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Synthesis of Composite Materials based on TiB_2–TiC–Al_2O_3 and CrB_2-Al_2O_3 in the Combustion Conditions

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Abstract

Borides and carbides attract the attention of developers of heat-resistant and super hard structural materials due to a unique combination of their resistance to high-temperature oxidation, high hardness, wear resistance, electrical and thermal conductivity and etc. The article presents experimental results on obtaining composites based on TiB_2-TiC-Al_2O_3, CrB_2-Al_2O_3 by a method combining self-propagating high-temperature synthesis (SHS) and mechanical activation (MA). The influence of the composition of the initial components, the conditions of SHS and preliminary MA on the formation of the microstructure and phase composition of the SHS-composite based on titanium carbide and titanium, chromium borides has been studied. The SHS products were examined by X-ray diffraction analysis and a scanning electron microscope. High-temperature phases of borides of chromium, titanium, aluminum oxide and their spinel are found in SHS products.

1. Introduction

Transition metal borides with unique properties (high refractoriness, wear resistance, thermal conductivity) are of interest for the preparation of ceramic composites intended for use in high-temperature abrasive wear [1]. Synthesis of borides directly from elements is one of the simplest but at the same time the most expensive methods providing the most accurate composition and maximum degree of purity of borides. Synthesis of borides from simple substances by sintering, hot compaction realized at temperatures lower than the melting points of the initial materials is based on solid phase interaction [1].

However, strong covalent bonds inherent in the phases of transition-metal diborides lead to low plasticity and low bending and strength, which largely limits their application in pure form. In this regard, currently much attentions paid to the technology of obtaining composite materials based on borides of transition metals in combination with more plastic materials that act as a binder. For example, alumina can play the role of a high-temperature binder and filler, which reduces the content of trandition-metal diboride in composite materials. The production of these materials by traditional methods of powder metallurgy is hindered by high energy costs, multistageness complexity of process equipment and low productivity [1, 2].

TiB_2 is an important and promising transition metal boride with its unique properties such as high strength, hardness, durability, melting point, wear resistance, thermal conductivity and low electrical resistivity [2]. Its crystal structure was reported as hexagonal with space group of P6/mmm. The melting point of TiB_2 reaches up 3.523 K and its hardness can be enhanced to the values as high as 45 GPa due to its covalently bonded atomic structure [3]. Current usage areas are impact resistant armors, cutting tools, aluminum evaporation crucibles, wear resistant coatings and aluminum electrolysis cathodes as a new application area.

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It has been predicted that the development of other applications strictly depend on improve of its electrical discharge machining [3]. Many synthesis techniques are available in lab or industrial scale for the production of TiB_2. Carbothermic and metallothermic reduction of mixed oxides of titanium and boron, mechanical alloying synthesis from elemental forms of titanium and boron, sol-gel and aluminum melt reaction [4] processes are among the most remarkable processes to synthesize TiB_2 [5].

Self-propagating high-temperature synthesis (SHS) is an efficient way of producing ceramic and metal-ceramic composites [6]. Advantage of the method are fast heating(seconds) of the target product, simplicity of technology, low power consumption and low cost of the target product. To obtain SHS product, the following conditions must be met:

1) to carry out the synthesis of the desired product of a given composition,

2) to ensure the level of plasticity necessary to consolidate the target product to a non-porous state.

3) to ensure formation of a homogeneous microstructure with a minimum size of structural components.

The key parameter of the process is the combustion temperature. The use of a heterogeneous mixture with a high combustion temperature, at which the liquid phase forms, allows the first two conditions to be met. However, under these conditions, SHS products with a large-dispersed microstructure are formed. Recently, a combination of preliminary mechanochemical activation and subsequent SHS [7], has become very popular, which allows obtaining materials with improved characteristics. The use of the preliminary MA to SHS in a planetary mill significantly reduces the temperature of the onset of exothermic interaction of the mixture components, shortens the synthesis time of the combustion product, leads to a more complete course of chemical reactions in the combustion wave. With the help of MA, it is possible to accelerate chemical reactions by increasing the reactivity of mixtures.

The accumulation of energy by the reaction mixture (charge) in the form of structural defects (dislocations, vacancies, grain boundaries, stacking faults, etc.) and the formation of metastable phases increase free energy of the system, which leads to an increase in the reaction ability. Grinding of components reduces kinetic hindrances the course of chemical reactions in heterogeneous media. Thanks to MA heat release and its rate in combustion reactions increase, the temperature of the beginning of the reaction, the chemical and structural homogeneity of synthesis products. Therefore, the use of MA at the stage pretreatment of slightly exothermic and difficult to ignite mixtures for synthesis in the combustion mode, in particular for technologies of power SHS-compacting, significantly expands the class obtained ceramics and composites [8–12].

2. Experimental part

2.1. Materials

Boron oxide (B_2O_3 purity 99.9%), chromium oxide (Cr_2O_3 purity 99.8%), aluminum powder (Al purity 99.1%), carbonized rice husk (C). All chemicals were used without further purification

2.2. SHS-process

The process of carbonization of rice husk was carried out under isothermal conditions in a rotating reactor in an inert atmosphere at a temperature of 300–800 °C; argon feed rate of 50 cm^3/min, contact time 30–60 min [13].

The components were weighed in a stoichiometric ratio on an electronic balance and then a certain amount of distilled water was added, sufficient to prepare a semi-moist mixture for the purpose of preparing the samples by pressing. Preliminary mechanical activation was carried out in the high-energy planetary-centrifugal mill Pulverizette 5. The rotating platform is equipped with nests for two grinding jars. The contents of the grinding jar, consisting of grinding mass and grinding balls, act as a centrifugal force of rotation of the glasses around its axis, and the centrifugal force of the rotating support disk. Due to the resulting centrifugal force, the grinding balls reach a 40-fold acceleration of gravity. The rotation speed of the rotating reference wheel is 380 rpm.

The object of the study was a ceramic composite synthesized based on titanium and chromium borides by the reaction:

$$Cr_2O_3 + 2B_2O_3 + 6Al \rightarrow 2CrB_2 + 3Al_2O_3 \qquad (1)$$

$$3TiO_2 + B_2O_3 + 6Al + 2C \rightarrow TiB_2 + 2TiC + 3Al_2O_3 \qquad (2)$$

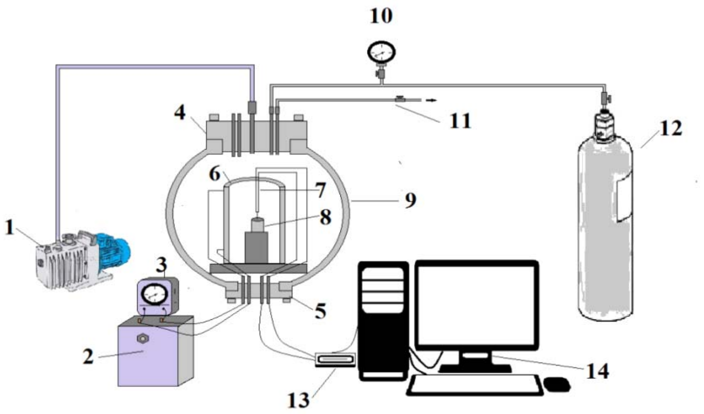


Fig. 1. SHS-reactor of high pressure: 1 – vacuum pump; 2 – transformer; 3 – ammeter; 4 – upper reactor cover; 5 – lower reactor cover; 6 – tube heating furnace; 7 – thermocouple; 8 – sample; 9 – reactor vessel; 10 – manometer; 11 – inlet and outlet valves; 12 – argon balloon; 13 – LTR-U-1 data acquisition unit; 14 – computer.

The SHS was carried out in an argon medium at a research facility in a high-pressure reactor, shown in Fig. 1. The setup provided argon pressure inside the reactor to 10 MPa. The temperature of the sample after the initiation of the combustion process was recorded using a computer and special software that reads the data in real time from tungsten-rhenium thermocouples WR5/20 with a junction thickness of 200 μm, for which an opening of 6 mm in depth and 2 mm in diameter was drilled in the sample. Charge billets with a diameter of 20 mm, a height of 16 mm and a relative density of 0.6 MPa were placed in the reactor. The initiation was carried out by a heated tungsten helix.

The microstructure of the ceramic composites was studied by scanning electron microscopy (QUANTA 3D 200i, FEI, USA). The phase composition of the obtained composites was studied using a diffractometer "DRON-4M" using cobalt Kα radiation in the range 2θ=10°-70°. To study the microstructure and phase composition, the surface of the sample was prepared in the form of pure cleavage and polishing.

3. Results and discussion

3.1. The patterns of combustion in the Cr_2O_3-B_2O_3-Al system

The SHS of the system under investigation was carried out in a high-pressure reactor. At high temperatures, developing in the SHS process, some components of the system become gaseous. In this case, the change in the external pressure makes it possible to control the depth of the synthesis, preventing or reducing the loss of the volatile elements of the system, contributing to the retention of the basic reducing agents in the system. The maximum combustion temperature corresponds to the moment of the thermal explosion.

An important parameter of SHS systems, which ultimately affects the quality of the synthesized product, is the combustion temperature. It is at the maximum temperature developed in SHS systems that the phase and structure formation of the material takes place. SHS-systems are characterized by a rapid increase in temperature in the zone of chemical reactions followed by cooling.

The diagram in Fig. 2 shows the heat of formation from the elements and the adiabatic combustion temperature (i.e., the maximum temperature that the combustion products have in the absence of heat losses). The diagram shows a general pattern: all compounds that have a great heat of formation from the elements can be synthesized under conditions of gas-free combustion.

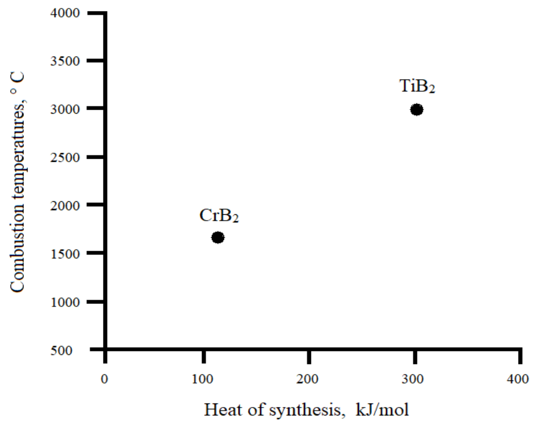


Fig. 2. Adiabatic combustion temperature and heat of formation from the elements for some two-component systems.

The thermodynamic analysis allows calculating the adiabatic combustion temperature of exothermic mixtures (T_{ad}). For the stoichiometric composition, the maximum combustion temperature is T_{ad} ~ 1900 °C, that is, above the melting point (T_m = 660 °C) of aluminum, boron oxide (T_m = 480 °C), but below the melting point of aluminum oxide (T_m = 2044 °C), chromium oxide (T_m = 2435 °C) and chromium boride (T_m =2000 °C), which makes it possible to judge the possibility of obtaining combustion products based on CrB_2-Al_2O_3. According to the thermodynamic calculations using “Thermo” among equilibrium products, along with chromium diboride and aluminum oxide, B_2O_2 is formed with gas evolution under such temperature conditions. The adiabatic combustion temperature and synthesis compositions were calculated using the “Thermo” program developed at the Institute of Structural Macrokinetics and Materials Science Problems of the Russian Academy of Sciences (Chernogolovka, Russia) [6].

Compounds with a moderate heat of formation can also be obtained by SHS, but require additional external heating.

Previously, the effect of argon pressure on the SHS parameters was studied, the argon pressure in the reactor varied from 0.5 to 3 MPa [10, 11]. The experiments showed that the optimum for SHS is the pressure of 1 MPa. The main heat release of exothermic compositions occurs due to aluminothermic reduction of oxides, and with increasing argon pressure the thermal conductivity of the gas increases, which leads to an increase in heat losses and a decrease in temperature in the system.

Figure 3 presents the dependence of the SHS temperature on the aluminum content, it can be seen from the figure that an increase in the amount of aluminum leads to a decrease in temperature, while samples with a content of 40% and a higher amount of Al do not retain the shape of the sample – they melt. The optimum aluminum content in the initial mixture corresponds to 30–35 wt.

The combustion temperature in the unactivated system Cr_2O_3-Al-B_2O_3 is 1556 °C (Fig. 3). The use of preliminary MA leads to a decrease in the synthesis temperature, for example, to 1200 °C for a system with a 10 min preliminary MA. Probably, the acceleration of the chemical reaction during mechanical activation occurs due to the «pumping» of additional (excess) energy into the reactants, which is accumulated in the resulting structural defects. Excess energy lowers the activation barrier of a chemical reaction. The preliminary MA of the system intensifies the process of solid-phase interaction during SHS and leads to self-acceleration of reactions at low temperatures. It was found that it is unreasonable to continue preliminary MA for more than 10 min since prolonged preliminary MA leads to a loss of the energy accumulated by the system due to the agglomeration of particles of the powder mixture [10].

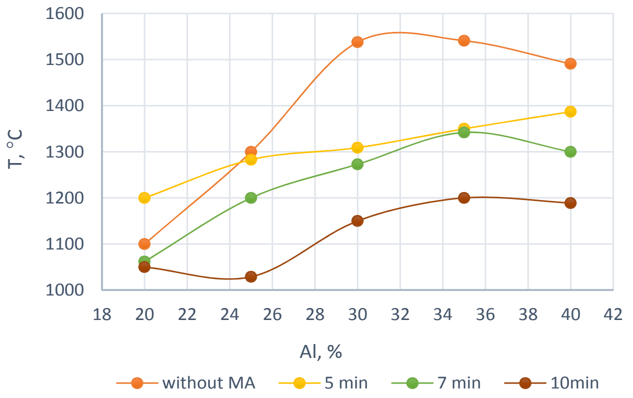


Fig. 3. Dependence of the combustion temperature in the Cr_2O_3-Al-B_2O_3 system on the content of aluminum (1 MPa).

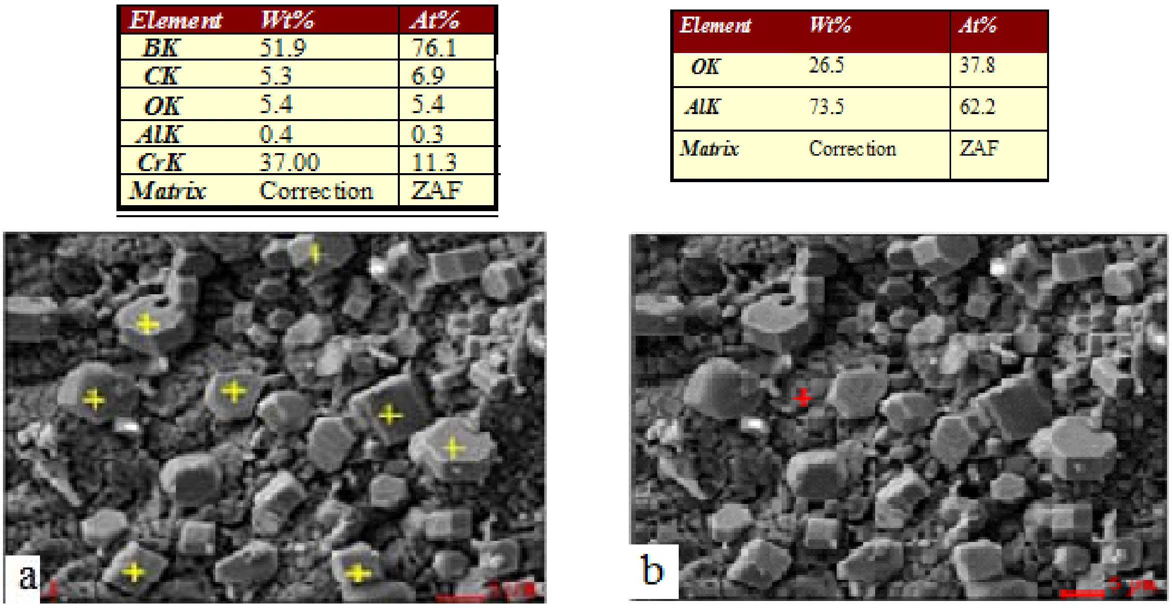
The process of formation of the structure of products in a chemical reaction is called primary structure formation, and the resulting microstructure is the primary microstructure of the product. Based on the studies of morphology, microstructure and literature data [10], we can assume the following mechanism of phase and structure formation for the investigated system Cr_2O_3-Al-B_2O_3.

$$B_2O_3 + 2Al = 2B + Al_2O_3 \tag{3}$$

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3 \tag{4}$$

$$Cr + 2B = CrB_2 \tag{5}$$

The initial mixture is heated in the front of the combustion wave to the melting point of boron oxide (753 K). At this temperature, boron oxide melts and very quickly wets solid particles of aluminum and chromium oxide, thus significantly increasing the specific contact surface between the reactants, which can contribute to the reduction of boron (3). The combustion process of the system begins with the melting of aluminum (933 K), then the solid phase of aluminum oxide (4) begins to crystallize from the melt, the melting point of which is 2317 K, i.e., higher than the maximum combustion temperature of the system under study. A further increase in temperature leads to the final formation of the chromium diboride and aluminum oxide phases (5).



Element	Wt%	At%
BK	51.9	76.1
CK	5.3	6.9
OK	5.4	5.4
AlK	0.4	0.3
CrK	37.00	11.3
Matrix	Correction	ZAF

Element	Wt%	At%
OK	26.5	37.8
AlK	73.5	62.2
Matrix	Correction	ZAF

Fig. 4. Microstructure of SHS products and elemental analysis (SEM) of the Cr_2O_3-B_2O_3-Al system: (a) – borides of chromium; (b) – aluminum oxide.

Thus, in the SHS process, boron oxide first melts, then aluminum melts. The combustion products are formed in the melt of these reagents as a time-increasing product layer, and the chemical transformation occurs as a result of diffusion of the reagents through this layer. The formation of refractory compounds of transition metal borides occurs simultaneously with the chemical reaction in the combustion front, because they have very strong covalent bonds. Available at present experimental data allow us to conclude that refractory compounds such as carbides and borides of transition metals are formed in a combustion wave with an almost equilibrium crystal structure. This is apparently due to the fact that they usually have a simple structure and very strong interatomic bonds.

The effect of the amount of aluminum on the temperature of the synthesis was studied. Figure 4 shows electron microscopic images of SHS products of the Cr_2O_3-B_2O_3-Al system. Crystals of a regular cubic and hexagonal structure, the elemental analysis of which corresponds more to boron and chromium; i.e. borides of chromium – CrB, CrB_2 (Fig. 4a). Between the regular geometric crystals of chromium borides is a phase of Al_2O_3 (aluminum oxide), which is confirmed by elemental analysis (Fig. 4b). Apparently, the matrix of the obtained composite material is Al_2O_3, which is closely bound with the phases of chromium borides, having submicron dimensions [11].

A qualitative and semi-quantitative X-ray phase analysis of the composition of SHS products for the Cr_2O_3-Al-B_2O_3 system (1 MPa) was carried out. The presence of high-temperature aluminum oxide, chromium boride was determined by the X-ray diffraction method (Table 1) in the final combustion products.

Table 1

SHS products of the Cr_2O_3-Al-B_2O_3 system (1 MPa)

Cr_2O_3-B_2O_3-nAl	Activation time, min	Content,%						
		CrB	CrB_2	Cr_2B	Cr_5B_3	CrB_6	Al_5BO_9	Al_2O_3
30%	5	11.5	9.1	3.5	-	5.5	14.5	55.9
30%	7	13.3	2.4	2.6	6.6	6.7	5.3	63.1
30%	10	12.9	7.6	2.1	6.5	2.6	3.5	64.8
35%	5	17.4	1.4	-	-	-	-	81.2
35%	7	16.5	5.6	5.0	3.5	3.3	-	66.1
35%	10	20.3	3.7	-	-	-	-	76.0

The presence of high-temperature phases of chromium borides in SHS products (melting point 2200 °C) in combination with corundum (melting point 2050 °C) give the resulting composite material refractoriness.

According to X-ray phase analysis, it is seen that the combustion products of the charge contain intermediate products of the borides CrB, CrB_2, Cr_2B, Cr_5B_3 and Cr_3B_4 reactions.

These results are consistent with combustion temperature data. The use of 35% by weight of aluminum and 7, 10 min preliminary MA contributes to a more complete synthesis.

3.2. The patterns of combustion in the TiO_2-B_2O_3-Al-C system

To obtain a composite based on titanium carbide under the conditions of SHS, an aluminothermic combustion reaction of the TiO_2-B_2O_3-Al-C mixture was chosen, where carbonize SHS produced rice husk is used as a carbon component.

In recent years, the interest to multi-tonnage restorable wastes as a promising raw material for the production of different materials has increased [13].

Rice husk is a waste of agricultural production. It is a fibrous substance containing moisture, lignin, cellulose, pentozanes, a small amount of protein and vitamins as well as silica [14]. Rice husk is a new and promising source of raw material for the production of carbide as it contains about 50% of carbide in its composition [15, 16].

Such materials can be characterized as cheap and ecologically friendly. Availability and annual resumption of the raw material, a small number of mineral impurities, a developed porous structure, ecologically friendly production allow predicting its wide usage.

It was found that the maximum combustion temperature of the unactivated TiO_2-B_2O_3-Al-C system is 1280 °C. Figure 5 shows an increase in the combustion temperature of the system with the use of mechanical activation; the highest temperature of 1480 °C is achieved using 5 min MA. When using a preliminary MA for 7, 10 min, the combustion temperature is lower.

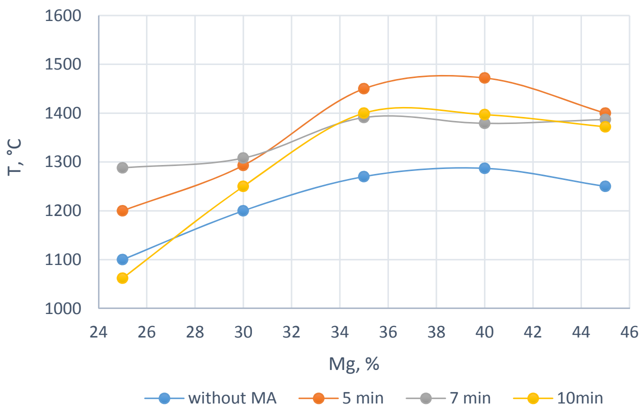


Fig. 5. Dependence of the combustion temperature in the TiO_2-B_2O_3-Al-C system on the content of aluminum and time MA (1 MPa).

As a result of the experiments carried out to determine the combustion temperature, it is stated that the combustion temperature depends strongly on the time of mechanochemical activation 5–7 min.

XRD results for SHS products (Table 2) show that high temperature TiC, TiB_2, TiB and Al_2O_3 phases are present in SHS products. The insignificant content of SiO_2 can be explained by its content in carbonized rice husk.

An important stage determining the nature of the formation of TiB_2 phases is the reduction of boron and titanium oxides by aluminum. As a result of combustion, high temperatures develop, at which aluminum partially evaporates from the combustion zone and, as a result, there is no complete reduction of the oxides. Intermediate products of the reaction are aluminum suboxides Al_2O and AlO_2. The existence of these unstable oxides has been known for a long time, it is also known that these suboxides are unstable and when they are cooled to normal temperatures, they are disproportionated on Al_2O_3 and Al. The formation of titanium carbide occurs due to the reaction diffusion of carbon into the titanium melt [16].

Table 2

Combustion products of the TiO_2-B_2O_3-Al-C system (1 MPa)

$TiO_2 + B_2O_3 + C + nAl$	Activation time, min	Content,%						
		Al_2O_3	SiO_2	TiO_2	$Al_3Ti_5O_2$	TiC	TiB_2	TiB
30%	10	70.6	0.8	1.2	2.6	10.3	8.1	6.4
30%	5	73.2	1.8	1.6	2.3	6.4	5.3	9.4

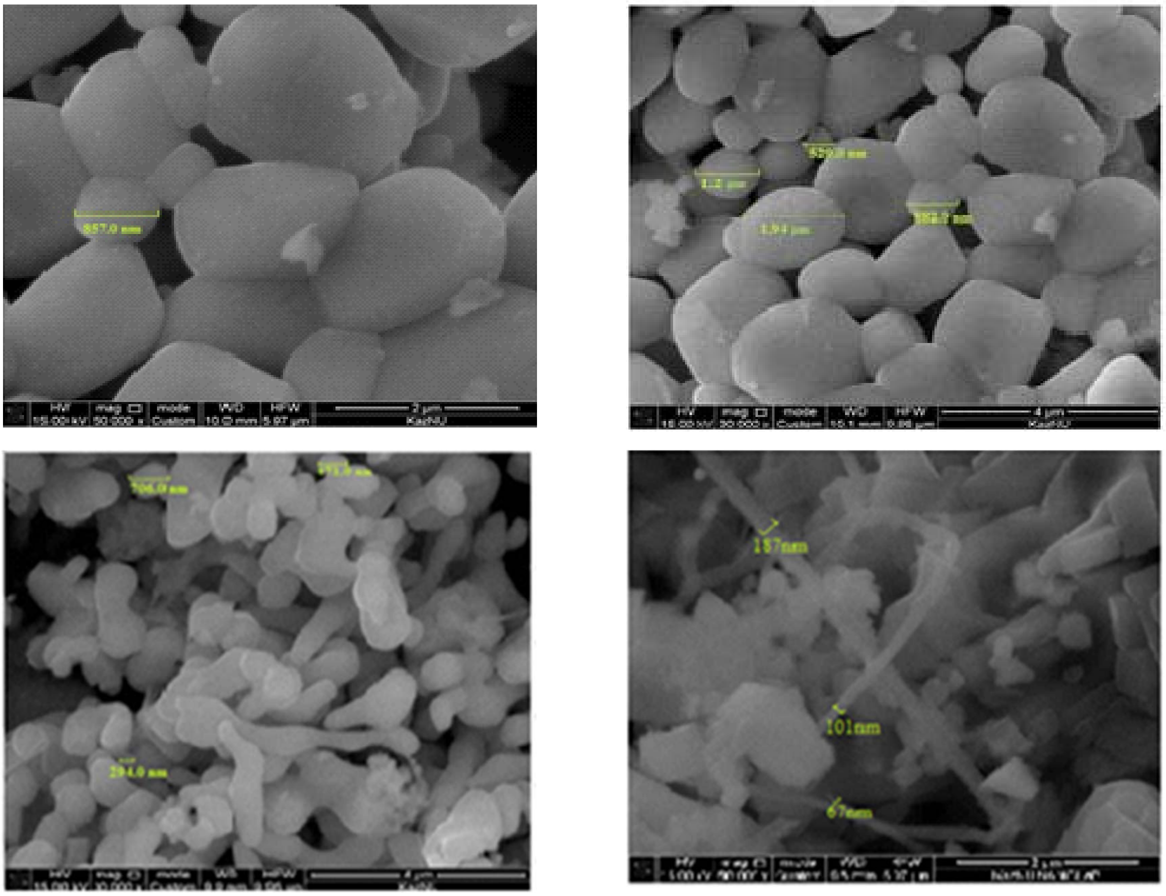


Fig. 6. Microstructure of SHS products of the TiO_2-B_2O_3-Al-C system.

Microscopic images were obtained for the TiO_2-B_2O_3-Al-C system (Fig. 6) presents the fragments of the SHS products of this system. The structure of TiC particles differs significantly; it occurs in the form of separate inclusions of a globular, faceted or dendritic form. The preferential formation of TiC in the TiO_2-B_2O_3-Al-C system is due to the greater diffusion mobility of carbon compared to boron. The TiC particles formed at the first stages of SHS facilitate the nucleation and growth of TiB_2 crystals, i.e. they also play the role of modifiers in the formation of a more wear-resistant phase [17]. In this way, the main structural components of the deposited layer are TiB_2, TiB.

The formation of a melt in SHS products consisting only of TiC and TiB_2 at the maximum temperatures of 1500 °C is unpredictable. The melting points of TiC and TiB_2 are 2940 °C and 2920 °C, respectively. Therefore, the appearance of a melt in SHS products, apparently, is explained by the melting of the eutectic. It is known that in the systems TiB_2-TiC_x and $B_4C_{0.89}$-TiB_2 eutectics exist [18].

The structure of TiC particles differs significantly; it occurs in the form of separate inclusions of a globular, faceted or dendritic form.

According to the data of [18] in the TiB_2-TiC_x system, when the value of x varies from 0.95 to 0.68, the temperature of the eutectic formation decreases from 2520 to 2350 °C. In, several other eutectic formation temperatures are given in this system, namely: when the value of x varies from 0.6 to 0.8, the melting temperature of eutectic increases from 2637 °C to 2688 °C, but at $x = 1$ it decreases to 2663 °C.

It was found that as a result of mechanochemical activation of the initial mixtures, the sizes of titanium oxide particles decrease to micrometer values even with a short activation time.

According to the data of [19], this effect can reduce the temperature of formation of eutectic by hundreds of degrees suggesting that the formation of a melt in SHS products consisting only of TiC and TiB_2 is due precisely to the formation of a non-equilibrium eutectic.

The combined use of MA and SHS makes it possible to produce an ultra disperse material. Thus, the possibility of obtaining nano-sized TiO_2 in the TiO_2-B_2O_3-Al-C system is shown. The effect of MA on the amount and particle size of the synthesized TiO_2 powder is stated.

4. Conclusion

Thus, the conditions for obtaining ceramic materials based on high-temperature transition metal borides, carbides, and Al_2O_3 in the solid-flame combustion model are optimized.

It was also found that the preliminary MA of the initial components and the implementation of SHS in a reactor with an argon pressure of 1 MPa makes it possible to achieve the final yield of chromium, titanium borides and titanium carbide in SHS products. A possible mechanism of phase and structure formation during SHS was proposed. The formation of submicron crystals of chromium borides in the alumina matrix for the Cr_2O_3-Al-B_2O_3 system has been established. The combined use of MA and SHS makes it possible to obtain titanium boride and titanium carbide phases in the TiO_2-B_2O_3-Al-C system.

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