Synthesis and characteristics of the B_4C–ZrB_2 composites

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Bulk ceramic materials based on B_4C–ZrB_2 systems have been produced by means of pressure-assisted Self-propagating High temperature Synthesis (SHS) using a mixture of elementary powders B, C and Zr. Reactant mixture compositions were chosen based on thermodynamic calculations to obtain synthesis regimes with the formation of a liquid phase, ensuring proper compaction. The liquid phase in the SHS products consisted from molten B_4C. The influence of a "chemical oven" on densification of the SHS-products was studied. Significant reducing of ceramic residual porosity was obtained at mass ratio of the reaction mixture and the "chemical oven" 1 : 4. The minimum residual porosity of SHS composites obtained by a "chemical oven" is 1.7%. X-ray analysis showed that SHS products were equilibrium and contain refractory compounds ZrB_2 and B_4C, which formed a dispersed phase and a ceramic binder. The influence of the composition of the reaction mixture on the formation of the microstructure and phase composition of ceramic composites was studied. It is established that microstructure of SHS-composites depends on the B_4C content. At the B_4C content less than 10% wt. the B_4C–ZrB_2 ceramic composite has uniform microstructure with ZrB_2 grain sizes of $10-20$ µm. Increasing of the B4C contents up to 20% wt. leads to decreasing of the ZrB_2 grain size up to $2-5$ µm. Vickers Hardness of the SHS composites are $21-24.5$ GPA.

Keywords: SHS, compacting, ceramic composite B_4C–ZrB_2, microstructure, hardness.

1. Introduction

Zirconium diboride and boron carbide have high refractoriness, heat resistance, hardness, strength, low density [1, 2]. Zirconium diboride (ZrB_2) and B_4C are used as material for high-temperature structural applications, such as thermal protection structures in the aerospace industry, crucibles for molten metal, cutting tools due to a combination of high melting point, high strength, high thermal and electrical conductivity [3 – 6]. However, the use of boron carbide as the material of construction is limited by its low fracture toughness. Adding TiB_2 and B_4C particles improves the mechanical characteristics of the composite. It was found [10] that the addition of 30.5% wt. TiB_2 increases the B_4C 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 strength of 621 MPa and a fracture toughness of 6.1 MPa·m$^{1/2}$.

The B_4C–ZrB_2 ceramic composites are promising for production the parts working in corrosive environments at high temperatures. The B_4C–ZrB_2 composites are obtained by hot pressing (HP) at a temperature close to the melting point of boron carbide [7 – 9] and by spark plasma sintering (SPS) [10 – 11].

A promising method of producing ceramic composites is SHS-compaction [12]. The peculiarity of this method is that a ceramic composite is heated in the course exothermic synthesis of refractory compounds.

The advantages of this method include the simplicity of equipment, lack of electricity costs and the possibility of making large-scale products from ceramic composites.

The purpose of this work is to study the possibility of obtaining high-temperature the B_4C–ZrB_2 composites by means of pressure-assisted self-propagating high temperature synthesis (SHS). The main goal is to study the influence of the reaction mixture composition on microstructure formation and physical and mechanical characteristics of the SHS composites.

2. Experimental procedure

Exothermic reactions of synthesis were carried out according to the scheme

$$(1-x)(Zr + 2B) + x(4B + C) \rightarrow (1-x)ZrB_2 + xB_4C. \quad (1)$$
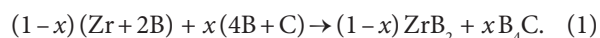
The reaction mixtures compositions were calculated on formation the final product with different content of the refractory compounds. The reaction mixtures compositions are given in the Table 1.

The powders of zirconium (PZRk-1), boron (amorphous black B-99A) and carbon (P804) were used for preparation the reaction mixtures for synthesis the composites. The initial powders were pre-dried at a temperature of 373 – 393 K and mixed in a two-liter ball mill of the "drunk cylinder" type.

To increase the efficiency of compaction and to reduce the residual porosity of the target product, exothermic synthesis was carried out using additional heating. For this goal was carried out with a chemical stove pressed from a stoichiometric mixture of titanium powders (PTM grade) and boron (amorphous black grades). The exothermic reaction in the "chemical oven" was carried out by the scheme

$$\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2. \qquad (2)$$
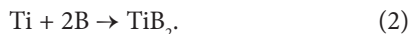
Exothermic synthesis and consolidation of the B_4C–ZrB_2 composite were carried out in the reaction press-form a schematic of which is shown in Fig. 1 and described in [13]. The green compacts and "chemical ovens" were pressed with a diameter of 60 mm, a height of 16 mm with relative density of 0.6. The green compact was placed in a reaction press-form between the layers of the "chemical oven", which were separated from each other by a graphite foil. The exothermic reactions in the compact and "chemical ovens" were initiated by tungsten spiral heated with the electric current. Exothermic synthesis was carried out at 10 MPa of pressure, and consolidation of SHS product at 100 MPa of pressure. Consolidation time (holding under pressure) was varied from 5 to 30 seconds.

Table 1. Compositions of the reaction mixtures and SHS-products.

	Reactants*, % wt.			SHS-product, % wt.		T_{ad}, K	Liquid phase, % wt.
x	Zr	B	C	ZrB_2	B_4C		
0.05	76.81	22.1	1.09	95	5	3320	5
0.1	72.77	25.06	2.17	90	10	3280	10
0.125	70.74	26.54	2.72	87.5	12.5	2700	12.5
0.15	68.72	28.02	3.26	85	15	2700	5
0.2	64.68	30.972	4.348	80	20	2700	0

*Compositions of green mixture and SHS-product are given as weight percentage.
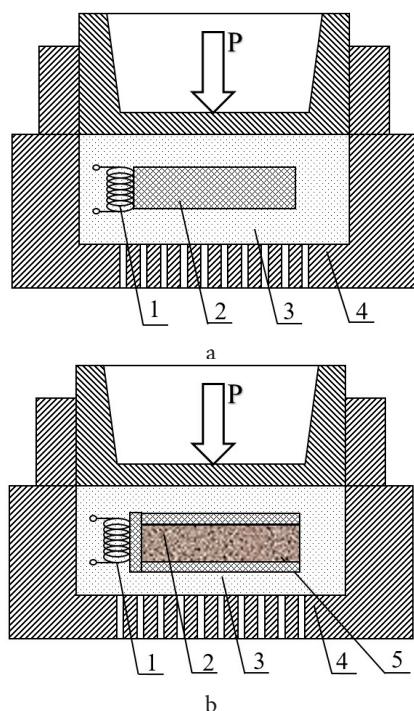

Fig. 1. Schematic of the reaction molds for preparation of ceramic composites by SHS-pressing without a "chemical oven" (a) and with a "chemical oven" (b): 1 — tungsten spiral; 2 — green samples; 3 — disperse heat insulator (SiO_2); 4 — mold; 5 — "chemical oven".

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-Kα 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 and a dwell time of 10 s in accordance with GOST 3450 – 76. The density of ceramic samples was determined by hydrostatic weighing in accordance with GOST 25281 – 82 on analytical scales with an accuracy of 10^{-4} g.

3. Experimental results

Characteristics of composites are largely determined by value of residual porosity. So an important task is to select the thermal mode of SHS-pressing, in which the final product contains a molten ceramic binder. The formation of a liquid phase allows a significant increase in ductility of hot SHS product and consolidates the composite to minimum residual porosity.

The thermodynamic calculations carried out using the THERMO program [14, 15] showed that increasing the B_4C content from 6 to 22% wt. result to decreasing adiabatic combustion temperature from 3320 K (melting point ZrB_2) to 2540 K (melting point B_4C).

At these conditions ZrB_2 is in the solid and B_4C is in the liquid state. The maximum amount of the molten binder (B_4C) is 12.5 wt. %. It is shown that the equilibrium products of the synthesis are refractory compounds, which are used as the dispersed phase (ZrB_2) and the ceramic binder (B_4C).

The Table 2 presents the data on influence of the binder content on density and residual porosity of the SHS composites. The experiment results showed that the minimum residual porosity 8.2% is achieved at the B_4C content of 12.5%. The high residual porosity of SHS composites is due to low content of the liquid phase and rapid cooling, which makes difficult to consolidate the synthesized product.

In order to increase the fraction of the liquid phase and the time of its existence, the green compact was placed in a

Table 2. Characteristics of the SHS-composites.

x	ρ_{theor}, g/cm³	Out of "chemical oven"		"chemical oven"		
		ρ_{theor}, g/cm³	Π, %	ρ_{exp}, g/cm³	Π, %	HV, GPa
0.05	5.7	5.4	10.3	5.5	3.5	20.4
0.1	5.3	4.8	8.7	5.2	2.8	22.1
0.125	5.15	4.7	8.2	5.2	1.7	24.5
0.15	5	4.5	9.4	4.7	5.6	24.6
0.2	4.73	4.2	12.1	4.4	7.4	20.9

"chemical oven". Thermodynamic calculations have shown that varied mass ratio of green compact and "chemical oven" from zero to $1:9$ result to increasing maximum proportion of the molten binder from 10 to 100%.

The synthesis of SHS-composites was carried out at mass ratio of green compact and "chemical oven" equal $1:4$. The adiabatic combustion temperature of the chemical furnace is $T_{ad} = 3500$ K.

The results of the experiments are presented in Table 2. It is seen that consolidation SHS-product in the "chemical oven" reduces the residual porosity of composites. In this conditions minimum residual porosity of the composite is $\Pi = 1.7\%$.

According to X-ray phase analysis the SHS-products are only two compounds — ZrB_2 and B_4C. The good agreement between thermodynamic calculations and experimental results has confirmed synthesis of equilibrium products.

The microstructural investigations have confirmed influence of the B_4C content on densification and the ZrB_2 grain size in the SHS ceramic materials. Fig. 2 shows the microstructures of the B_4C–ZrB_2 composites. It is seen that they consist of a dispersed phase of ZrB_2 (light phase) and a ceramic binder B_4C (dark phase).

Due to good wetting, the molten boron carbide evenly spreads over the surface of the ZrB_2 particles. At the B_4C content less than 10% wt. the ceramic composite has uniform microstructure with ZrB_2 grain sizes of $10-20$ μm.

The increasing of the B_4C contents up to 20% wt. leads to decreasing of the ZrB_2 grain size up to $2-5$ μm. At the B_4C content more than 20% wt. the ceramic composite has formed with nonuniform microstructure (Fig. 2c-d).

Hardness of the five samples is presented in Table 2. As the proportion of B_4C binder increased, there was increase in hardness of the composites. This is due to a corresponding change in density of the composites. Measurement of hardness by Vickers showed at the B_4C content $12.5-15\%$ wt. is achieved maximum value of $HV = 20.4-24.6$ GPa. These values exceed the hardness of the B_4C–ZrB_2 composites obtained by hot pressing in [9, 16].

4. Conclusions

The B_4C–ZrB_2 composites have been successfully produced by means of pressure-assisted self-propagating high temperature synthesis (SHS). The use of a "chemical oven" provided an optimal thermal regime for the synthesis of ceramic composites, which significantly reduced their residual porosity. It is shown that an increase in the B_4C content to 20% leads to a decrease in the particle size of ZrB_2 to $2-5$ μm and the formation of a composite with a Vickers hardness of $21-24.5$ GPa.
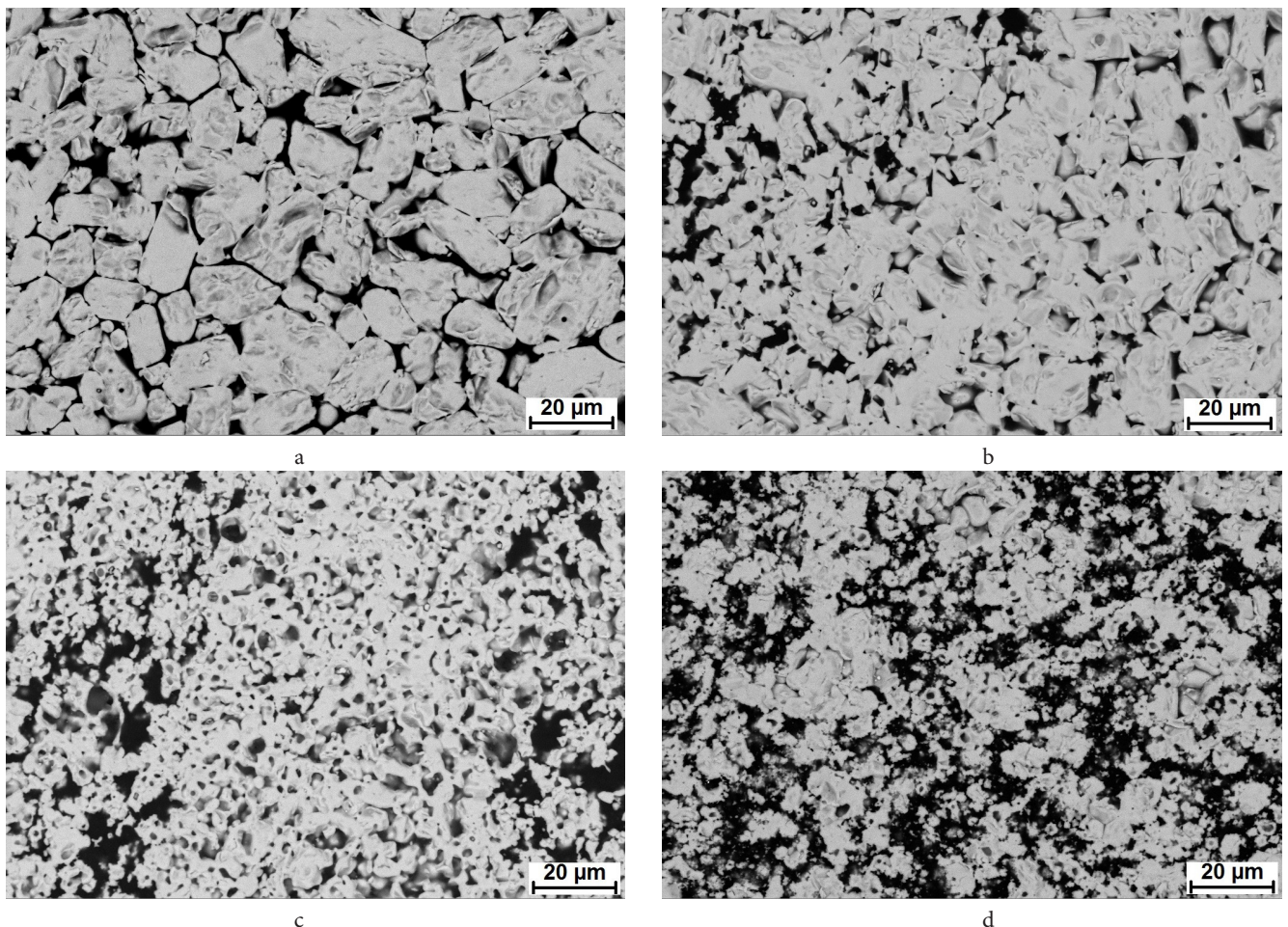
Fig. 2. SEM images of the ZrB_2–xB_4C composites: $x = 5$ (a), 10 (b), 15 (c), 20 (d) %. The light phase is ZrB_2, the dark phase is B_4C.

References

1. S. M. Zhu, W. G. Fahrenholtz, G. E. Hilmas, S. C. Zhang, E. J. Yadlowsky, M. D. Keitz. Composites Part A. 39 (3), 449 (2008). DOI: 10.1016/j.compositesa.2008.01.003

2. W. Han, J. Gao, J. Zhang, J. Yu. Int. J. Eng. Innov. Technol. (IJEIT). 3 (1), 163 (2013).

3. M. M. Opeka, I. G. Talmy, E. J. Wuchina, J. A. Zaykoski, S. J. Causey. J. Eur. Ceram. Soc., 19 (13–14), 2405 (1999). DOI: 10.1016/S0955–2219 (99) 00129–6

4. W. G. Fahrenholtz, G. E. Hilmas, I. G. Talmy, J. A. Zaykoski. J. Am. Ceram. Soc. 95 (5), 1347 (2007). DOI: 10.1111/j.1551–2916.2007.01583.x

5. V. Domnich, S. Reynaud, R. A. Haber, M. Chhowalla. J. Am. Ceram. Soc. 94 (11), 3605 (2011). DOI: 10.1111/j.1551–2916.2011.04865.x

6. F. Thevenot. J. Eur. Ceram. Soc. 6 (4), 205 (1990). DOI: 10.1016/0955–2219 (90) 90048-K

7. A. L. Chamberlain, W. G. Fahrenholtz, G. E. Hilmas. J. Eur. Ceram. Soc. 29 (16), 3401 (2009). DOI: 10.1016/j.jeurceramsoc.2009.07.006

8. W. M. Guo, L. X. Wu, Y. You, H. T. Lin, G. J. Zhang. J. Eur. Ceram. Soc. 36 (4), 951 (2016). DOI: 10.1016/j.jeurceramsoc.2015.11.022

9. X. G. Wang, W. M. Guo, Y. M. Kan, G. J. Zhang. Adv. Eng. Mat. 12 (9), 893 (2010). DOI: 10.1002/adem.201000012

10. J. Zou, S. G. Huang, K. Vanmeensel, G. J. Zhang, J. Vleugels, O. Van der Biest. J. Am. Ceram. Soc. 96 (4), 1055 (2013). DOI: 10.1111/jace.12284

11. S. Chakraborty, P. K. Das, D. Ghosh. Rev. Adv. Mater. Sci. (RAMS). 44, 182 (2016).

12. A. N. Pitjulin. In the book "Self-Propagating High Temperature Synthesis: Theory and Practice". Chernogolovka: "Territoriya". Ed. Sychev A. E., 432 p. (2001), pp. 333–353 (in Russian) [Питюлин А. Н. Силовое компактирование в СВС процессах, С. 333–353 в книге "Самораспространяющийся высокотемпературный синтез: теория и практика". Черноголовка: "Территория", 432 с. (2001)]

13. V. A. Scherbakov, A. N. Gryadunov, M. I. Alymov. Advanced Materials & Technologies. 4, 16 (2016). DOI: 10.17277/amt.2016.04.pp.016–021

14. A. A. Shiryaev. Int. J. of SHS. 4 (4), 351 (1995).

15. S. S. Mamyan, A. A Shiryaev, A. G. Merzhanov. Journal of Engineering Physics and Thermophysics. 65 (4), 974 (1993). DOI: 10.1007/BF00862769

16. S. Chakraborty, D. Debnath, A. R. Mallick, P. K. Das. Int. J. Appl. Ceram. Technol., 12. (3). 568 (2015). DOI: 10.1111/ijac.12290