Production of Homogeneous Composite Press-Powders Based on ZrB2 and SiC for UHTCs

G. Bokuchava[1], E. Sanaia1, Z. Mestvirishvili[2*], N. Jalagonia[1], T. Prikhna[3], T. Kuchukhidze[1], N. Darakhvelidze[1]

[1]Ilia Vekua Sukhumi Institute of Physics and Technology. 7 Mindeli Str., Tbilisi, Georgia
[2]Ilia Vekua Sukhumi Institute of Physics and Technology. 7 Mindeli Str., Tbilisi, Georgia
Georgian Institute of Stable Isotopes. 1 Alio Mirtskhulava Str, Tbilisi, Georgia, zviad.mst@gmail.com
[3]V.Bakul Institute for Superhard materials, 2, Avtozavodskaya Str., Kiev, Ukraina

The aim of the research was to obtain superfine homogeneous composite powders, which, due to their unique composition and morphology, will be used to obtain ceramics with improved properties for the thermal protection of supersonic aircraft. The novelty of research was microstructure refining methods, selection of sintering additives/dopants and their combining action. As regards sintering additives and dopants, B4C and graphite powder, carbon black and graphene structures were used. The use of the latter individually and in combination sintering additives was one of the innovations of the research. Several variants of zirconium boride nano powder with different stoichiometry and graphene nanostructures were produced by us. Composite nano powders were made on the basis of zirconium boride and silicon carbide. Scanning electron microscopy with Energy-dispersive X-ray spectroscopy method was used to study the mentioned composite micro and nano powders.

Keywords: ceramic, aircraft, hypersonic, extreme environment.

1. Introduction

Materials working in the extreme environment are subject to permanent research. The extreme environment is the joint impact of temperature, chemically reactivity, mechanical stress, wear, etc. Such an environment is formed on the nose cone, wing leading edges and the propulsion system components of the hypersonic space vehicle (HSSV), generally during the HSSV's atmospheric re-entry and rocket propulsion. Already in its early reports, NASA underlined the necessity for rocket nozzles and thermal protection systems (TPSs) [1-4]. A

particular attention was paid to the conditions associated with the entry into atmosphere, the rocket engine and the requirements to the materials of the leading edges and propulsion system of vehicles [4]. A whole series of recommendations contained in the reports are still being prioritized for modern research.

Studying the properties of refractory borides and carbides for hypersonic aerospace vehicles is a part of research carried out in the U.S.A. [5-6].

A great impact in the NASA reports was made in the definition of Ultra-High Temperature Ceramics (UHTCs), where zirconium and hafnium borides are the main candidates for HSSV [7-11]. As a result of B-1 and B-2 testing of the SHARP program, UHTCs have been defined as a potential candidate for a HSSV, despite failure of the UHTC strakes due to problems traced back to processing issues [12, 13].

Since the 1960s, the Air Force Research Laboratory (AFRL) has funded a series of studies that focused on refractory diborides and carbides as candidates for a number of potential future aerospace vehicles.

Based on the properties of zirconium boride ceramics, the ZrB2-based UHTCs are rather promising in the TPS materials. Of special interest is the ZrB2-SiC composite ceramics, on which the major part of the ZrB2 research falls.

The strong covalent bonding and low-volume self-diffusion coefficients of ZrB2 phase make densification difficult. Therefore, ZrB2 ceramics are prepared by a reactive hot pressing (RHP), hot pressing (HP) and spark plasma sintering (SPS) methods [14]. The enumerated methods cause grain growth in size, which adversely affects the composite's properties. An interesting method is described in [15] works, where ZrB2, HfB2 and composites on their bases are obtained by the high quasi isostatic pressure (4.1 GPa). ZrB2 ceramic obtained by the mentioned method demonstrated HV (9.8 N) = 17.7 ± 0.6 GPa, HV (49 N) = 15.4 ± 1.2 GPa, and HV (98 N) = 15.3 ± 0.36 GPa and K1C (9.8 N) = 4.3 MPa·m0.5, K1C (49 N) = 4.2 MPa·m0.5 and K1C (98 N) = 4.0 MPa·m0.5. Addition of 20 wt. % of SiC to ZrB2 allowed essential increase of hardness to HV (9.8 N) = 24.2 ± 0.7 GPa, HV (49 N) = 16.7 ± 0.5 GPa, and HV (98 N) = 17.6 ± 0.4 GPa and fracture toughness to K1C (49 N) = 7.1 MPa·m0.5, K1C (98 N) = 6.2 MPa·m0.5 [15].

Boride powder surfaces always contain B2O3 and ZrO2 impurities that adversely affect its densification, because oxygen impurities promote coarsening mechanisms, which reduces surface area and the driving force for sintering.

In addition to the above, a problematic matter in the fabrication of the above-mentioned composites is the production of homogeneous mixtures from the powders with different density and grain sizing [16].

The novelty of our research is the improvement of properties of ZrB2-SiC ceramic by innovative techniques: microstructure refining methods, selection of sintering additives/dopants and their combining action. The microstructure refining is possible by forming homogeneous micro- and nanostructures in ceramics (ZrB2 and SiC), the ends of which will equally locate nanosized inhibitors – third phase. Here the SiC phase will also serve as inhibitor of the grain growth of the main phase and will slow down the crack

propagation. A similar method is described in [16] work, however, the hardening phase there is much larger in size - several microns. In the present work, various methods and nano additives are used, which ensure the maintenance of nano dimensions of the components.

As regards sintering additives and dopants, B4C and carbon as graphite, carbon black, and graphene structures were used. The use of the latter (graphene structures) individually and in combination sintering additives is one of the innovations of the research.

Boron carbide nano-powder is the latest discovery of ceramics sintering additive [17]. In addition, its role includes removal of oxide impurities from the surface of ZrB2 grains in the presence of carbon:

$$2ZrO_2 + B_4C + 3C \rightarrow 2ZrB_2 + 4CO \uparrow \quad (1)$$

In parallel, carbon (as carbon black) conditions the removal of boron oxide admixtures:

$$2B_2O_3 + 5C \rightarrow B_4C + 6CO \uparrow \quad (2)$$

2. Experimental procedure

In the first stage, ZrB2 powders were produced. ZrO2 was used as a transition metal source, and B4C (Grade HP, H.C. Starck) was used as a boron source for the production of the mentioned powders. Technical carbon (ENSACO 250P, Imerys Graphite and Carbon) and graphite powder (TIMREX-KS6, Imerys Graphite and Carbon) was added to the components to balance the chemical reaction.

According to thermodynamic calculations, the reaction takes place in several steps, and the summery reaction is similar to the (1). Under different conditions, intermediate reactions take place in different ways, for example, with a deficiency or an excess of boron oxide. Because of this, it is well known to take an excess of reactive components.

Considering the expected chemical reaction, mixtures with different stoichiometry were selected - Table 1. ZBT - theoretical stoichiometry, ZBC5 and ZBC15 with an excess of carbon and ZBBC5 and ZBBC10 with an excess of boron carbide.

Mixing of the raw powders were carried out in the tungsten carbide jar with zirconium oxide milling balls by the planetary micro mill PULVERISETTE 7 (FRITSCH, Germany). Zirconium oxide balls eliminated contamination of the powders with new elements. A small amount of tungsten carbide that contaminates the mixture from the planetary mill jar may be used as a reductant to remove the boron oxide according to the following reaction:

$$B_2O_3 + WC + 2C \rightarrow WB_2 + 3CO \uparrow \quad (3)$$

An 80 ml tungsten carbide jar, 100 g 5 mm ZrO2 balls, and a powder to liquid (water + ethyl alcohol) weight ratio of 1/2 were used. The mixing parameters were as follows - rotation speed 350 rpm, one cycle time 3 min, interval 2 min, total mixing time 60 min. After mixing, the powder was dried at 120°C for 16 hours. The dry powder was cold pressed with a pressure of 100 MPa.

Table 1 Composition of mixture

#	Mixture index	Excess component	ZrO_2, wt.%	B_4C, wt.%	C, wt.%
1	ZBT	-	72.97	16.36	10.67
2	ZBBC5	B_4C, 5wt.%	72.52	17.07	10.41
3	ZBBC10	B_4C, 10wt.%	72.05	17.77	10.18
4	ZBC5	C, 5wt.%	72.59	16.27	11.14
5	ZBC15	C, 15wt.%	71.82	16.10	12.08

Production of ZrB2 fine powders were carried out by carbo/borothermal reduction at 1550-1600°C in the high-temperature vacuum furnace FR210-30T-A-200-EVC (OXY-GON, USA) according to the (1) reaction. The Fig. 1 shows the synthesis process as a graph - pressure and temperature changes over time for the ZBBC5 mixture. Holding time at 1550°C was 20 minutes.

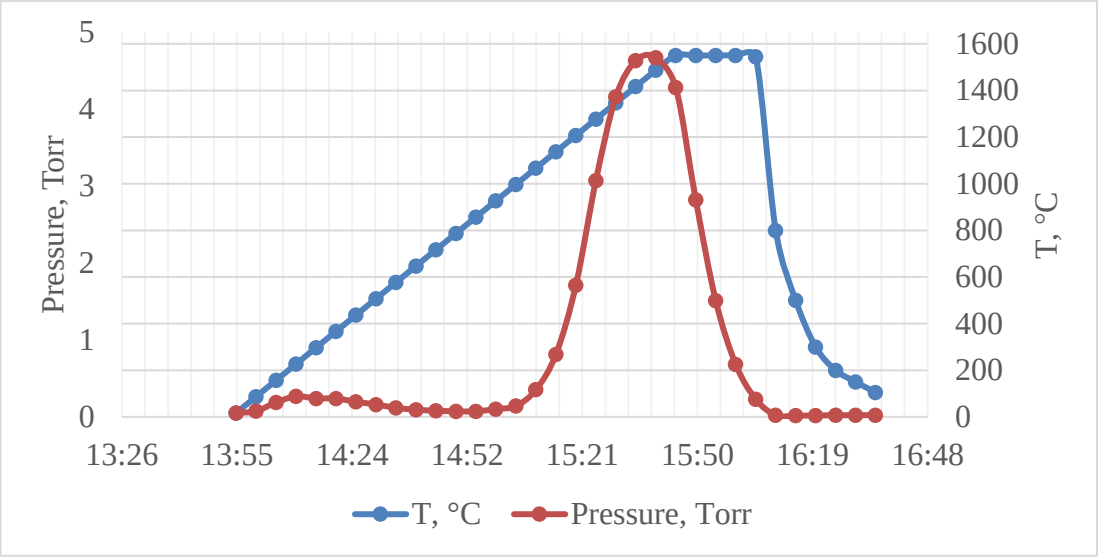

Figure 1. Synthesis parameters interdependence for ZBBC5

X-ray-structural analysis was done using DRON-3 diffractometer. Electron microscopic examination of the ZrB2 powder was performed on a JEOL JSM-510LV electron microscope, equipped with an energy dispersive micro-X-ray analyzer (EDXA) "X-MaxN" (OXFORD INSTRUMENTS, ENGLAND). The particle size distribution was studied using a nano sizer Analysette 12 Dynasizer (FRITSCH, Germany).

In parallel, graphene structures were synthesized using modified Hummer's method; thereafter reduction of the produced graphene oxide were carried out by chemical reagents using ultrasonic and a microwave oven (Fig. 2). Because graphene structures are characterized by the ability to aggregate, which prevent its homogeneous distribution in the matrix and have an affect the mechanical properties of the final product, graphene was prepared in the form of stable suspensions [18]. For which an organic solvent was selected, where we placed graphene and treated by ultrasound for 1-2 hours. Graphene structures obtained in this way are ideal for use as additives in composites. Reduction with ascorbic

acid was carried out as follows: the solution volume 200 ml, concentrations of reagents: GO - 0.1 mg/ml, ascorbic acid - 0.5 mg/ml, sodium alkali 0.4 mg/ml. We subjected the solution to sonication for half an hour, (40 kHz, 600 w), delayed at 80 0C for 24 hours and re-sonicated for another 1 hour. Also we poured a small portion of the graphene oxide suspension obtained by the intercalation method into a quartz glass and placed it in an 800 Watt microwave oven at 6000C for 3 minutes. The obtained graphene oxide was studied using SEM.

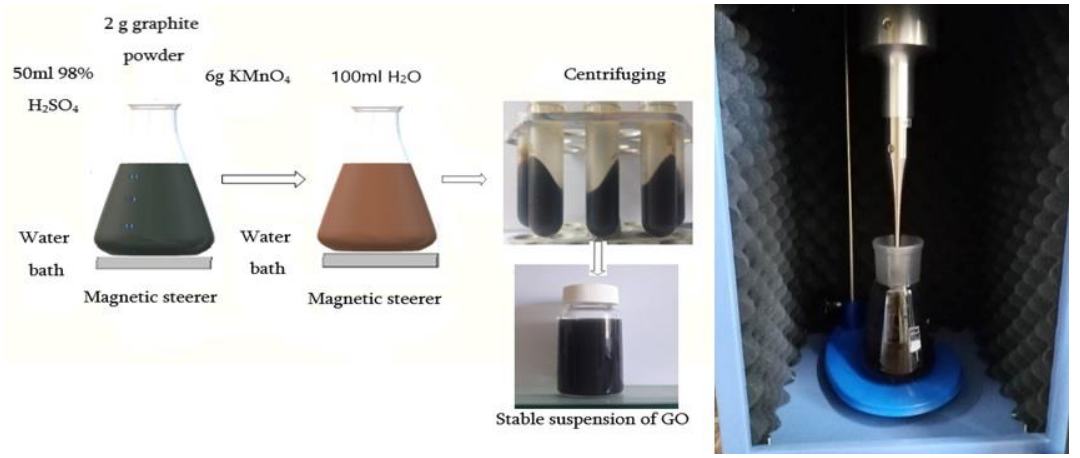

Figure 2. Illustration of the preparation of GO

At last, homogenous composite press-powders (mixture) with different stoichiometry - ZrB_2+SiC+B_4 C(C) were produced based on ZrB2 and SiC using sintering additives/dopants by planetary milling. In order to obtain homogeneous composite powders, we selected three compositions (Table 2). ZBTSC – ZBT with SiC, B4C (grade HD20) and graphene oxide. ZBC15SC - ZBC15 with same admixtures and ZBBC10SC - ZBBC10 with same admixtures.

Table 2 Composition of the composite powders

#	**Composite powders**				
	Composite powder Index	ZrB_2, wt. %	SiC, wt. %	B_4C, wt. %	C_{GO}, wt. %
1	ZBTSC	75	20	4	1
2	ZBC15SC				
3	ZBBC10SC				

The milling/mixing parameters were as follows - rotation speed 400 rpm, one cycle time 3 min, interval 2 min, total mixing time 2 h (3min*40 cycle). After mixing, the powder was dried at 120°C for 16 hours. Electron microscopy and energy dispersive micro-X-ray analysis (EDXA) were carried out for the composite powders. A novelty was the production of a multiphase mixture with equally distributed phases of different size and inhibitors, using ultrasonic (Ultrasonic homogenizer TF-1000N) and the planetary milling machine.

3. Results and discussions

It can be seen from the graph (Fig. 1) that the intensive release of gases starts at 1000°C. At this time, one of the intermediate reactions begins with the release of CO. At 1400°C gas release decreases and at 1500-1550°C the reactions are completed. Fig. 3 show the x-ray analyses of the ZBT powders. As we assumed, the powder obtained from the mixture with theoretical stoichiometry contains impurities in addition to the main phase. Basically, it is zirconium carbide and ZrB. This applies more to ZrB2 powder obtained from graphite powder (KS6). Zirconium boride powder obtained from carbon black (250P) is relatively free of impurities.

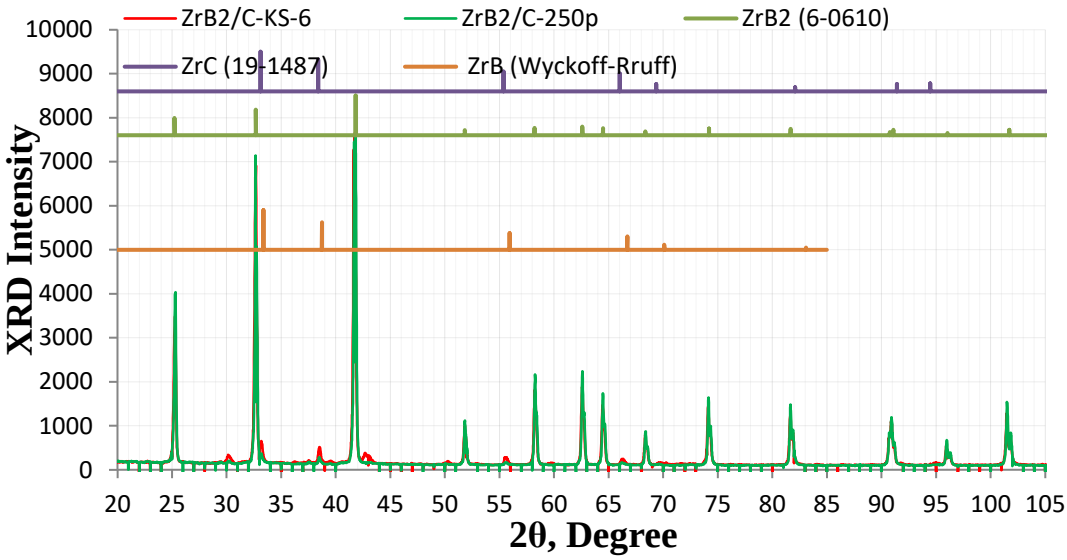

Figure 3. X-ray analyses of the ZBT powders, red from KS6 and green from P250

The ZBT powder obtained from P250 is slightly finer grained than the powder obtained from KS6. Their PSD50 are 786 and 823 nanometers, respectively. Their scanning electronic images are presented in the Fig. 4.

The grain sizes of the powders do not exceed one micron. Since carbon is the crystallization center of the zirconium boride grains, its size determines the grain size of the ZrB2 grains. Therefore, there is a difference in size, even though the synthesis process was carried out under the same conditions - one synthesis in one crucible.

Zirconium boride powders, which are obtained from the mixture taken with an excess of carbon also contain zirconium carbide admixture. Fig. 5 presents the PSD measurement results and scanning microscopy image of the ZBC15 powders obtained as from KS6, as from P250.

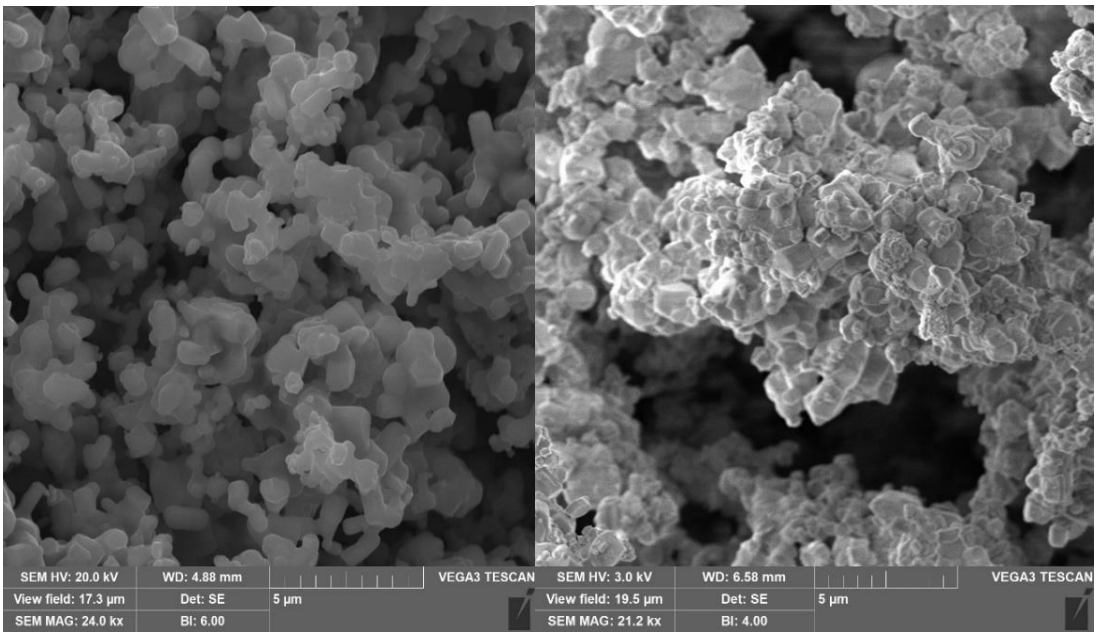

Figure 4. Scanning electron microscopy images of the ZBT powders, left – KS6, right – P250

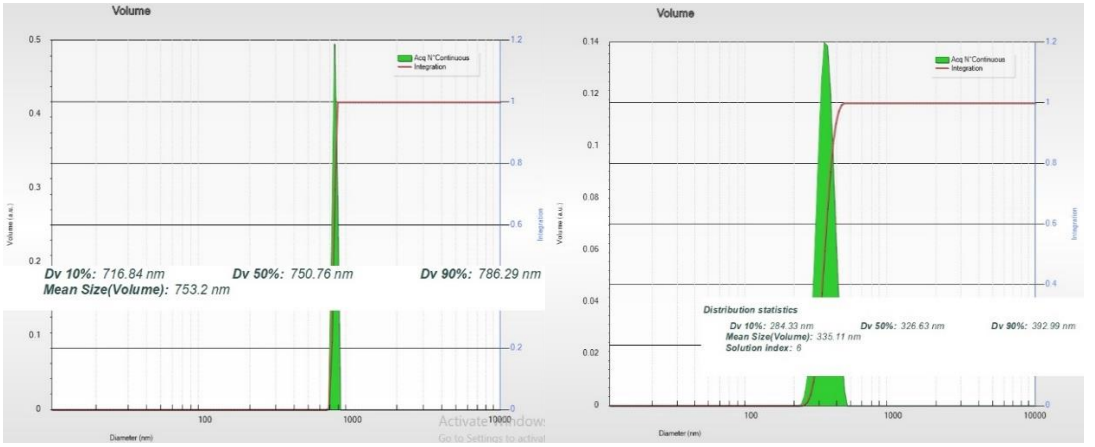

Figure 5. Particle size distribution of the ZBC15 powders, left – KS6, right – P250

The ZBC15 powder obtained from P250 is much finer than the powder obtained from KS6. Their PSD50 are 326 and 750 nm, respectively. The synthesis reaction of these powders was carried out under absolutely equal conditions, they were made in one technological process, in one crucible and therefore under the same conditions. The only difference is the carbon source. The fact is that when carbon black is taken in excess, the grain size of the ZrB2 powder is completely determined by the carbon - the crystallization center of the zirconium boride grain. ZBC15 powders scanning electron microscopy images are given in Fig. 6.

The photos make it clear, that the powder obtained from KS6 is more homogeneous in both

grain shape and size, although it is much coarser. The advantage of the powder obtained from P250 is its fineness, in addition, its homogeneity area is wide (Fig. 5. right), this last parameter has a positive effect for a press-powder.

Fig. 7 shows the x-ray diffraction of the ZBBC10 powder. As we assumed, the powders obtained from the mixture taken with an excess of boron carbide (ZBBC5 and ZBBC10) do not contain impurities. They contain only one phase - zirconium boride.

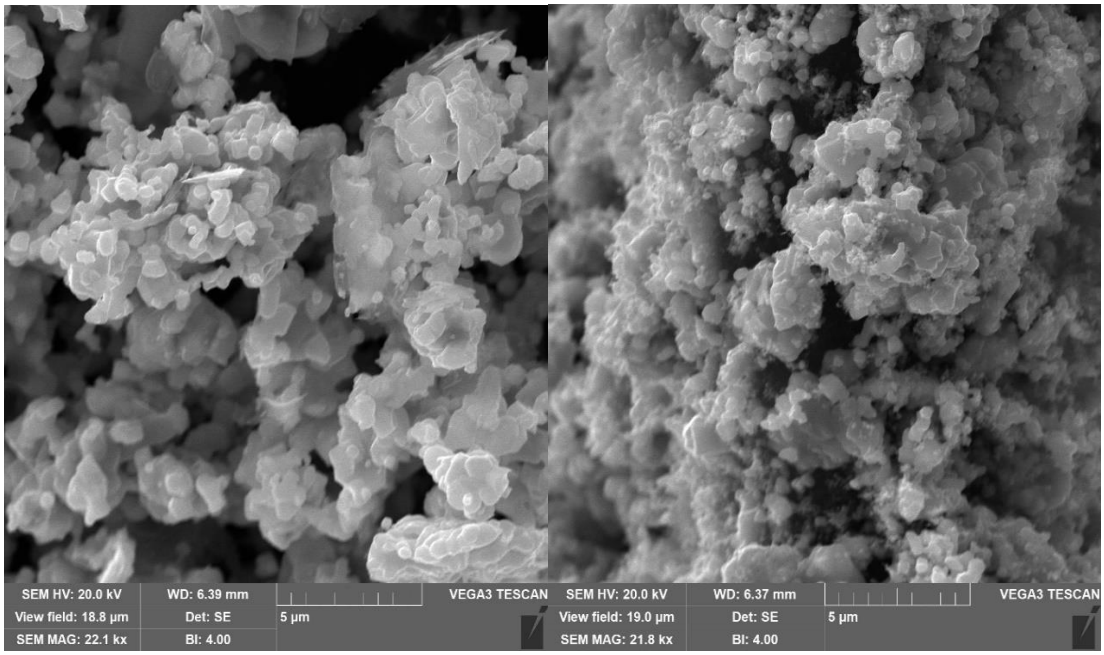

Figure 6. Scanning electron microscopy images of the ZBC15 powders, left – KS6, right – P250

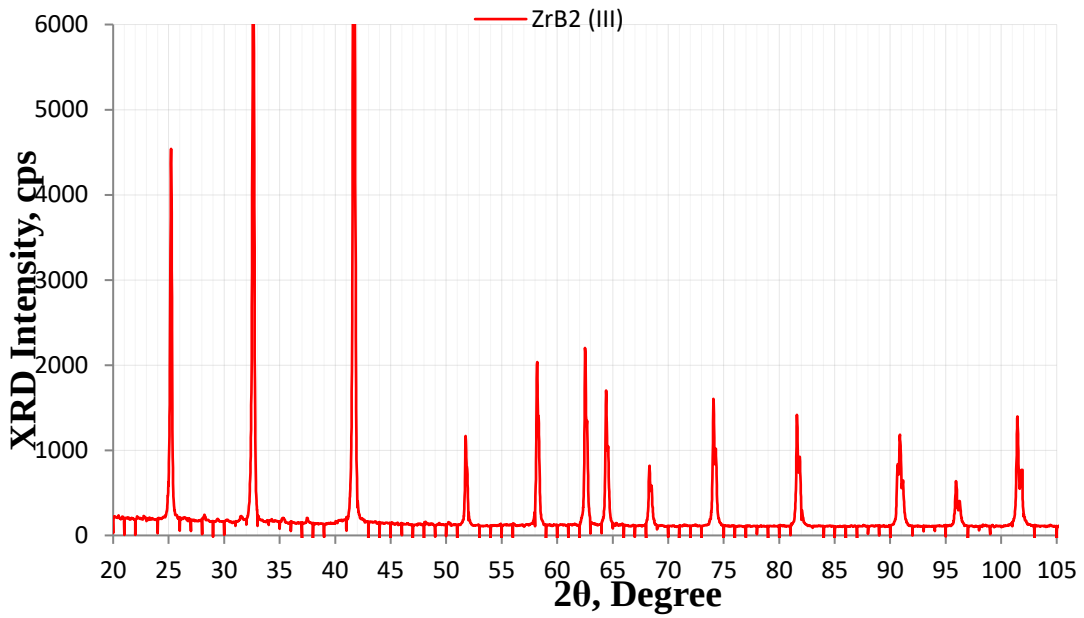

Figure 7. X-ray diffraction of the ZBBC10 powder from P250

As for their grain sizes, they are relatively large compared to the powders obtained with an excess of carbon. The PSD of the ZBBC5 and ZBBC10 powders are 596 and 473 nm, respectively (Fig. 8). While PSD of the ZBC5 and ZBC15 powders are 495 and 326 nm (Fig. 5), respectively.

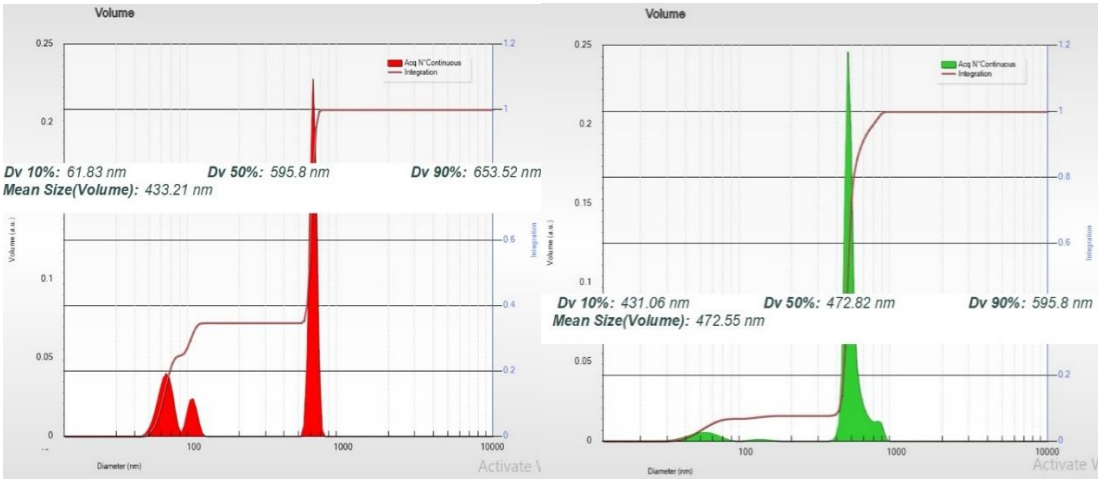

Figure 8. Particle size distribution of the ZBBC5 (left) and ZBBC10 (right) powders obtained from P250

Scanning electron microscopy images of the ZBBC5 and ZBBC10 powders are given in Fig. 9. If we compare the all considered powders with each other, we can see that the deviation

from the theoretical stoichiometric of the mixture leads to a decrease in the particle size of the ZrB2 powder. Although the synthesis temperature of ZBC15 powder (1600°C) was higher than that of ZBT (1550°C). In addition, the polyhedral shape characteristic of the zirconium boride particle changes to a spherical shape.

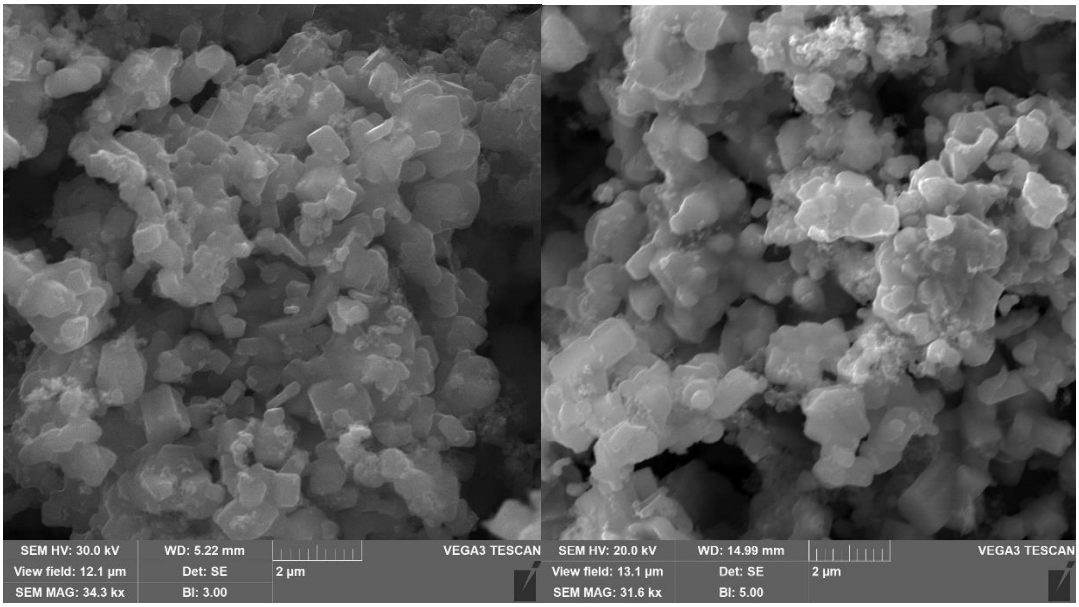

Figure 9. Scanning electron microscopy images of the ZBBC5 (left) and ZBBC10 (right) powders obtained from P250

The Fig. 10 shows the results of the study of graphene oxide. A highly wrinkled stack of ultra-thin graphene oxide nanosheets with agglomerated part can be observed. Obtained GO layers have thickness ≈20-40 nm. The XRD is the most widely used technique for general crystalline material characterization. In XRD peak at 100 is observed which shows the presence of GO. In the Raman, the G-band and D-band of GO appear at 1595 cm−1 and 1347 cm−1, respectively.

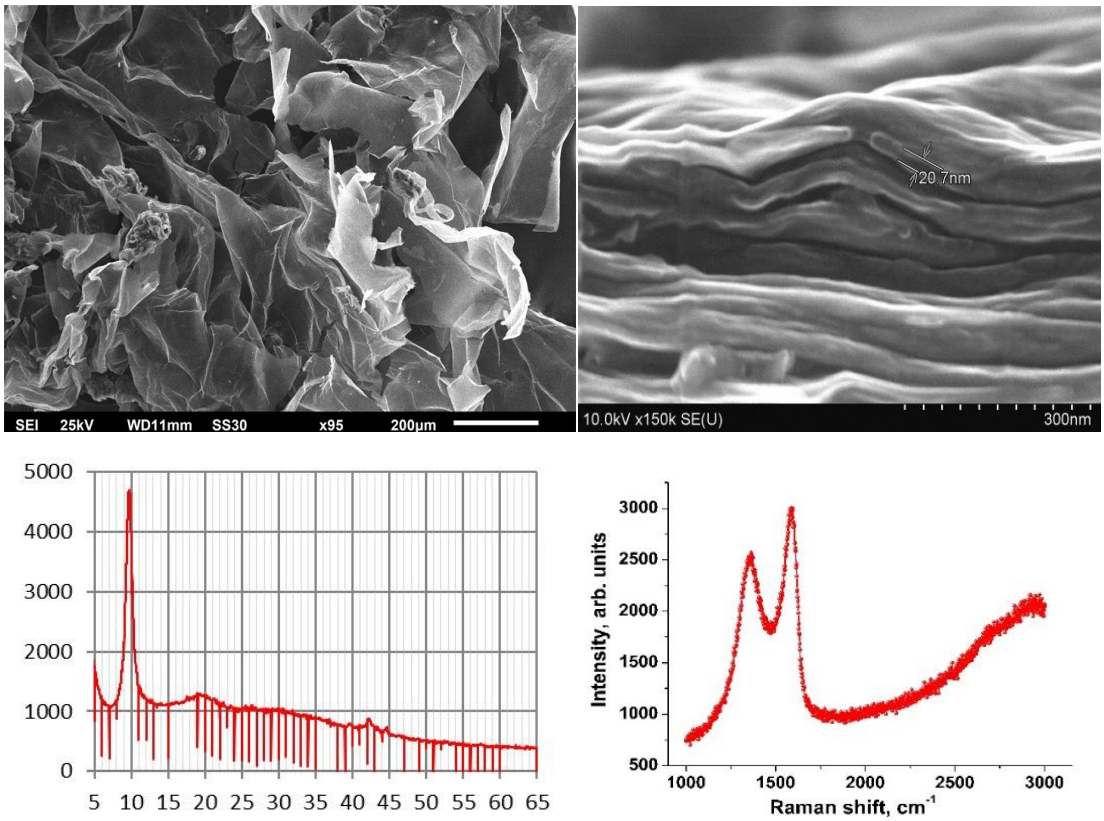

Figure 10. The results of the study of GO

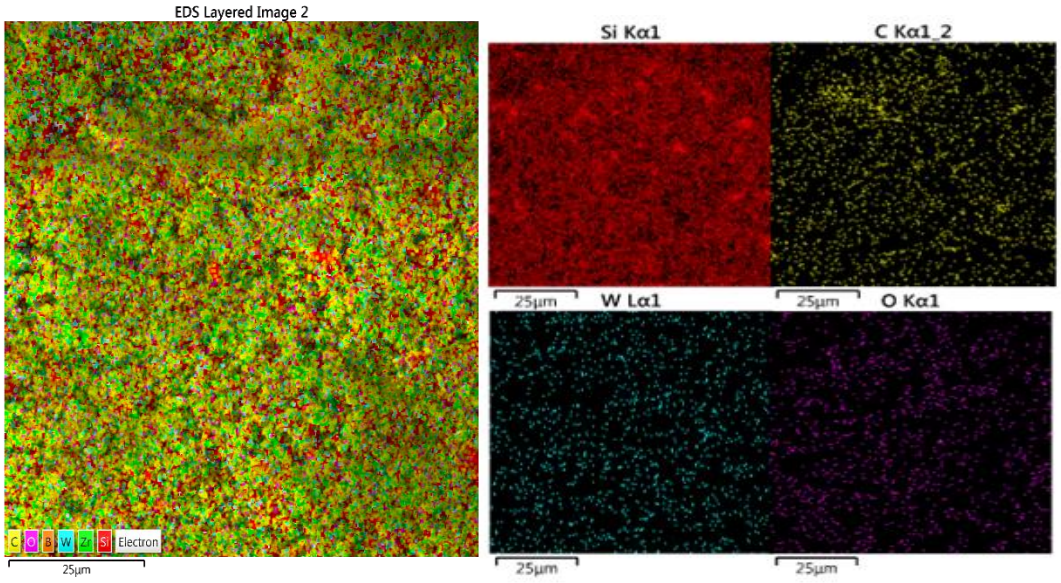

Figure 11. Energy-dispersive X-ray spectroscopy analyses of ZBTSC composite powder

Figure 11 shows EDS images of ZBTSC composite powder, common image and images of the elements. Images of zirconium and boron are not shown because ZrB2 is the main phase. The presented images belong to elements of SiC, WC and ZrO2 phases. According to EDS images, composite powders are homogeneous. Both the main phases and the impurities, even WC and ZrO2 are evenly distributed in the volume. The picture is the same in powders of another stoichiometry, both in powders with an excess of boron carbide and in powders with an excess of carbon. To prove the above, the results of one of our previous works [16] Energy-dispersive X-ray spectroscopy analyzes are presented in the form of images (Fig. 12). The given pictures show that the grain size of the ZrB2 phase is 0.5-1um. Even though these are small grains, they are well illustrated by energy-dispersive X-ray spectroscopy analysis.

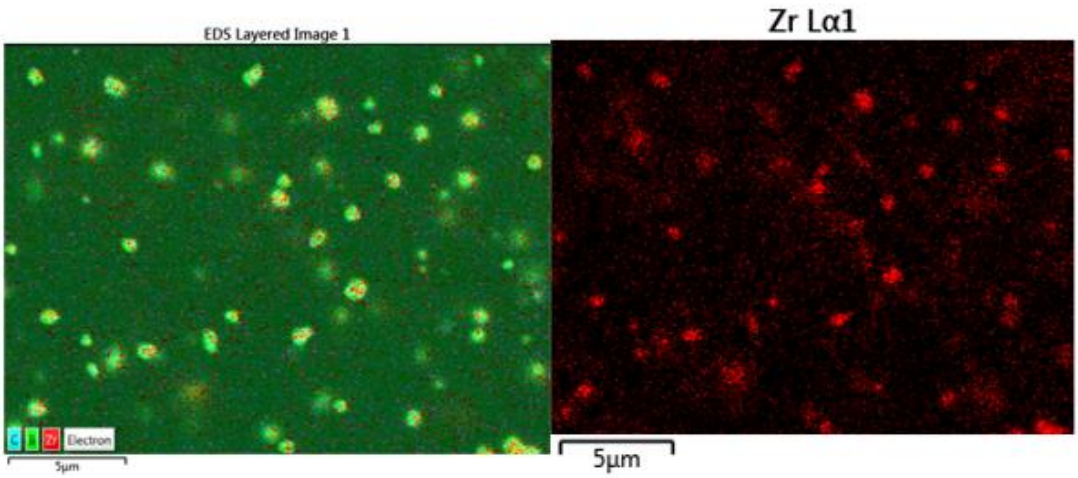

Figure 12. EDS analyses of B4C-ZrB2 composite, left – summery image, right – Zr [16]

In the current work, impurity elements appear as dots (Fig. 11), and they are homogeneously distributed in the entire volume. The comparison of the presented similar works confirms once again that we have obtained composite powders with ideal distribution of phases with micro and nano sizes. Such a result was due to the fact that the wet milling/mixing method was used with correctly selected parameters (milling media, milling time, ball diameter) and the ratio of liquid to powder was taken so that the mixed suspension was of gel consistency. Otherwise, aggregation of graphene oxide and separation of heavy and light phases would definitely occur. The obtained results most likely lead to the fact that ceramics made from the obtained homogeneous composite press-powders will have improved physical-mechanical characteristics.

4. Conclusions

The method of obtaining super fine ZrB2 powder has been developed, where, by adjusting the stoichiometry, the powder of the desired chemical composition is obtained. An excess of nano Carbon Black determines the fineness of the product, and an excess of boron carbide determines the purity of the product.

The method has been developed of production of the superfine homogeneous composite press-powders based on ZrB2 and SiC. For this, both methods of mechanical processing of powders and selection of sintering additives/dopants and their combining action were used.

According to the developed method correctly selected milling/mixing parameters - milling media, milling time, ball diameter and the ratio of liquid to powder determined that the mixed suspension was of gel consistency.

Aggregation of graphene oxide and separation of heavy and light phases, which is a big problem in the process of obtaining composite powders, was avoided by the above.

The production of superfine homogeneous composite press-powders leads to obtaining UHTCs with an improved microstructure and physical-mechanical characteristics in the end.

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