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INVESTIGATION OF MECHANICAL CHARACTERISTICS OF MATERIALS BASED ON REFRACTORY BORIDES

The object of research is the effect of sintering under pressure (10 MPa–4.1 GPa) on the formation of the structure and properties of ZrB_2, HfB_2, and composites on their bases. It has been found that high pressure consolidation results in an improvement of mechanical characteristics. In particular, the hardness and fracture toughness of the materials sintered under 4.1 GPa pressure are higher than those of the materials obtained under hot pressing conditions at 20–30 MPa and spark-plasma sintering at 50 MPa.

High-pressure sintered HfB_2 demonstrated hardness H_V (9.8 N) $= 21.3 \pm 0.8$ GPa, H_V (49 N) $= 19.3 \pm 1.3$ GPa, and H_V (98 N) $= 19.2 \pm 0.5$ GPa and fracture toughness K_{1C} (49 N) $= 7.2$ MPa·$m^{0.5}$ and K_{1C} (98 N) $= 5.7$ MPa·$m^{0.5}$. The HfB_2 sintered by hot pressing at 1850 °C and 30 MPa demonstrated hardness: H_V (9.8 N) $= 19.0$ GPa, H_V (49 N) $= 18.7$ GPa, and H_V (98 N) $= 18.1$ GPa, K_{1C} (9.8 N) $= 7.7$ MPa·$m^{0.5}$, K_{1C} (49 N) $= 6.6$ MPa·$m^{0.5}$ and K_{1C} (98 N) $= 5.3$ MPa·$m^{0.5}$. High pressure sintered ZrB_2 ($a = 0.3167$ nm, $c = 0.3528$ nm, $\gamma = 6.2$ g/cm^3) demonstrated H_V (9.8 N) $= 17.7 \pm 0.6$ GPa, H_V (49 N) $= 15.4 \pm 1.2$ GPa, and H_V (98 N) $= 15.3 \pm 0.36$ GPa and K_{1C} (9.8 N) $= 4.3$ MPa·$m^{0.5}$, K_{1C} (49 N) $= 4.2$ MPa·$m^{0.5}$ and K_{1C} (98 N) $= 4.0$ MPa·$m^{0.5}$. Addition of 20 wt. % of SiC to ZrB_2 and sintering under high pressure (4.1 GPa) allowed essential increase of hardness to H_V (9.8 N) $= 24.2 \pm 0.7$ GPa, H_V (49 N) $= 16.7 \pm 0.5$ GPa, and H_V (98 N) $= 17.6 \pm 0.4$ GPa and fracture toughness to K_{1C} (49 N) $= 7.1$ MPa·$m^{0.5}$, K_{1C} (98 N) $= 6.2$ MPa·$m^{0.5}$; the material density was $\gamma = 5.03$ g/cm^3. Additions of SiC and Si_3N_4 to ZrB_2 lead to some increase in fracture toughness (up to K_{1C} (98 N) $= 9.2$ MPa·$m^{0.5}$).

The developed ZrB_2- and HfB_2-based materials and composites can be used for aerospace applications, in cutting and refractory industries, etc.

Keywords: *zirconium diboride, hafnium diboride, hot pressing, ultra-high temperature ceramics, high quasi isostatic pressure.*

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1. Introduction

For the manufacture of supersonic aircraft mainly aluminum aviation alloys are used, and metal super alloys are used in more critical areas (for example, for the manufacture of engine components). At speeds in excess of 2 Mach, the temperature at certain areas of a fuselage may approach the melting point of aluminum thus carbon composites are useful and employed there. Although the production of carbon composites is well-developed and there is a wide range of materials based on those that can be used to design aircraft, a development of new materials with improved physic-mechanical characteristics. These materials must have a set of parameters: more resistant to ablation at high energy, oxygen- and radiation-resistant and stable to aggressive media, thermal shocks and temperature gradients, cheap and with improved performance characteristics. The further progress in this direction can be achieved due to the development of simpler and less costly manufacturing technologies of these materials. Recently, aluminum oxide reinforced with aluminum fibers have also been used for high-speed aircraft bodies. Carbides, nitrides, and diborides of transition metals are of constant theoretical and practical interest because of such unique properties as extremely high melting points, high hardness, electrical and thermal conductivity, and superconductivity, which are closely related to their electronic structure [1]. Ceramic composites based on refractory borides exhibit high resistance to oxidation and corrosion at ultra-high temperatures and suitable for their use in hypersonic apparatus. Boride-based composites are also rather promising for the manufacture of high-temperature thermoelectric converters.

The promising materials for aerospace application can be AlB_{12}- and B_4C-based. Almost all modifications of boron have a common structural element: 12 boron atoms are located at the vertices of an almost regular icosahedron and are connected to each other in different ways. All boron-rich compounds with a bulk modulus of ~200 GPa are actually constructed from B_{12} icosahedra, as in pure boron. This leads to strong covalent bonds and, as a result, hardness of at least 30 GPa. Obviously, such high values of hardness and bulk modulus are largely associated with the nature of chemical bonds in complex boron compounds. It has been shown recently [2, 3] that using as initial the nanopowders, sintering temperature of aluminum dodecaboride-based ceramics can be reduced by 300 °C under hot pressing (30 MPa) and by 750 °C under high pressure (2 GPa) – high temperature conditions, what made the process cheaper. The formation of solid solutions during consolidation allowed achieving the higher level of the materials mechanical characteristics. The aluminum dodecaboride and boron based composites demonstrated the following mechanical characteristics. The composite contained $AlB_{12}C_2$ (74 mass %)+TiB_2 (22 mass %), having density γ=3.12 g/cm^3, showed Vickers microhardness H_V (49 N)=37.7±6.7 GPa, fracture toughness K_{1c} (49 N)= =6.9±0.6 MPa·m$^{1/2}$, K_{1c}(three point bending)=6.1 MPa·m$^{1/2}$, bending strength σ_{bend}=646 MPa, compression strength σ_{comp}=1143 MPa. The composite contained B_4C (78 mass %)+ +SiC (22 mass %), having density g=2.63 g/cm^3, showed H_V (49 N)=34.6±0.5 GPa, K_{1c} (49 N)=5.4 MPa·m$^{1/2}$, K_{1c} (three point bending)=7.4 MPa·m$^{1/2}$, bending strength σ_{bend}=474 MPa, compression strength σ_{comp}=1878 MPa.

Only four of the known elements have a melting point above 3000 °C, W, Re and Ta, but ThO_2 is the only oxide compound having a melting point above 3000 °C. Most materials with melting point above 3000 °C are borides, carbides, and nitrides of the early transition metals. Therefore, most of the studies concerning ultra-high temperature ceramics (UHTCs) are focused on compounds like ZrB_2, HfB_2, TaC, TaB_2, ZrC and HfC. Any compound containing a transition metal (Zr, Hf, Ta, Mo, W or Nb together with B, C or N) can be referred to ultra-high temperature. However, there is uncertainty in the melting point of these compounds. For example, ZrB_2 usually melts at 3250 °C according to phase diagrams obtained by [4, 5], nevertheless other researchers report different melting temperatures, including 3040 °C [6] and 3517 °C [7]. The reason for these discrepancies is not only the difficulty in accurate measurement of melting points at high temperatures, but also the fact that these compounds melt incongruously, i. e. they may decompose or dissociate before melting.

To be employed on the open air at temperatures up to 1600 °C alumina, magnesium, silicon carbide and silicon nitride are good enough, but many hypersonic applications involve higher temperatures. When compounds with a melting point higher 3000 °C specially combined with other phases (for example, to intensify sintering, grain size reducing additives, additives to elevate oxidizing resistance, etc.), or when in a ceramic there is an impurity contributing to a formation of a liquid, the material has melting temperature lower than 3000 °C. For the most common high temperature composite material ZrB_2–SiC solidus temperature makes about 2300 °C due to eutectic reaction. Zirconium diboride ZrB_2 is one of the promising materials for space shuttles of new generation. This material has high melting temperature >3000 °C [8], significant values of fracture strength, durability and heat resistance. Also, it has high thermal conductivity, which provides rapid heat removal and dissipation from the surface that is in contact with oxidative gas stream which is an extremely important advantage of composites based on ZrB_2. Development of effective methods of manufacturing erosion-resistant and ultra-refractory materials based on HfC ($T_{melting}$=3900 °C), TaC ($T_{melting}$=3800 °C), HfB_2 ($T_{melting}$=3380 °C), ZrB_2 ($T_{melting}$=3200 °C), TaB_2 ($T_{melting}$= =3200 °C), and NbB_2 ($T_{melting}$=3050 °C) is a pressing problem. Solid solutions have a higher melting point than the individual compounds. Thus, the melting point of single-phase carbide and C with 20 % HfC dissolved therein, i. e. (Ta, Hf)C is ~3950 °C. In addition to the high melting point, solid solutions are characterized by a remarkable correlation between hardness, thermal expansion coefficient (TEC), or thermal conductivity and a composition of solid solution. A combination of high thermal conductivity and low TEC determines material's heat resistance. Therefore, the synthesis of single-phase solid solutions $(Ta,Zr)B_2$ and $(Ta,Hf)B_2$, (Ta,Zr)C, (Ta,Hf)C is an important task.

Currently, UHTC developments are one of the crucial points of interest of material science. The recent study of diborides that form UHTC basis, demonstrated that mechanical properties and high temperature oxidation resistance are strongly improved with the addition of silicon carbide (SiC). To tackle a problem of thermal shock, UHTCs were reinforced with beams/fibers SiC_f or C_f [9]. In case HfB_2–SiC_f (SiC fibers) the best ceramic composition had H_V=21.6 GPa and fracture toughness K_{1C}=6.2 MPa·m$^{1/2}$ [9]. Nevertheless, fibers SiC broke into pieces at temperature of consolidation 2000 °C and higher; some silicides melt thus sintering temperature has to be close or lower than 1800 °C.

The UHTC is usually synthesized by hot pressure (HotP) or spark plasma sintering (SPS) methods. The present paper deals with the mechanical characteristics (hardness and fracture toughness) study of high pressure (4 GPa) – high temperature (HP-HT) sintered ZrB_2 and HfB_2 ceramics and composites on their bases which are compared with that of ceramics and/or composites prepared by HotP and SPS methods.

The relevance of this study is due to the need to develop new heat-resistant materials with improved physical and mechanical characteristics. It is expected to be achieved by using high and moderate pressures during their consolidation, as well as the creation of fundamentally new composite materials with the required set of physical and mechanical properties, in particular, due to the formation of solid solutions.

Thus, *the object of research* is the effect of sintering under pressure (10 MPa–4.1 GPa) on the formation of the structure and properties of ZrB_2, HfB_2, and composites on their bases. *The aim of research* is to study the correlations between manufacturing pressure (10 MPa–4.1 GPa) – temperature conditions, structure and mechanical characteristics of the consolidated ZrB_2- and HfB_2-based refractory materials.

2. Methods of research

As initial materials were used powders of ZrB_2 (Technical specification 6-09-03-46-75) and HfB_2 (Ukraine, Technical specification 6-09-03-418-75) with grain sizes <10 µm which contained 0.1 mass % and 0.2 mass % of admixture carbon, respectively. The unite cell parameters of the initial powders obtained by Reitveld refinement of X-ray patterns are given in Table 1.

Table 1

Unit cell parameters *a, b, c* and phase composition of the initial powders

Initial powder	Phase composition, mass. %	*a, b, c,* nm
ZrB_2	ZrB_2 – 97 %	*a* – 0.3168, *c* – 0.3530
	ZrO_2t – 1 %	*a* – 0.3604, *c* – 0.5208
	ZrO_2m – 2 %	*a* – 0.5153, *b* – 0.5210, *c* – 0.5310
HfB_2	HfB_2 – 100 %	*a* – 0.3143, *c* – 0.3476
Si_3N_4	A – 4 %	*a* – 0.7747, *c* – 0.5620
	B – 96 %	*a* – 0.7599, *c* – 0.2907

The additions of SiC (5–10 μm), Si_3N_4 were mixed with ZrB_2 and HfB_2 powders for 24 hours using «drunken barrel» mixture. For high pressure (under 4.1 GPa) – high temperature (at 1800 °C) sintering was used «recessed-anvil» type high pressure apparatus described everywhere [2]. Besides, consolidated samples were obtained by hot pressing technique (under 20 or 30 MPa pressure at 1800–2000 °C).

The structure of the samples was examined by X-ray diffraction using a DRON-UM1 diffractometer (USSR). X-ray diffraction patterns were obtained using monochromatic Cu°Kα radiation ($\lambda = 0.1541841$ nm) in the range of angles $2\theta = 8–88°$, with a scanning step of 0.05° and an exposure time at the point of 2 sec. The analysis of experimental data was performed using the software package PowderCell 2.4 using the full-scale Rietveld method [10], which makes it possible to obtain data concerning the structure of crystalline materials, including unit cell parameters, atomic coordinates, thermal vibration parameters, etc. The materials structures were as well studied using a JAMP-9500F microscope (Japan) equipped by EDX and Auger detectors.

Microhardness and fracture toughness were estimated by Vickers indenter using hardness tester FALCON 500, Netherlands (equipped with an optical microscope, digital 5-MP camera and computer) under the loads of 9.8 N, 49 N and 98 N. At least 5 measurements were performed for each sample. For the samples with a large discrepancy of data at different points up to 15 measurements for each sample were performed.

3. Research results and discussion

Table 2 shows the compositions of the initial mixtures, details of the preparation method, the phase composition of the consolidated materials and the unit cell parameters of the phases present, determined by X-ray diffraction analysis. Table 3 demonstrates results of hardness and fracture toughness tests of the materials described in Table 2 (the numbering in Tables 2 and 3 are the same). Table 4 demonstrates the highest found in literature Vickers hardness of the HfB_2 and ZrB_2-based materials prepared using SPS technique [11].

Fig. 1 shows microstructures of ZrB_2 (No. 1), HfB_2 (No. 5) and ZrB_2+20 % SiC (No. 2) (Tables 2, 3) sintered under 4.1 GPa (or 4100 MPa) pressure at 1800 °C. Comparing the results of hardness tests one can see the pronounced sintering pressure effect (please compare samples No. 1 with 4, No. 5 with 6 and No. 7 with 8 (Tables 2, 3). The materials prepared under 4.1 GPa pressure demonstrated higher mechanical characteristics than that sintered under 20–30 MPa by hot pressing even at higher temperatures. The method of spark plasma sintering (Table 4) allowed obtaining materials with somewhat higher or similar hardness than that sintered using hot pressing technique, but the materials shown in Table 1 were obtained under higher pressure (50 MPa).

Table 2

Compositions of the initial mixtures, details of the preparation method (temperature, *T*, pressure, *p*, holding time, τ), the phase composition, density, γ, of the consolidated materials and the unit cell parameters (*a*, *b*, *c*) of the phases present in ZrB_2- and HfB_2-based materials

No.	Initial composition	Conditions of preparation			Phase composition, wt. %, density, g/cm^3	Unit cell parameters, nm, *a*, *b*, *c*
		T, °C	*P*, *MPa*	τ, h		
1	ZrB_2	1800	4100	0.13	ZrB_2 = 100 %, γ = 6.2	*a* – 0.3168
						c – 0.3528
2	ZrB_2+20 % SiC	1800	4100	0.13	ZrB_2 = 79.53 %, β-SiC = 20.47 %, γ = 5.04	*a* – 0.3169
						c – 0.3508
						a – 0.4359
3	ZrB_2+20 % SiC+ +4 % Si_3N_4	1800	4100	0.13	ZrB_2 = 77.58 %, β-SiC = 19.92 %, β-Si_3N_4 = 2.50 %, γ = 4.98	*a* – 0.3168
						c – 0.3529
						a – 0.4357
						a – 0.7609
						c – 0.2906
4	ZrB_2	2000	30	0.18	ZrB_2 = 100 %, γ = 5.97	*a* – 0.3168
						c – 0.3531
5	HfB_2	1800	4100	0.13	HfB_2 = 100 %, γ = 10.42	*a* – 0.3141
						c – 0.3473
6	HfB_2	1850	30	1	HfB_2 = 100 %, γ = 10.79	*a* – 0.3142
						c – 0.3473
7	HfB_2+30 % SiC	1800	4100	0.13	HfB_2 = 72.40 %, β-SiC = 27.60 %, γ = 6.21	*a* – 0.3143
						c – 0.3475
						a – 0.4358
8	HfB_2+30 % SiC	1900	20	0.083	HfB_2 = 100 %, β-SiC = 29.74 %, γ = 5.84	*a* – 0.3141
						c – 0.3474
						a – 0.4357

Table 3

Vickers hardness and fracture toughness of the ZrB_2 and HfB_2-based materials. Numbering is the same as in the Table 2

No.	Initial composition	Vickers hardness, GPa, under the load			Fracture toughness, K_{1C}, MPa·m$^{0.5}$, under the load		
		9.8 N	49 N	98 N	9.8 N	49 N	98 N
1	ZrB_2	17.7	15.4	15.3	4.3	4.2	4.0
2	ZrB_2+20 % SiC	24.2	16.7	17. 6	–	7.1	6.2
3	ZrB_2+20 % SiC+4 % Si_3N_4	20.5	18.3	15.8	–	–	9.2
4	ZrB_2	13.6	11.2	11.39	4.37	3.1	3.0
5	HfB_2	21.3	19.3	19.2	–	7.2	5.7
6	HfB_2	19.0	18.7	18.1	7.7	6.6	5.3
7	HfB_2+30 % SiC	38.0	27.7	26.3	8.2	6.8	6.4
8	HfB_2+30 % SiC	20.1	18.9	16.1	7.3	6.4	5.9

Table 4

Hardness of the materials prepared by spark plasma sintering (SPS) [11]

No.	Composition	Conditions of preparation	Vickers hardness	Reference
1	HfB_2	2100 °C, 50 MPa	H_V(9.8 N) = 19.8 ± 0.7 GPa	[11]
2	ZrB_2	2000 °C, 50 MPa	H_V(9.8 N) = 16.5 ± 0.9 GPa	[11]
3	ZrB_2–SiC	1950 °C, 50 MPa	H_V(9.8 N) = 21.1 ± 0.6 GPa	[11]

Additions of SiC to ZrB_2 and HfB_2 allowed to increase hardness and fracture toughness and in combination with high 4.1 GPa pressure allowed to obtain whatever high mechanical characteristics. The combination of SiC with Si_3N_4 additions to ZrB_2 (sample 3, Tables 2, 3) and high pressure sintering allowed obtaining materials with lower hardness, but higher fracture toughness.

The works of other researchers inform that ZrB_2 obtained by pressureless sintering at 2150 °C had hardness H_V (9.8 N) $= 15.5 \pm 0.05$ GPa [11]. The hardness of ZrB_2 obtained by hot pressing at 20 MPa, 1850 °C was H_V (9.8 N) $= 18.2 \pm 0.6$ GPa. The SPS sintered ZrB_2 at 50 MPa, 2000 °C demonstrated hardness H_V (9.8 N) $= 16.5 \pm 0.9$ GPa [11].

The high pressure effect on the sintering of ZrB_2, HfB_2 and composites on their bases was not described in literature before this study.

X-ray diffraction study showed (Table 2) that lattice parameters of ZrB_2 and HfB_2 after sintering stayed practically unchanged (compare data of Tables 1, 2). SEM EDX analysis demonstrated that composition of ZrB_2 (No. 1) was near the stoichiometry, while in the case of composite ZrB_2–20 % SiC (No. 2) the ZrB_2 matrix contained 5–6 at. % of carbon what can be the explanation of mechanical characteristics increase. Auger and EDX study showed that the structure of HfB_2 (No. 5) contained admixture carbon and oxygen in the amounts of about 3 at. %.

The available high-pressure apparatuses of big volume make promising application of the developed material in the different brunches of industry.

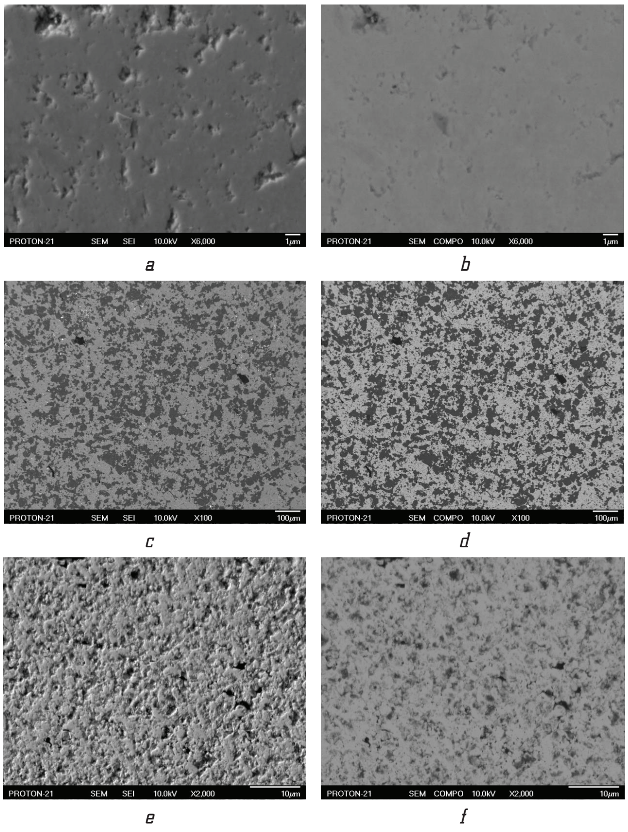

Fig. 1. Microstructures obtained by SEM of: *a, b* – ZrB_2 (No 1); *c, d* – ZrB_2+20 % SiC (No 2); *e, f* – HfB_2 (No 5) (Tables 2, 3) sintered under 4 GPa (or 4100 MPa) pressure at 1800 °C; *a, c, e* – secondary electron images (SEI); *b, d, f* – backscattering electron images (BEI or COMPO) of the same place of each sample under the same magnification

4. Conclusions

The paper deals with investigation of pressure effect on the mechanical characteristics (hardness and fracture toughness) of the consolidated ZrB_2, HfB_2 and composites on their bases with SiC and Si_3N_4 additions. The synthesis of the investigated materials was carried out under following conditions:

1) high quasihydrostatic pressure (4.1 GPa) – high temperature;

2) hot pressing (20–30 MPa).

The characteristics of the materials obtained under high pressure conditions and by hot pressing were compared with that of the materials obtained by spark plasma sintering (50 MPa). The results demonstrated positive effect on the mechanical characteristics of these materials.

High-pressure sintered HfB_2 ($a = 0.3141$ nm, $c = 0.3473$ nm, $\gamma = 10.42$ g/cm^3) demonstrated hardness H_V (9.8 N) $= 21.3 \pm 0.8$ GPa, H_V (49 N) $= 19.3 \pm 1.3$ GPa, and H_V (98 N) $= 19.2 \pm 0.5$ GPa and fracture toughness K_1C (49 N) $= 7.2$ MN·m$^{0.5}$ and K_1C (98 N) $= 5.7$ MN·m$^{0.5}$. According to the literature [11], HfB_2 which demonstrated the same density, but obtained by spark plasma sintering (SPS) at 50 MPa and 2100 °C, had lower hardness: H_V(9.8 N) $= 19.8 \pm 0.7$ GPa. The HfB_2 sintered by hot pressing at 1850 °C and 30 MPa demonstrated hardness similar with SPS prepared material: H_V (9.8 N) $= 19.0$ GPa, H_V (49 N) $= 18.7$ GPa, and H_V (98 N) $= 18.1$ GPa, K_1C (9.8 N) $= 7.7$ MPa·m$^{0.5}$, K_1C (49 N) $= 6.6$ MPa·m$^{0.5}$ and K_1C (98 N) $= 5.3$ MPa·m$^{0.5}$.

High pressure sintered ZrB_2 ($a = 0.3167$ nm, $c = 0.3528$ nm, $\gamma = 6.2$ g/cm^3) demonstrated H_V (9.8 N) $= 17.7 \pm 0.6$ GPa, H_V (49 N) $= 15.4 \pm 1.2$ GPa, and H_V (98 N) $= 15.3 \pm 0.36$ GPa and K_1C (9.8 N) $= 4.3$ MPa·m$^{0.5}$, K_1C (49 N) $= 4.2$ MPa·m$^{0.5}$ and K_1C (98 N) $= 4.0$ MPa·m$^{0.5}$. Other researchers inform that ZrB_2 obtained by SPS sintering at 50 MPa, 2000 °C demonstrated H_V (9.8 N) $= 16.5 \pm 0.9$ GPa [11].

Addition of 20 wt. % of SiC to ZrB_2 and sintering under high pressure (4.1 GPa) allowed essential increase of hardness to H_V (9.8 N) $= 24.2 \pm 0.7$ GPa, H_V (49 N) $= 16.7 \pm 0.5$ GPa, and H_V (98 N) $= 17.6 \pm 0.4$ GPa and fracture toughness to K_1C (49 N) $= 7.1$ MPa·m$^{0.5}$, K_1C (98 N) $= 6.2$ MPa·m$^{0.5}$; the material density was $\gamma = 5.03$ g/cm^3. The EDX SEM analysis demonstrated presence of 5–6 at. % of carbon what can be possible explanation of mechanical property increase. Additions of SiC and Si_3N_4 to ZrB_2 and high pressure sintering lead to some decrease in hardness as compare to ZrB_2-20 wt. % SiC material, but it demonstrated an increase in fracture toughness (up to K_1C (98 N) $= 9.2$ MPa·m$^{0.5}$).

The developed ZrB_2- and HfB_2-based materials are promising for different aerospace applications cutting tools and in refractory industries in general.

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