

Synthesis of Composite Materials Based on Borides of Metals and Aluminum Oxide under the Combustion Conditions

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Abstract: The article presents experimental results on obtaining composites based on the systems $TiB_2-Al_2O_3$, $CrB_2-Al_2O_3$ and $ZrB_2-Al_2O_3$ by a method combining SHS (self-propagating high-temperature synthesis) and MA (mechanical activation). Using the thermodynamic calculation program "THERMO", the adiabatic temperature and the composition of the equilibrium combustion products are calculated. It is shown that the products of exothermic interaction are refractory compounds of metal borides and alumina, which in the ceramic composite form a dispersed phase and a ceramic binder. The effect of duration of the activated mixing on the morphology of the reaction mixture and formation of the microstructure of the ceramic composite was studied. The realization of solid-state SHS is due to the formation of the initial powder mixture of ultradisperse reagent sizes during mechanochemical activation. The SHS products were examined by X-ray diffraction analysis and a scanning electron microscope. High-temperature phases of borides of chromium, titanium, zirconium, aluminum oxide and their spinel are found in SHS products. The purpose of this work is to investigate the influence of regimes for preparing reaction mixtures on formation of the microstructure of a ceramic SHS composite based on titanium, chromium and zirconium borides.

Key words: Composite materials, metal borides, SHS, MA.

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, 2]. 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 attention is 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 expensive 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 [2].

SHS (self-propagating high-temperature synthesis) is an efficient way of producing ceramic and metal-ceramic composites [2]. Advantages 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 composites, 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) ensure formation of a homogeneous microstructure with a minimum size of

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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 [3].

Recently, a combination of preliminary mechanical charge activation and subsequent SH-synthesis [4], has become very popular, which allows obtaining materials with improved characteristics. The use of the pre-MA to SH synthesis in a planetary mill significantly reduces the temperature of the onset of exothermic interaction of the mixture components, shortens the synthesis time of the final product, leads to a more complete course of chemical reactions in the combustion wave. Using MA, it is possible to accelerate chemical reactions by increasing the reactivity of mixtures. The grinding of components reduces the kinetic difficulties of chemical reactions in heterogeneous media. Accumulation of energy in the form of structural defects (dislocations, vacancies, grain boundaries, packing defects, etc.) and formation of metastable phases increase the free energy of the system, which leads to an increase in reactivity in the SHS process [5].

2. Experimental Part

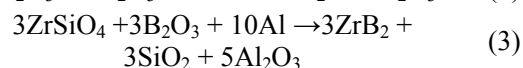
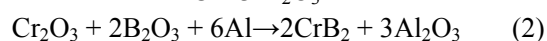
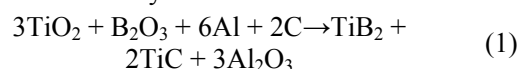
In operation, the following reagents were selected as the main initial components:

- B₂O₃—boron oxide, a crystalline substance of white color with a purity of at least 99.9%.
- Cr₂O₃—chromium oxide powder of not less than 99.8% pure.
- TiO₂—titanium oxide powder of not less than 99.8% purity.
- ZrSiO₄—natural zircon of the Obukhov deposit of the RK (Republic of Kazakhstan).
- Al—aluminum powder with a purity of at least 99.1%.

The components were weighed in a stoichiometric

ratio on an electronic balance, 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 Pulverzette 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 own 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 on the basis of titanium, chromium and zirconium borides by the reaction:



The SH-synthesis 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.

The SH-synthesis of the system under investigation was carried out in a high-pressure reactor (Fig. 1). 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

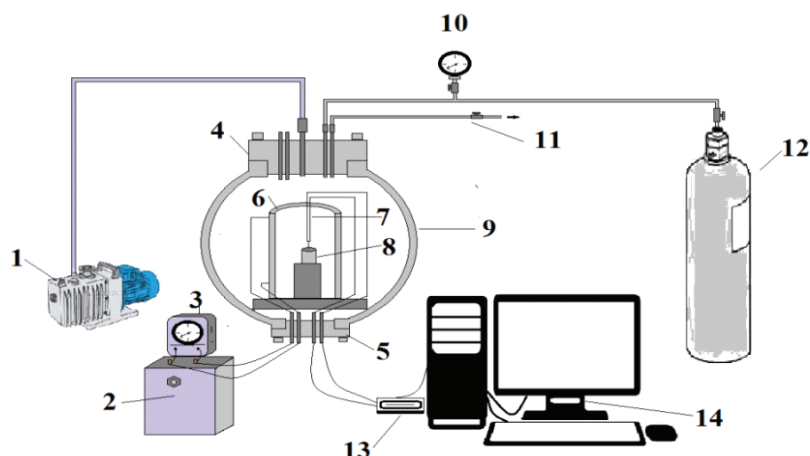


Fig. 1 SHS-reactor of high pressure.

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.

obtained composites was studied using a diffractometer “DRON-4M” using cobalt K_{α} radiation in the range $\theta = 10^{\circ}$ - 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 SH-synthesis 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.

Thermodynamic analysis allows calculating the adiabatic combustion temperature of exothermic mixtures

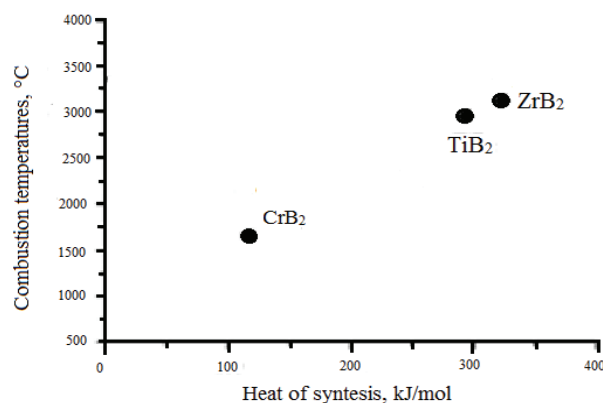


Fig. 2 Adiabatic combustion temperature and heat of formation from the elements for some two-component systems.

(T_{ad}). For the stoichiometric composition, the maximum combustion temperature is $T_{ad} \sim 1,900$ °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 ($T_m = 2,044$ °C), chromium oxide ($T_m = 2,435$ °C) and chromium boride ($T_m = 2,000$ °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 [6]. 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 (ISMAN) in Chernogolovka.

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 of in the reactor varied from 0.5 to 3 MPa [7]. The experiments showed that the optimum for SHS is the pressure of 1 MPa.

Fig. 3 shows an increase in the aluminum content

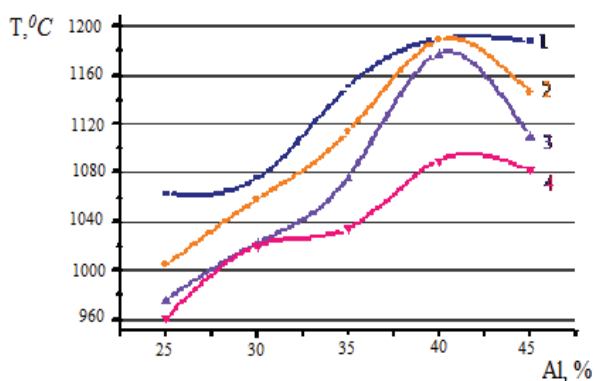


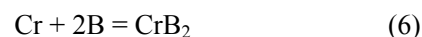
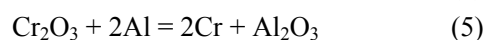
Fig. 3 Dependence of the combustion temperature in the $Cr_2O_3-Al-B_2O_3$ system on the content of aluminum (1 MPa). 1—MA 10 min; 2—MA 7 min; 3—MA 5 min; 4—without MA.

of up to 45%, the content over the stoichiometric amount leading to a decrease in temperature.

Obviously, an excess of aluminum affects the completeness of the reduction of oxides, and an increase in the amount of reduced chromium and boron causes an increase in temperature. The combustion temperature rises to 1,200 °C. The time of preliminary mechanical activation of the charge also affects the combustion temperature, the longer the activation time, the higher the combustion temperature, and therefore the reaction in the combustion wave proceeds more fully.

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 [8]. A further increase in the aluminum content leads to a change in the shape of the sample after SHS. The optimal content of aluminum is set at 30-40 wt. %.

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 [8], we can assume the following mechanism of phase and structure formation for the investigated system $Cr_2O_3-Al-B_2O_3$.



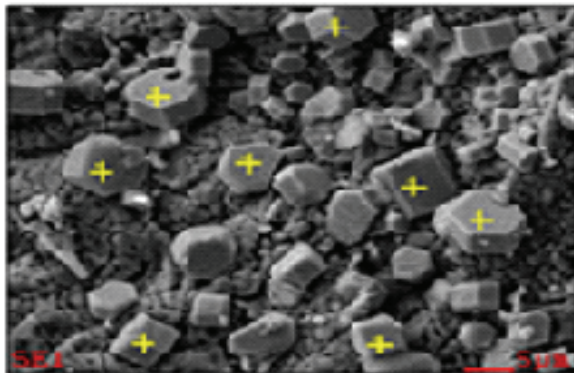
First, boron oxide, then aluminum melts. The final products are formed in the melt of these reagents as a time-increasing product layer, and the chemical transformation occurs as a result of diffusion of the reagents through this layer. Formation of refractory compounds of transition metal borides occurs 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 [9].

The effect of the amount of aluminum on the temperature of SH-synthesis was studied. Fig. 4 shows electron microscopic images of SHS products of the $\text{Cr}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Al}$ system. SEM images present 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,

a)

| 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 |



a—borides of chromium;

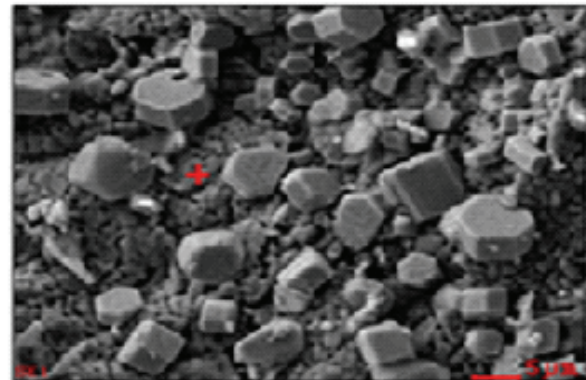
Fig. 4 Microstructure of SHS products and elemental analysis (SEM) of the $\text{Cr}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Al}$ system.

CrB_2 (Fig. 4a). Between the regular geometric crystals of chromium borides is a phase of corundum (aluminum oxide), which is confirmed by elemental analysis (Fig. 5). Apparently, the matrix of the obtained composite material is corundum, which is closely bound with the phases of chromium borides, having submicron dimensions.

A qualitative and semi-quantitative X-ray phase analysis of the composition of SHS products for the $\text{Cr}_2\text{O}_3\text{-Al-B}_2\text{O}_3$ 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 products of SH-synthesis.

b)

| Element | Wt% | At% |
|---------|------------|------|
| OK | 26.5 | 37.8 |
| ALK | 73.5 | 62.2 |
| Matrix | Correction | ZAF |



b—aluminum oxide

Fig. 5 Microstructure of SHS products and elemental analysis (SEM) of the $\text{Cr}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Al}$ system.

Table 1 SHS products of the $\text{Cr}_2\text{O}_3\text{-Al-B}_2\text{O}_3$ system (1 MPa).

| $\text{Cr}_2\text{O}_3\text{-B}_2\text{O}_3\text{-nAl}$ | Activation time (min) | Content (%) | | | | | | |
|---|-----------------------|-------------|----------------|-----------------------|-------------------------|----------------|--------------------------|-------------------------|
| | | CrB | CrB_2 | Cr_2B | Cr_3B_3 | CrB_6 | Al_3BO_9 | Al_2O_3 |
| 30% | 5 | 11.5 | 5.2 | 3.5 | - | 5.5 | 14.5 | 55.9 |
| 30% | 7 | 13.3 | 2.4 | 2.6 | 6.6 | 6.6 | 5.3 | 63.1 |
| 30% | 10 | 12.9 | 7.6 | 2.0 | 6.5 | 2.6 | 3.5 | 64.8 |
| 35% | 5 | 17.4 | 1.4 | - | - | - | - | 81.3 |
| 35% | 7 | 16.5 | 5.6 | 5.0 | 3.5 | 3.3 | - | 66.1 |
| 35% | 10 | 20.3 | 3.7 | - | - | - | - | 76.0 |

3.2 The Patterns of Combustion in the System $ZrSiO_4-B_2O_3-Al$

Similar studies with the aim to obtain composite materials were carried out for the $ZrSiO_4-B_2O_3-Al$ system. Natural zirconium- $ZrSiO_4$ of the Obukhov deposit of the RK was investigated.

Fig. 6 shows the temperature dependence of the combustion temperature on the aluminum content and the time of the MA of the $ZrSiO_4-Al-B_2O_3$ system. The content of aluminum in all systems varied from 25 to 45 wt. %. An increase in the aluminum content leads to an increase in the combustion temperature. The optimum aluminum content is 30-40 wt. % and the MA time is 10 min.

Acceleration of the chemical reaction during mechanical activation is due to the “pumping” of additional (excess) energy in the reacting substances, which accumulates in the resulting structural defects. Excess energy reduces the activation barrier of the chemical reaction. The effect of excess energy on the reaction rate is the kinetic factor of the acceleration of the chemical reaction acceleration [10].

It can be seen in Fig. 7 that the sizes of zirconium boride have diameters of 251.5 nm, 829.6 nm and it can be judged from the elemental composition that all components of the system participated in chemical transformations in the SH-synthesis wave, the products are represented by the crystal components.

According to X-ray phase analysis (Table 1), the use of preliminary MA 5 and 10 min leads to an increase in the yield of zirconium diboride and aluminum oxide. The final products of SH-synthesis by the XRD (X-Ray Diffraction) method (Table 2) show the presence of high-temperature alumina,

zirconium diboride, and a negligible amount of SiO_2 formed upon the decomposition of $ZrSiO_4$.

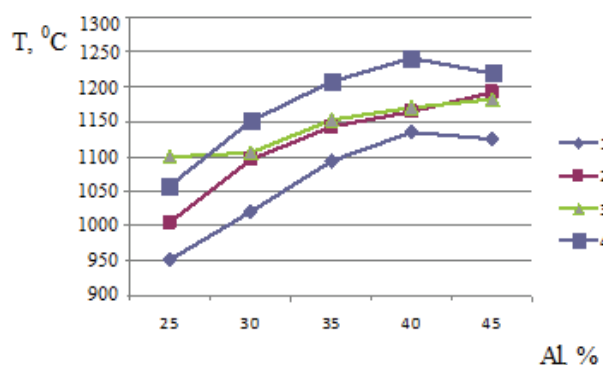


Fig. 6 Dependence of the combustion temperature in the $ZrSiO_4-B_2O_3-Al$ system on the content of aluminum (10 MPa).

1—MA 10 min; 2—MA 7 min; 3—MA 5 min; 4—without MA.

| Element | Wt% | At% |
|---------|------------|------|
| OK | 29.7 | 48.9 |
| AlK | 28.8 | 31.2 |
| SiK | 6.2 | 5.8 |
| BK | 8.9 | 6.5 |
| ZrK | 26.4 | 7.6 |
| Matrix | Correction | ZAF |

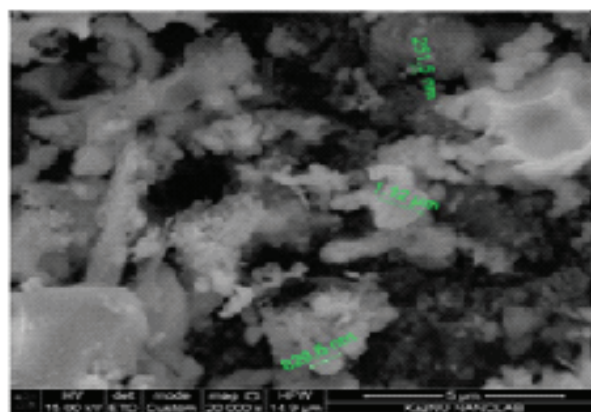


Fig. 7 Microstructure of SHS products and elemental analysis (SEM) of the $ZrSiO_4-B_2O_3-Al$ system.

Table 2 Combustion products of the system $ZrSiO_4-B_2O_3-Al$ (1 MPa).

| $ZrSiO_4-B_2O_3-nAl$ | Activation time (min) | Content (%) | | | | |
|----------------------|-----------------------|-------------|---------|-----------|---------|---------|
| | | ZrB_2 | ZrO_2 | Al_2O_3 | ZrO_2 | SiO_2 |
| 15% | 5 | 15.7 | 70.0 | 12.8 | 1.5 | - |
| 25% | 10 | 11.4 | 69.9 | 17.6 | 1.1 | - |
| 15% | 5 | 23.6 | 24.4 | 33.6 | 3.9 | 1.8 |
| 25% | 10 | 21.5 | 25.4 | 43.8 | 6.7 | 2.7 |

3.3 The Patterns of Combustion in the TiO_2 - B_2O_3 -Al-C System

In order to obtain a composite based on titanium carbide under the conditions of SH-synthesis, an aluminothermic combustion reaction of the TiO_2 - B_2O_3 -Al-C mixture was chosen, where carbonized rice husk is used as a carbon component [11].

In recent years, the interest to multi-tonnage restorable wastes as a promising raw material for the production of different materials has increased [12-14].

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 [12].

Rice husk is a new and promising source of raw material for production of carbide as it contains about 50% of carbide in its composition [13]. Here, an important thing is, first of all, purity and dispersion of the material obtained from rice husk.

Such materials can be characterized as cheap and ecologically friendly. Availability and annual resumption of the raw material, a small amount of mineral impurities, a developed porous structure, ecologically friendly production allow predicting its wide usage [14].

The maximum experimental combustion temperature of the system determines the possibility of performing synthesis in the combustion regime. The value of the maximum combustion temperature corresponds to the moment of thermal explosion. It was found that the maximum combustion temperature of the TiO_2 - B_2O_3 -Al-C system is 1,380 °C. As a rule, the first period of temperature increase is due to oxidation of aluminum in the sample, followed by ignition and directly by SH-synthesis.

Fig. 8 shows an increase in the combustion temperature of systems with an increase in the time of mechanochemical activation, so for 10 min of MA the

maximum temperature is 1,380 °C in a system with an excess of aluminum of 40% and for an inactive system of 1,258 °C, which indicates the completeness of the reaction after activation. In the course of mechanochemical activation, the specific surface area of the charge increases due to the grinding of the powder particles, the formation of cracks, the accumulation of microstructural and surface defects, which contributes to the increase in the reactivity of the components in SH-synthesis.

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. The optimal time for MA is 10 min.

An important stage determining the nature of the formation of TiB_2 phases is 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 [15].

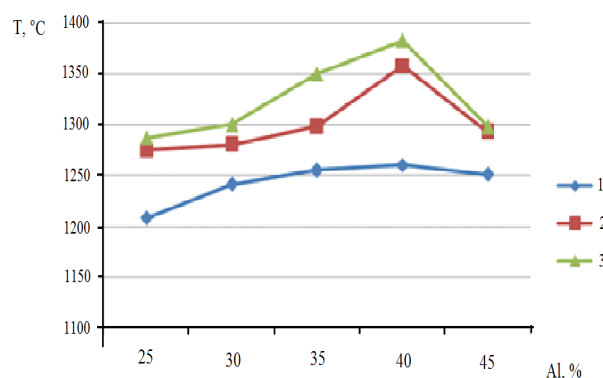


Fig. 8 Dependence of the combustion temperature in the TiO_2 - B_2O_3 -Al-C system on the content of aluminum (1 MPa).

1—MA 10 min; 2—MA 5 min; 3—without MA.

Microscopic images were obtained for the $\text{TiO}_2\text{-B}_2\text{O}_3\text{-Al-C}$ system (Fig. 9) which shows the fragments of the SHS products of this system. The preferential formation of TiC in the $\text{TiO}_2\text{-B}_2\text{O}_3\text{-Al-C}$ 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 [16]. In this way, the main structural components of the deposited layer are: TiB_2 , TiB.

SHS products of the same samples have practically a similar microstructure that is observed, but these products are much better melted.

The formation of a melt in SHS products consisting only of TiC and TiB_2 at the maximum temperatures of 1,400-1,200 °C is very strange. The melting point of TiC and TiB_2 is 2,940 °C and 2,920 °C [13], 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 $\text{TiB}_2\text{-TiC}_x$ and $\text{B}_4\text{C}_{0.89}\text{-TiB}_2$ eutectics exist [17, 18]. According to the data of Ref. [17] in the $\text{TiB}_2\text{-TiC}_x$ system, when the value of x varies from 0.95 to 0.68, the temperature of the eutectic formation rises from 2,520 °C to 2,350 °C. In Ref. [18], 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 2,637 to 2,688 °C, but at $x = 1$ it decreases to 2,663 °C.

It was found that as a result of mechanical 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 Ref. [18], this effect can reduce the temperature of formation of eutectic by hundreds degrees suggesting that formation of a melt in SHS products consisting only of TiC and TiB_2 is due precisely to formation of a nonequilibrium eutectic

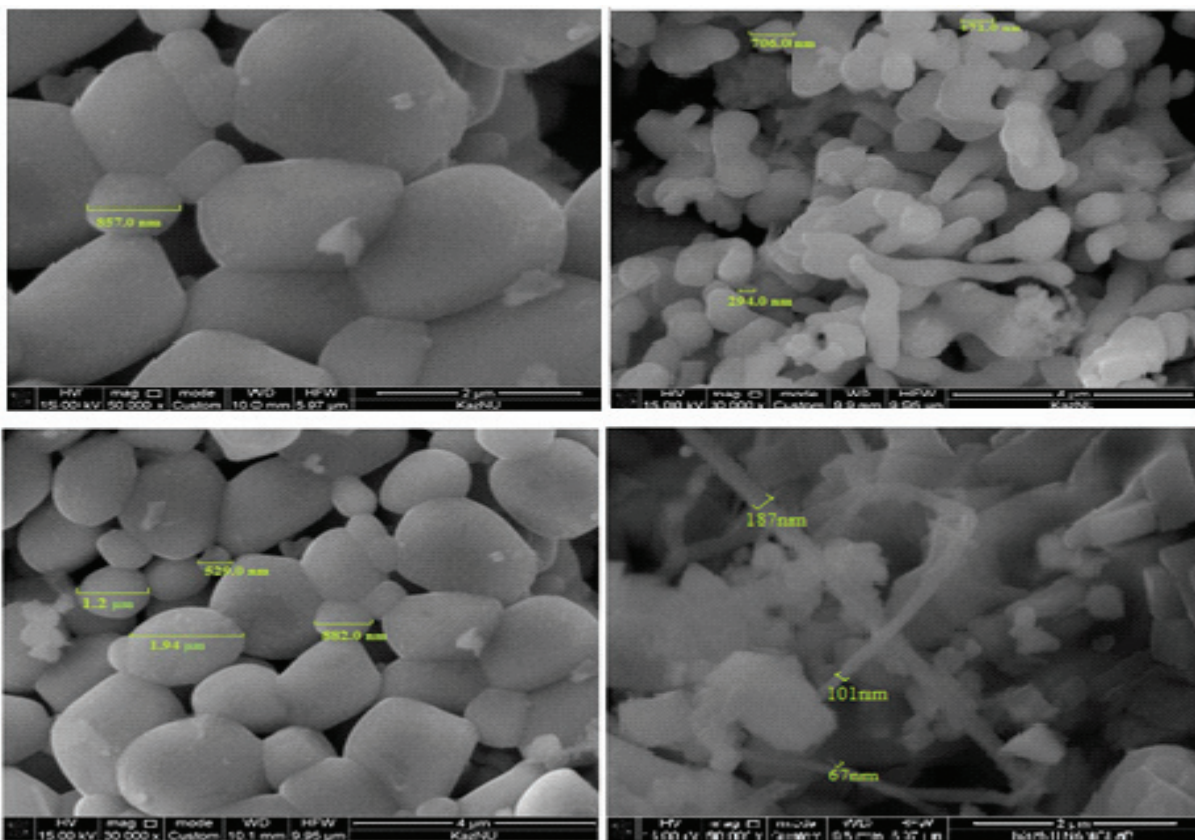


Fig. 9 Microstructure of SHS products of the $\text{TiO}_2\text{-B}_2\text{O}_3\text{-Al-C}$ system.

Table 3 Combustion products of the TiO₂-B₂O₃-Al system (1 MPa).

| TiO ₂ + B ₂ O ₃ + C + nAl | Activation time (min) | Content (%) | | | | | | |
|--|-----------------------|--------------------------------|------------------|------------------|--|------|------------------|-----|
| | | Al ₂ O ₃ | SiO ₂ | TiO ₂ | Al ₃ Ti ₅ O 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 |

The XRD results for SHS products (Table 3) shows that this phase contains the amount of TiB equal to 14.5%, TiC = 10.3% and Al₂O₃ = 70.6% by weight. The structure of TiC particles differs significantly; it occurs in the form of separate inclusions of a globular, faceted or dendritic form.

The combined use of MA and SHS makes it possible to produce an ultradisperse material. Thus, the possibility of obtaining nano-sized titanium diboride in the TiO₂-B₂O₃-Al-C system is shown. The effect of MA on the amount and particle size of the synthesized titanium diboride powder is stated.

4. Conclusions

Thus, the conditions for obtaining ceramic materials based on borides of transition metals and high-temperature aluminum oxides in the regime of solid flame combustion are optimized. The possibility of SH-synthesis of materials at the initial room temperature is shown, which makes the production of ceramic materials based on borides of titanium, chromium and zirconium cheaper.

Composite materials based on the systems Cr₂O₃-B₂O₃-Al, ZrSiO₄-B₂O₃-Al and TiO₂-B₂O₃-Al-C were obtained by SH-synthesis.

An important stage for optimizing the conditions for studying the regularities of synthesis of boron-containing compounds in a combustion wave was carried out in a constant-pressure reactor in the atmosphere of argon. The effect of preliminary mechanoactivation, initial temperature on the synthesis of nanostructured composite materials is shown.

Formation of the phase composition and microstructure of SHS-ceramic materials based on transition metal borides and high-temperature

aluminas was investigated. A possible mechanism for the procedure of SH-synthesis is proposed. Formation of submicron crystals of titanium, chromium borides and zirconium diboride crystals in an alumina matrix has been stated.

Acknowledgments

Authors thank the financial support for this work by grant funding of Scientific Research of the Ministry of Education and Science of the Republic of Kazakhstan (3793/GF4).

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