Peculiarities of Self-Propagating High-Temperature Synthesis and Structure Formation of TiB_2-Al_2O_3 and CrB_2-Al_2O_3 Composites

Z.A. Mansurov[1], D.S. Abdulkarimova[1]*, O. Odawara[2], A. Gubarevich[2], A.S. Rogachev[3], N.F. Shkodich[3], N.N. Kochetov[3]

[1] al-Farabi Kazakh National University, Institute of Combustion Problems, Bogenbay str.172, Almaty, Kazakhstan
[2]Tokyo Institute of Technology, 4259 Nagatsuta-cho Midori-ku, Yokohama, Kanagawa 226-8502, Japan
[3] Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, Moscow Region, 142432, Russia

Abstract

Preparation of TiB_2-Al_2O_3 and CrB_2-Al_2O_3 composites with a broad range of phase composition was conducted by self-propagating high-temperature synthesis (SHS) involving reaction of different types. The formation of fibrous crystals of aluminum oxide with length of about 10-25 microns and with diameter of 200-500 nm at self-propagating high-temperature synthesis in the system $2B_2O_3$-Cr_2O_3-6A1 was established. Thermite mixtures of Al-TiO_2 and Al-TiO_2-B_2O_3 were incorporated with the Ti-B combustion system to produce the composites of TiB_2-Al_2O_3, within which the increase of the thermite mixture for a higher content of Al_2O_3 decreased the reaction temperature and combustion wave velocity. This implies that the thermite reaction of Al with TiO_2 reduces the exothermicity of the overall SHS process. It was found that adoption of B_2O_3 as one of the thermite reagents improved the product formation effectively. For investigate the combustion wave in $0.75TiO_2$-0.25Ti-2B-Al system the «quenching» method was used. The XRD analysis shows that the final products containing diborides and aluminium oxide.

Introduction

Transition metal diborides like TiB_2 and CrB_2 posses many superior properties, such as high melting points, high hardness, good thermal and electrical conductivity, excellent wear and corrosion resistance, and chemical stability [1-3]. Moreover, addition of Al_2O_3 to these metal borides further improves their fracture toughness, flexural strength, and impact resistance, which renders the Al_2O_3-reinforced boride composites a promising candidate for a variety of the applications including cutting tolls, wear resistant parts, and high-temperature structural materials [4].

Among various reaction-based synthesis in the mode of self-propagating high-temperature synthesis (SHS) is particularly attractive, on account of its advantages of low energy requirement, short processing time, simplicity of facilities, and formation of high-purity products. Observing the microstructural transitions during a combustion synthesis will be of benefit to the understanding of the mechanism of the synthesis. The SHS technique has been extensively applied to produce a great number of advanced materials such as borides, carbides, nitrides, silicides, and intermetallics such as aluminides [1-3, 5]. When incorporated with thermite reactions based on Al as the reducing agents, the SHS approach represents an in situ procedure for preparing ceramic, intermetallic, and metal matrix composites reinforced by Al_2O_3, because such thermite reactions are highly exothermic and produce a stable oxide Al_2O_3 [4]. Rogachev et al. [5] invested the so called combustion front quenching method (CFQM) to study the structural transitions in the gasless combustion of Ti-C and Ti-B systems. In their work, the reaction mixture was placed in the wedge-shaped notch in a copper block, and the combustion reaction was initiated by an incandescent tungsten spiral at the base of the

*corresponding author. Email: abd.danara@mail.ru

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wedge. When the combustion wave traveled toward the apex, because of the intense transfer of heat to the cooling copper block, the combustion was quenched, so the intermediate and final products of the reaction were frozen. By investigating the structure of the specimen in the regions where the front is quenched, one can obtain information about the structural evolution and thus about the process mechanism. Recently, many studies on the SH-synthesis of boride composites were reported. For example, Mishra at al. [6] successfully fabricated the ZrB_2-Al_2O_3 composite through the SHS process by using the powder compact composed of Al, ZrO_2, and B_2O_3 as the raw materials. Similarly, an in situ composite with TiB_2:Al_2O_3=3:5 was produced from the test specimen consisting of $3TiO_2$-$3B_2O_3$-10Al [7]. The reaction system of Ti-Al-TiO_2 was employed under different starting stoichiometries to prepare the TiAl-Al_2O_3 composites and Ti-Al_2O_3 cermets [8]. Vallauri et al. [9] applied the SHS route involving the thermite reagent of TiO_2 reduced by Al, Mg, and Zr to fabricate TiC-TiB_2-based composites reinforced by different metallic oxides including Al_2O_3, MgO, and ZrO_2. For direct formation of dense TiC-Al_2O_3-Al composites, Hu et al. [10] conducted the field-activated combustion synthesis to overcome thermodynamic limitations of the $3TiO_2$-3C-(4+x)Al system with $x\geq10$. One additional benefit from combining thermite-based displacement reactions with conventional combustion synthesis is the cost saving, since the metallic oxides like TiO_2, B_2O_3 and ZrO_2 are considerably less expensive than elemental titanium, boron, and zirconium.

The objective of this study is to investigate of the TiB_2-Al_2O_3 and CrB_2-Al_2O_3 composites with a broad range of phase composition by the SHS process involving thermite reactions of different types. On formation of the TiB_2-Al_2O_3 composite, two thermite mixtures, Al-TiO_2 and Al-TiO_2-B_2O_3, were added to the elemental combustion system. For investigate the combustion wave in $0.75TiO_2$-0.25Ti-2B-Al system the «quenching» method was used. In this study, the influence of the thermite reaction on the SHS process was explored in terms of the combustion sustainability, propagation rate of the reaction front, combustion temperature, and phase composition of the synthesized products.

Experimental

The starting materials used in this study included elemental powders: Ti (RP-Ti 280 (PTC) (99% purity, particles 80 μm), amorphous boron and disperse aluminium of a spherical form (ACD–4) (99,1 % purity, particles<40 μm), TiO_2 (98% purity, anatase), Cr_2O_3 (98 % purity), B_2O_3 (96% purity). The initial stoichiometry of the powder blend for the synthesis of the TiB_2-Al_2O_3 and CrB_2-Al_2O_3 composites was prepared according to different thermite mixtures involved in the SHS process and described in Reactions (1)-(5):

$$(1\text{-}y)\,(\mathrm{Ti}+2\mathrm{B}) + y\,(\mathrm{TiO_2} + 2\mathrm{B} + \tfrac{4}{3}\mathrm{Al}) = \mathrm{TiB_2} + \tfrac{2}{3}y\mathrm{Al_2O_3} \quad (1)$$

$$(1\text{-}x)\,(\mathrm{Ti}+2\mathrm{B}) + x\,(\mathrm{TiO_2} + \mathrm{B_2O_3} + \tfrac{10}{3}\mathrm{Al}) = \mathrm{TiB_2} + \tfrac{5}{3}x\mathrm{Al_2O_3} \quad (2)$$

$$(\mathrm{Ti}+2\mathrm{B}) + x\mathrm{Al_2O_3} = \mathrm{TiB_2} + x\mathrm{Al_2O_3} \quad (3)$$

$$\mathrm{TiO_2} + 2\mathrm{B} + 1{,}33\ \mathrm{Al} = \mathrm{TiB_2} + 0{,}67\ \mathrm{Al_2O_3} \quad (4)$$

$$6\mathrm{Al} + 2\mathrm{B_2O_3} + \mathrm{Cr_2O_3} = 2\mathrm{CrB_2} + 3\mathrm{Al_2O_3} \quad (5)$$

Where the stoichiometric parameters x and y represent the mole fraction of Al_2O_3 formed in the TiB_2-Al_2O_3 composite. The maximum value of x adopted in reaction (2) was 0.75. The parameter y was varied form 0 to the upper limit of 1, under which the sample was composed of three thermite reagents Al, TiO_2 and B_2O_3.

SHS was carried out in the constant-pressure chamber in argon atmosphere at 1 atm (Fig.1). The air was pumped out from the chamber using vacuum pump 1, then argon 15 was introduced into the chamber. Pressure in chamber was controlled using vacuum gauge 2. When combustion should have been done at the initial temperature, higher than room temperature, sample is 13, being on the ceramic substrate 14 was heated using molybdenum furnace 3, which was powered by electrical current form the power supply unit 4. The heating was controlled with tungsten-rhenium thermocouple 5 with the thickness of juncture of 200 μm, connected to the controller 6. The combustion was initiated from the upper surface of the sample using incandescent tungsten spiral heated by electrical current 7, supplied by the power supply unit 8. Video camera Panasonic CCTV 10, connected to the videotape recorder 11 and the TV set Supra 12, fixed the process through the peep hole 9 and optical filter 16. The velocity of combustion was

determined using videotapes. The video camera shoots 30 shots per second, taking it into account, the obtained imagining is treated using shot viewing.

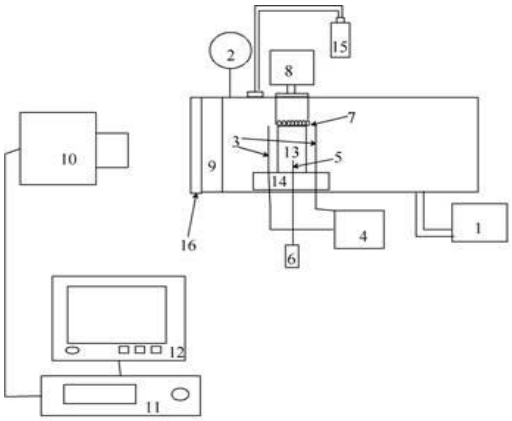


Fig. 1. Scheme of experimental unit: 1 – vacuum pump, 2 – vacuum gauge, 3 – molybdenum furnace, 4 – power supply unit of molybdenum furnace, 5 – thermocouple, 6 – thermocouple controller, 7 – electrical current, 8 – power supply unit, 9 – peep hole, 10 – video camera, 11 –-videotape recorder, 12 –TV set, 13 – sample, 14 – ceramic substrate, 15 – argon, 16 – optical filter

The experimental unit allows making the video recording of combustion at different initial temperature of the sample and also fixing combustion temperature. When defining combustion velocity, the dependence of combustion velocity on temperature. Then effective kinetic parameters were calculated-temperature coefficient of combustion velocity and activation energy of combustion using the following formulas:

$$k=d(\ln (u))/dT \quad (6)$$

$$E=2*R*T_r^2*k \quad (7)$$

where k – temperature coefficient of combustion velocity,

u – combustion velocity,

T – temperature,

T_r – combustion temperature,

R – universal gas constant of 8,31 J/mol*K.

The «quenching» of the combustion wave in the process of SHS was carried out for $75TiO_2$-0.25Ti-2B-A system using the contact of the rolled thin bands of the charge with cold metallic wall. Reaction mixture is burnt under a wide edge of a copper block and during combustion specific heat losses increase resulting finally in extinction. Thus, the velocities of «quenching» of a few thousand degrees per second can be reached.

The combustion temperature of systems was calculated using "Thermo" program (Fig. 4).

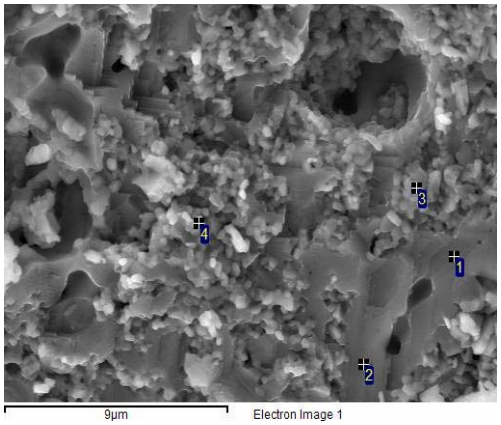
The microstructure and phases composition of synthesized products was investigated using microanalizer-scanning electron microscope JCXA-733 (JEOL) «Superprobe» and Hitachi S-4800 FE-SEM, Japan (Fig. 2, 7, 8), and XRD (Fig. 5-6).

Results and discussion

Hardening and analyze of samples

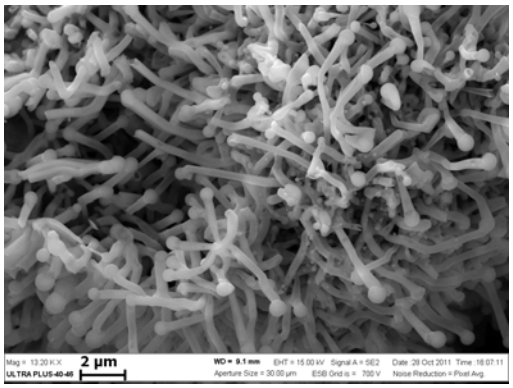
For investigate the combustion wave in $0.75TiO_2$-0.25Ti-2B-Al system the «hardening» method was used.

The holdup wave of SHS process followed by analysis of partially and completely part of $0.75TiO_2$-0.25Ti-2B-Al mixture. On Fig. 2a it can be seen that initial reagents melt and with boron oxide can be formed the titanium diboride crystals. Thus during initial structural formation infusible reagent dissolves in melt of other reagent (or contact melting) and fall out of solid granules of the product from oversaturated melt.



a

Zone No.	Atomic ratio, %			
	B	O	Al	Ti
1		57.32	39.69	2.99
2	7.76	52.99	37.93	1.32
3	44.13	24.23	20.69	10.95
4	49.98	13.43	7.44	29.14



b

Zone No.	Atomic ratio, %			
	B	O	Al	Ti
1		42.87	56.45	0.67
2	19.01	29.45	50.00	1.54
3	13.42	40.40	42.60	3.58

Fig. 2. Microstructure of products of system $0.75TiO_2$-0.25Ti-2B-Al produced by hardening method: a) microanalyses of zone reaction , b) formation of Al_2O_3 fibers in pores

The structure of the melt after SHS is a porous, strong material that has in some zones dendrite constituent and grainy inclusions, crystallized into six membered lamellar formation of titanium diboride in aluminium oxide matrix (Fig. 2 a). The presence of dendrites shows that the particles of initial powder are the centres melt crystallization. The figure 2 shows that the fibrous crystals of Al_2O_3 have different sizes. Fibrous crystals, having a branched structure too (Fig. 2 b). The length of fibers is about 5 microns and the diameter is 700 nm. It is known that the fibrous crystals can be formed by two mechanisms – either "vapor-solid" or "vapor-liquid-crystal." Aluminum can serve as concentrate for fibrous crystals growth, which is made by the mechanism of "vapor-liquid-crystal" [4]. It is explained by the fact that they have a simple structure and very strong interatomic bonds. One can assume that they are zones of metastable solid solution of chromium diboride in the matrix of aluminium oxide. Inside the product the grains of aluminium oxide cover plates and grains of titanium diboride.

Measurement of flame-front propagation velocity

The propagation velocity (Vf) of the combustion front was determined from the recorded SHS images. Fig. 3 plots the flame front velocity of the SHS process as a function of the Al_2O_3 content in the TiB_2-Al_2O_3 composites is considerably lower and decreases with increasing Al_2O_3 content formed in the products. The decrease in flame-front velocity is believed to be caused by reduced exothermicity of the overall synthesis reaction, in view of the fact that both the Al-TiO_2 and Al-TiO_2-B_2O_3 thermite systems yet releasing heat are less exothermic that the elemental reaction between Ti and B.

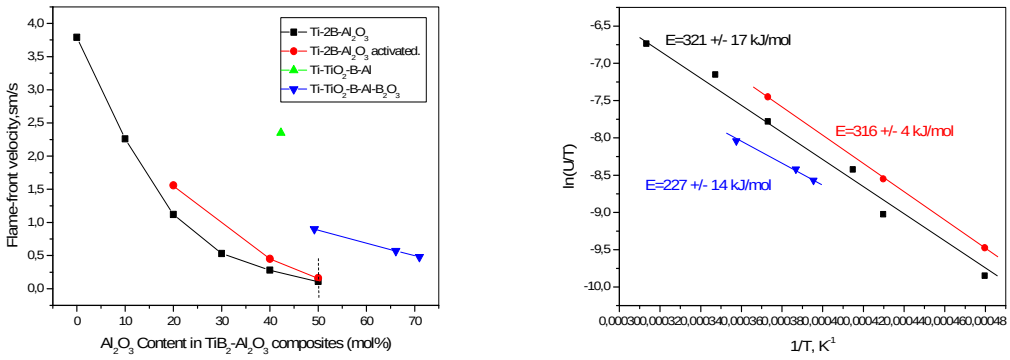


Fig. 3. Velocity and energy activation variation from Al_2O_3 content in TiB_2-Al_2O_3

Based upon Eq. (1) and (2), Fig. 4 shows the decrease in the calculated adiabatic temperature with increasing Al_2O_3 content in the TiB_2-Al_2O_3 composites, mainly because the elemental reaction of Ti with B is more exothermic that the displacement reaction within the thermite mixture. Additionally, on account of the higher heat of formation of B_2O_3 than TiO_2, the SHS processes

involving the thermite mixture Al-TiO_2-B_2O_3 exhibit adiabatic temperatures when compared with those using the Al-TiO_2 mixtures.

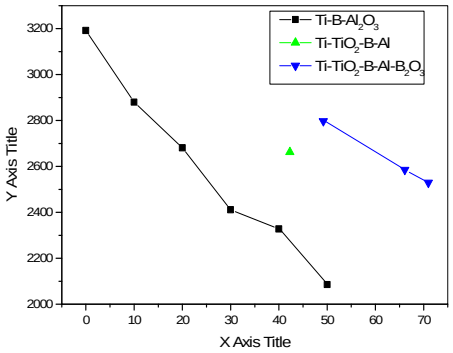
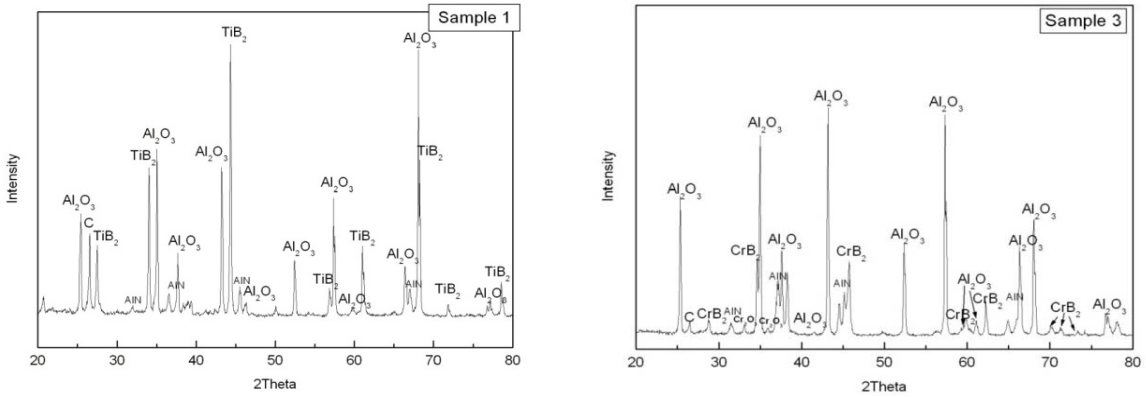


Fig. 4. Effect of Al_2O_3 content on adiabatic combustion temperatures associated with SHS formation of TiB_2-Al_2O_3 composites

Fig. 3 with the Al_2O_3 content of the product and the composition of the thermite mixture agree reasonably with those of the adiabatic combustion temperature presented in Fig. 4.

Composition and morphology analysis of combustion products

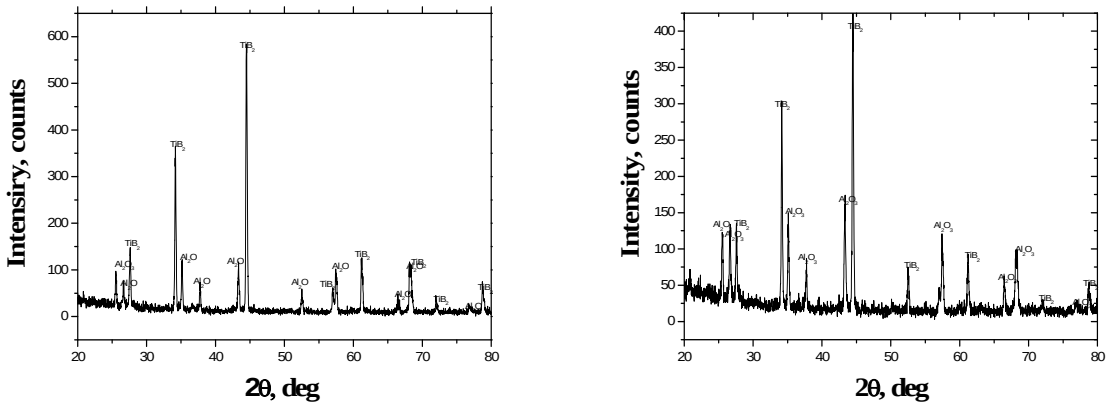
Composition of the samples after self-propagating high-temperature synthesis has been defined by X-ray fluorescence analysis method. Products containing titanium and chromium borides and aluminum oxide were obtained according to the X-ray fluorescence analysis. We see also that the insignificant fraction of aluminum interacts with the air forming nitride A1 (Fig. 5a, 5b).



a b

Fig. 5. XRD patterns of TiB_2-Al_2O_3 (a) and CrB_2-Al_2O_3 (b) composites produced by SH-synthesis

Fig. 6 shows the existence of two phases TiB_2 and Al_2O_3 for the preparation of the TiB_2-Al_2O_3 composites in (a) 0.75TiO_2-0.25Ti-2B-Al and (b) TiO_2-1.33Al-2B composites in the synthesized products.



a b

Fig. 6 XRD patterns of TiB_2- Al_2O_3 composites produced by SHS in (a) 0.75TiO_2-0.25Ti-2B-Al and (b) TiO_2-1.33Al-2B systems

It can be seen that peaks for system TiO_2-1.33Al-2B more intensive in comparison with system 0.75TiO_2-0.25Ti-2B-Al.

Fields of elemental microanalysis were selected using SEM Hitachi S-4800 FE-SEM, Japan for CrB_2-Al_2O_3 composite (Fig. 7).

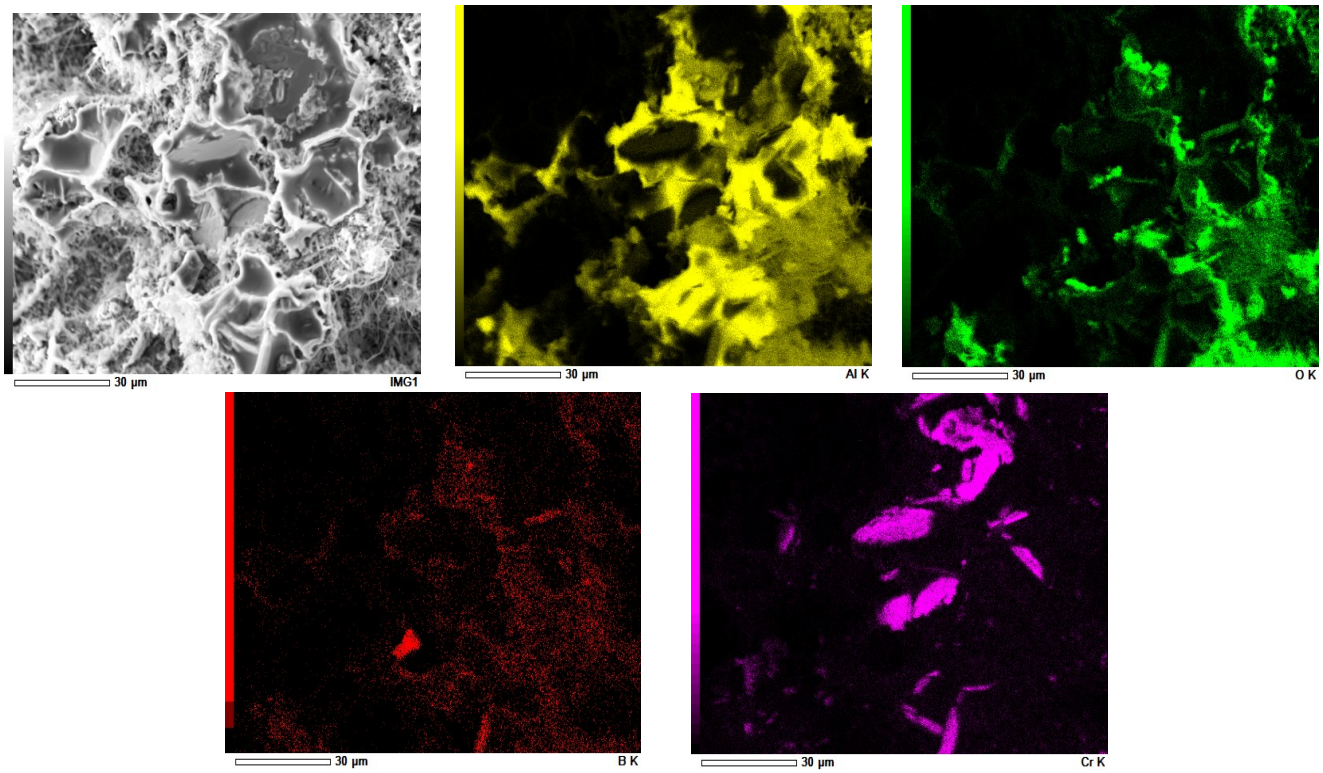
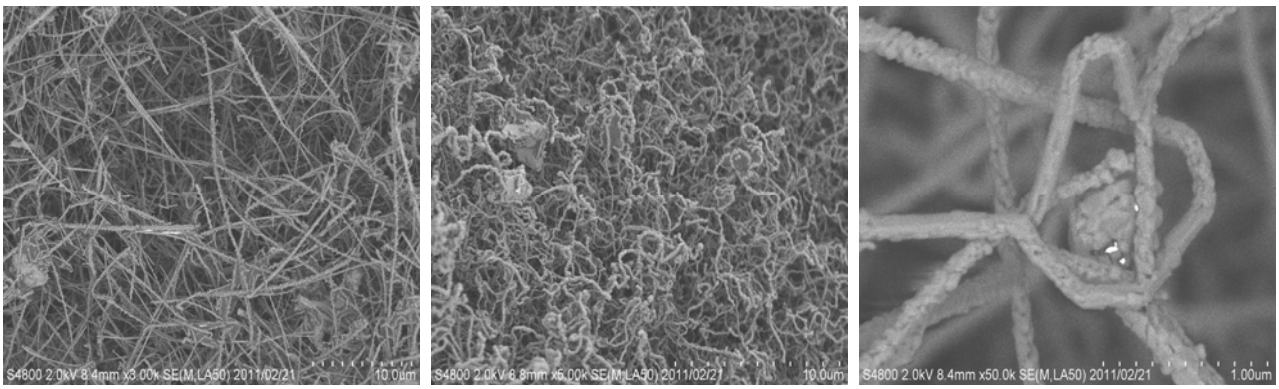


Fig. 7. Microstructure of Cr_2O_3-2B_2O_3-6Al system

Microanalysis showed the presence of aluminum, oxygen, boron and chromium. Typical SEM micrographs, shown in Fig. 2a, reveal the grains TiB_2 with a small and rather uniform particle size. This confirms the feasibility of applying the SHS technique to fabricate the soft-agglomerated composite powders with homogeneous distribution of the components. In comparison with conventional methods, the SHS-derived powders eliminate the less efficient mechanical mixing of both components, the prolonged grinding of disagglomeration, and the steps of removal of the impurities. Therefore, the SHS-derived powders enable the simplification of processing ceramic materials by shaping, sintering and hot-pressing of powders [1-3].

The formation of fibrous crystals of Al_2O_3 with length of about 10-25 microns and with diameter of 200-500 nm at SHS in the system 2B_2O_3-Cr_2O_3-6A1 was established. Crystals have direct, contorted and curly form (Fig. 8).



a b c

Fig. 8 SEM pictures of Cr_2O_3-2B_2O_3-6Al system, where (a) Al_2O_3 fibers, (b), (c, d, e) straight, curly fiber forms

Different values of the fibers diameter are resulted from system growth self-turbulency, namely the growth of diffusion temperature, chemical reaction, asperities between the interface, liquid and solid phases [11]. Fibers formation was also observed by employees of Borovinskaya in self-propagating high-temperature synthesis reactors when a refractory powders pilot plant operated. Fibers formation is also associated with gas-phase reactions that take place at partial gasification of reagents (evaporation, impurities reactions). The works of Mukosyan and Stepanov with coauthors suggest that crystals Si_3N_4 in reaction zone grows using mechanism: vapour-liquid-crystal. The realization of the mechanism vapour-liquid-crystal promotes by a small amount of the impurities Fe, Ca, Zn, Al. These impurities form stable drops of eutectic melt that are the centres of the formation of the product embryos [12, 13].

According to the formation sequence of TiB_2 and the XRD results f the synthesized products of this study, the reaction mechanism for the synthesis of the TiB_2-Al_2O_3 composite is proposed as follows. The interaction of Ti with B acts as the first reaction step, which proceeds with formation of TiB and triggers displacement reaction between the thermite reagents. The intermediate boride phase TiB then converts into TiB_2 through further reaction with B. The reaction steps involved in SHS formation of the TiB_2- Al_2O_3 composite are given below.

$$Ti + B = TiB \quad (8)$$

$$4Al + 3TiO_2 = 3Ti + 2Al_2O_3 \quad (9)$$

$$2Al + B_2O_3 = 2B + Al_2O_3 \quad (10)$$

$$TiB + B = TiB_2 \quad (11)$$

Conclusions

In this study, the SHS processes was conducted to prepare TiB_2-Al_2O_3 and CrB_2-Al_2O_3 composites. Composition and structure of synthesis products in the system B_2O_3-Cr_2O_3 and A1 were investigated. The formation of fibrous crystals of aluminum oxide with length of about 10-25 microns and with diameter of 200-500 nm at self-propagating high-temperature synthesis in the system B_2O_3-Cr_2O_3 and A1 was established. Experimental results indicate that the sustainability of the synthesis reaction, dynamics of the combustion wave, and phase composition of the synthesized product are substantially influenced by the addition of the thermite reactions to the elemental SHS process to produce TiB_2-Al_2O_3 composites. In order to produce the TiB_2-Al_2O_3 composites, two thermite mixtures of Al-TiO_2 and Al-TiO_2-B_2O_3 were incorporated with the Ti-B elemental combustion system. Because of the lower exothermicity, the flame-front propagation velocity and combustion temperature were decreased by increasing the extent of the thermite reaction for a higher content of Al_2O_3 formed in the composite. It was found that aluminum can serve as concentrate for fibrous crystals growth, which is made by the mechanism of "vapor-liquid-crystal".

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