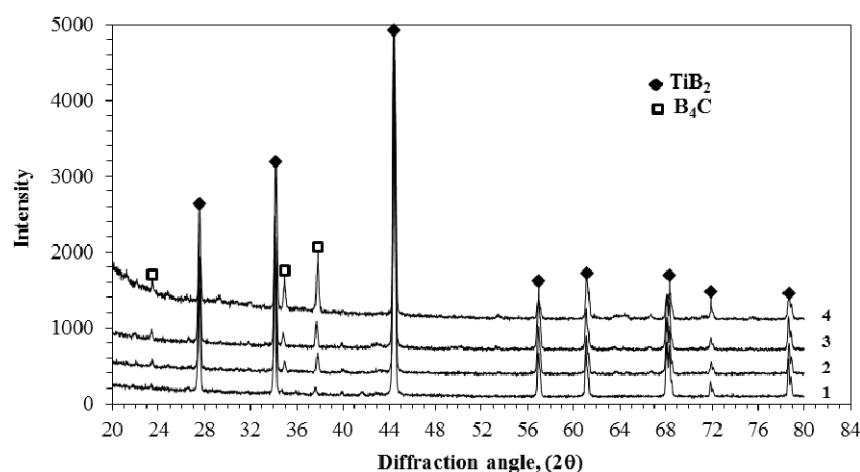


Fig. 4. XRD patterns of the $\text{TiB}_2\text{-xB}_4\text{C}$ composites, % wt.:
1 – $x = 20$; 2 – $x = 30$; 3 – $x = 40$; 4 – $x = 50$

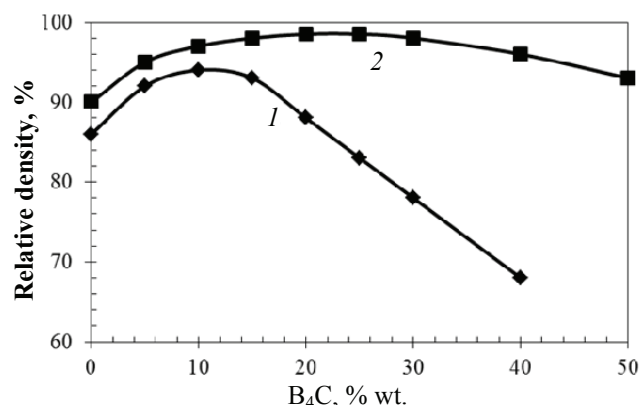


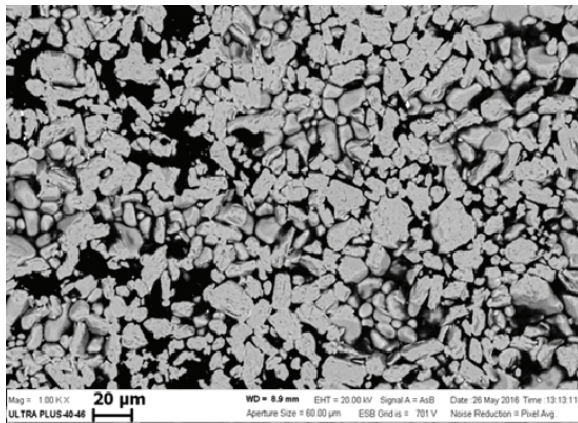
Fig. 5. Dependences of relative density of SHS-composites produced without a chemical oven (1) and with a chemical oven (2) on the B_4C content in the composite

relative density of the SHS-composite prepared using a chemical oven. We see that when the content of B_4C was 15–30 % wt., the relative density of the SHS-composite was 97–98 %. Increase in the content of boron carbide to 30 % wt. reduces the density of composites.

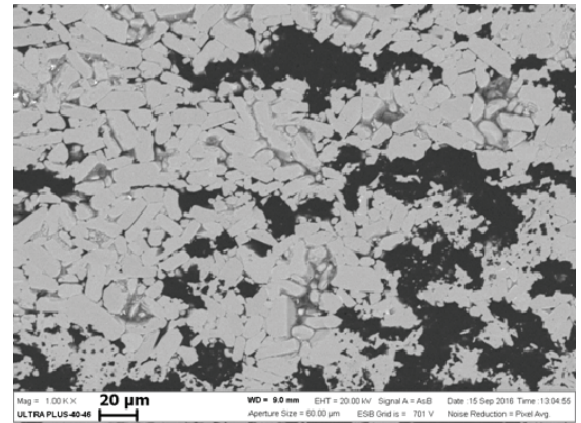
We consider the influence of the ceramic binder content on the composite microstructure. Figure 6 shows the microstructure of SHS-composites. It is seen that they consist of a dispersed phase – TiB_2 (light phase) and a ceramic binder – B_4C (dark phase). When the content of B_4C was 20 % wt., the average size of titanium diboride particles was 10–15 μm (see Fig. 6, a). Owing to the good wetting, the molten boron carbide uniformly flowed on the surface of TiB_2 particles. With increasing B_4C content in the final product to 50 %, an average TiB_2 particle size decreased to 1–0.5 μm (Fig. 6, d), which was caused by a decrease in the combustion temperature.

When the B_4C content was 50 % wt., the final product formed areas composed of colonies TiB_2 particles, in which B_4C was virtually non-existent. The formation of SHS-composite with uneven distribution of the ceramic binder was due to the low temperature combustion and the absence of molten B_4C .

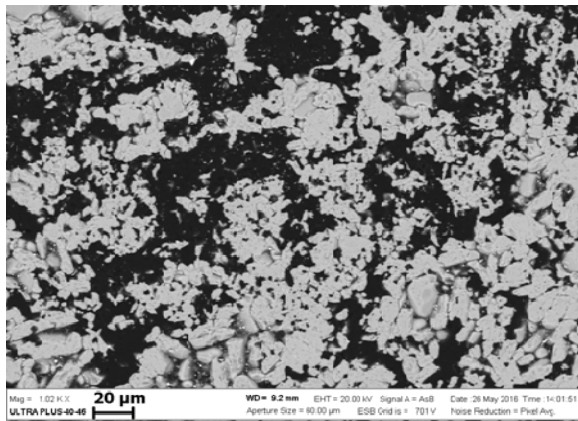
Table 2 shows physical and mechanical properties of SHS-composites. When the B_4C content in the final product increased from 20 to 40 % wt., the microhardness increased from 37.1 to 44.8 GPa and flexural strength increased from 90 to 210 MPa. Further increase in boron carbide content in the composite increased the residual porosity up to 7 %.



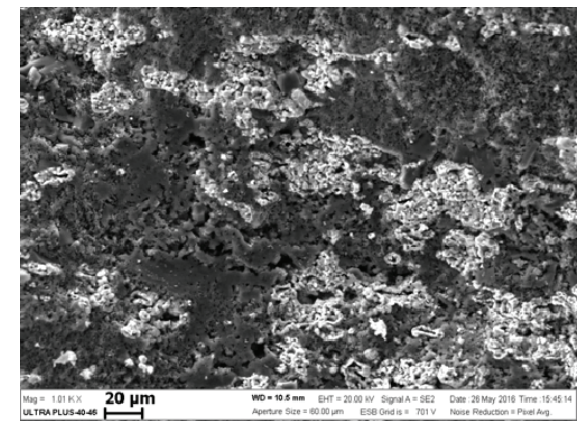
a)



b)



c)



d)

Fig. 6. SEM of the $\text{TiB}_2\text{-xB}_4\text{C}$ composites, % wt.:
 $a - x = 20$; $b - x = 30$; $c - x = 40$; $d - x = 50$

Table 2

Properties of SHS-composites preparation with a chemical oven

Composition	Composition of SHS-composites, % wt.		Flexural strength, MPa	Hardness, GPa
x	TiB_2	B_4C		
0	100	0	—	—
0.1	90	10	90	—
0.2	80	20	120	37.1
0.3	70	30	140	44.8
0.4	60	40	210	39.1
0.5	50	50	—	—

Conclusion

The SHS-compaction method was used to produce composites based on the $\text{TiB}_2\text{-B}_4\text{C}$ system, containing TiB_2 as a disperse phase, and B_4C as a ceramic binder. It is shown that for effective pressing of the synthesized composite it is necessary to use an additional source of heat in the form of a chemical oven with high heat capacity. This approach provided the necessary thermal conditions for the synthesis

of ceramic composites with a specified phase composition and melting of ceramic binder. The high content of liquid phase resulted in ceramic composites with minimal residual porosity of 1.5–2.0 %, bending strength of 140–210 MPa and microhardness of 37.1–44.8 GPa.

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References

1. Yamada S., Hirao K., Yamauchi Y., Kanzaki S. High strength $\text{B}_4\text{C-TiB}_2$ composites fabricated by reaction hot-pressing. J. Eur. Ceram. Soc., 2003, Vol. 23, No. 7, pp. 1123–1130, [http://dx.doi.org/10.1016/S0955-2219\(02\)00274-1](http://dx.doi.org/10.1016/S0955-2219(02)00274-1)
2. Srivatsan T.S., Guruprasad G., Black D., Petraroli M., Radhakrishnan R., Sudarshan T.S. Microstructural development and hardness of $\text{B}_4\text{C-TiB}_2$ composite samples: influence of consolidation temperature. J. Alloy Compd.,

2006, Vol. 413, No. 1–2, Pages 63–72, <http://dx.doi.org/10.1016/j.jallcom.2005.04.209>

3. Yue X.Y., Zhao S.M., Lü P., Chang Q., Ru H.Q. Synthesis and properties of hot pressed B_4C - TiB_2 ceramic composite. *Mat. Sci. Eng. A*, 2010, 527(27-28): 7215-7219, <http://dx.doi.org/10.1016/j.msea.2010.07.101>

4. Springer Handbook of Condensed Matter and Materials Data. Martienssen W, Warlimont H, editors. Berlin–Heidelberg–New York, Springer, 2005, pp. 451–458.

5. Kiffer R., Benezovskij F. Tverdye materialy [Solid materials]. Translated from German. M.: Metallurgija, 1968, 384 p. (Rus)

6. Samsonov G.V., Serebrjakova T.I., Neronov V.A. Boridy [Borides]. M.: Atomizdat, 1975. 376 p. (Rus)

7. Thevenot F. A review on boron-carbide. *Advanced Ceramics*, 1991, 56: 59–88, DOI: <http://dx.doi.org/10.4028/www.scientific.net/KEM.56-57.59m>.

8. Levine S.R., Opila E.J., Halbig M.C., Kiser J.D., Singh M., Salem J.A. Evaluation of ultra-high temperature ceramics for aero propulsion use. *J. Eur. Ceram. Soc.* 2012. vol. 22, pp. 2757-2767, DOI: [http://dx.doi.org/10.1016/S0955-2219\(02\)00140-1](http://dx.doi.org/10.1016/S0955-2219(02)00140-1)

9. Munro R.G. Material properties of titanium diboride. *J. Res. Natl. Inst. Stand. Technol.* 2000, 105, 709-720, DOI: <http://dx.doi.org/DOI: 10.6028/jres.105.057>

10. Sigl L.S., Kleebe H.J. Microcracking in B_4C - TiB_2 composites. *Journal of the American Ceramic Society*. 1995, 78 (9), 2374-2380.

11. Skorokhod V., Krstic V.D. High strength-high toughness B_4C - TiB_2 composites. *J. Mater. Sci. Lett.*, 2000, Vol. 19, No. 3, pp 237–239, DOI: <http://dx.doi.org/10.1023/A:1006766910536>

12. Itoh H., Sugiura K., Iwahara H. Preparation of B_4C - TiB_2 composites by high pressure sintering. *J. Alloy*

Compd. 1996, Vol. 232, No. 1–2, pp. 186-191, [http://dx.doi.org/doi:10.1016/0925-8388\(95\)01972-3](http://dx.doi.org/doi:10.1016/0925-8388(95)01972-3)

13. Yamada S., Hirao K., Yamauchi Y., Kanzaki S. High strength B_4C - TiB_2 composites fabricated by reaction hot-pressing. *J. Euro Ceram. Soc.*, 2003;23:1123–30, doi: [http://dx.doi.org/10.1016/S0955-2219\(02\)00274-1](http://dx.doi.org/10.1016/S0955-2219(02)00274-1)

14. Bellosi A., Monteverde F., Sciti D. Fast densification of ultra-high-temperature ceramics by spark plasma sintering. *Int. J. Appl. Ceram. Technol.*, 2006; Vol. 3, No. 1, Pages 32–40, DOI: <http://dx.doi.org/10.1111/j.1744-7402.2006.02060.x>

15. Dudina D.V., Hulbert D.M., Jiang D., Unuvar C., Cytron S.J., Mukherjee A.K.. In-situ boron carbide-titanium diboride composites prepared by mechanical milling and subsequent Spark Plasma Sintering. *J. Mater. Sci*, 43 (2008) 3569-3576, DOI: <http://dx.doi.org/10.1007/s10853-008-2563-8>

16. Pitjulin A.N. Silovoe kompaktirovanie v SVS processah [Power compacting in SHS processes] // V knige “Samorasprostranjajushhijsja vysokotemperaturnyj sintez: teorija i praktika” [In the book “Self-Propagating High-Temperature Synthesis: Theory and Practice”]. Chernogolovka: “Territorija”. 2001. pp. 333–353 (Rus)

17. Ziemnicka-Sylwester M. TiB_2 -Based Composites for Ultra-High-Temperature Devices, Fabricated by SHS, Combining Strong and Weak Exothermic Reactions *Materials*, 6, 1903 (2013); doi: <http://dx.doi.org/10.3390/ma6051903>

18. Shcherbakov V.A., Gryadunov A.N., Shteinberg A.S. Macrokinetics of the process of SHS compaction. *Journal of Engineering Physics and Thermophysics*, 63(5), 1111-1119 (1992), doi: <http://dx.doi.org/10.1007/BF00853507>