Self-propagating high temperature synthesis of composite materials based on boron carbide

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Received:
30 September 2018

Accepted:
20 October 2018

Available online:
25 December 2018

UDK 541.053:546.669

ABSTRACT

The experimental results on obtaining composites based on the system was wide variation of the concentration ratios of the components in the initial mixtures and the products of SH-synthesis of mechanically activated systems. It is shown that the products of exothermic interaction are refractory compounds of boron carbide and magnesium oxide, which in the ceramic composite form a dispersed phase and a ceramic binder. The effect of the duration of the activated mixing on the morphology of the reaction mixture and the formation of the microstructure of the ceramic composite was studied. The possibility of obtaining boron carbide-B_4C in the B_2O_3-Mg-MeO-C system is shown.The purpose of this study is to study the possibility of obtaining composite materials based boron carbide used on borate ore in the Inder deposit by the SHS method.The SHS products were examined by X-ray diffraction analysis and a scanning electron microscope.
Keywords: boron carbide, self-propagating high-temperature synthesis, mechanical activation, mineral raw materials.

1. Introduction

Boron carbide (B_4C) has excellent physical and chemical properties, such as high melting point, high thermal and chemical stability, and large neutron absorption cross-section from thermal to fast neutrons, therefore B_4C has been used for neutron absorbers of control rods for fast breeder reactor (FBR) [1]. However, cracks are induced and propagate in B_4C pellets caused by thermal stress and swelling during neutron irradiation, and failure of a cladding tube is also observed due to a mechanical interaction between the B_4C fragments and the cladding tube in a short period of time [2].

For extension of lifetime of control rods, and then for the safety of nuclear reactors, it is essential to improve mechanical and thermal properties of B_4C pellets [3]. Self-propagating high-temperature synthesis (SHS) is an efficient way of producing ceramic and metal-ceramic composites [4-6].

Due to the unique properties – such as high melting point, hardness, modulus of elasticity chemical and corrosion resistance, neutron-capture cross-section, and low density – boron carbide is exceedingly valuable for practical implementations. At present, self-propagating high temperature synthesis (SHS) allowed to obtain a wide range of such materials.

One of the problems in production of carbon containing composition systems is the use of different carbon additives which are able to substitute expensive carbon. The use of a cheap available raw material in production is of great interest. In this study, refractory boron carbide powder was obtained by the SHS of a mixture enriched borate ore containing a boron oxide, carbonized rice husk, magnesium. The most widespread was SHS-technology of refractory powders, characterized by simplicity and low energy intensity [5].

Recently, the SHS method is used along with mechanochemical activation (MA), the so-called MA SHS [7]. The mechanical activation (MA) of the reagents before carrying out the SHS process is a very important step. With the help of MA, it is possible to substantially intensify heterogeneous processes, MA leads to an increase in the chemical activity of the particles to be treated by increasing their defectiveness and/or increasing the reaction surface (by reducing the particle size). Thus, MA prepares particles for active response.

2. Experimental part

The adiabatic temperatures of SH-synthesis are calculated, which is 1500-1800 °C. The possibility of the synthesis of boron carbide in B_2O_3-Al-MeO-C systems, where C-carbonized rice husk, graphite, has been studied, but Al application was established did not have a significant effect, it was expedient to use as a reducing agent more active magnesium.

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Table 1
Combustion products of the Mg-C-B_4C-B_2O_3 (ore) system in an air atmospher

Composition of the initial charge	Products of SHS,%					
	MgO	$Mg_3(BO_3)_2$	SiO_2	$Mg(BO_2)_2$	$B_{13}C_2$	Mg_2C_3
Mg + B_2O_3 + C + B_4C (C – CRH)	51.9	-	9.3	-	37.3	1.5
Mg + B_2O_3 + C + B_4C (C – graphite)	72.0	7.0	3.5	-	17.4	-
Mg + B_2O_3 + B + C + B_4C (C – CRH)	71.3	7.8	4.1	-	13.5	3.3
Mg + B_2O_3 + B + C + B_4C (C – graphite)	59.9	11.7	4.4	3.5	10.4	10.0

SH-synthesis B_4C was carried out according to the reaction:

$$2B_2O_3 + C + 6Mg \rightarrow B_4C + 6MgO \quad (1)$$

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 in real time data 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 samples are 20 mm in diameter, 16 mm high and have a relative density of 0.6 MPa. The initiation was carried out with a tungsten helix. The microstructure of the ceramic composites was studied by scanning electron microscopy (QUANTA 3D 200i, FEI, USA) electron.

The phase composition of the obtained composites was studied using a diffract meter «DRON-4M» with the use of cobalt Ka radiation in the interval θ = 10°-70°. To study the microstructure and phase composition, the surface of the sample was prepared in the form of pure cleavage and polishing.

2. Results and disscustions

From Tables 1 and 2 it follows that in combustion products, along with B_4C, boron carbide of another modification of $B_{13}C_2$ is formed. Compound $B_{13}C_2$ has the same syngony as B_4C, but its crystal lattice parameters are somewhat larger than that of B_4C.

It has the same excellent properties as B_4C. Unlike previous results, it was possible to increase the content of boron carbide in SHS products.

When carrying out the synthesis in a high-pressure reactor at 10 atm argon, it was possible to increase the yield of boron carbide to 83.7 mass%.

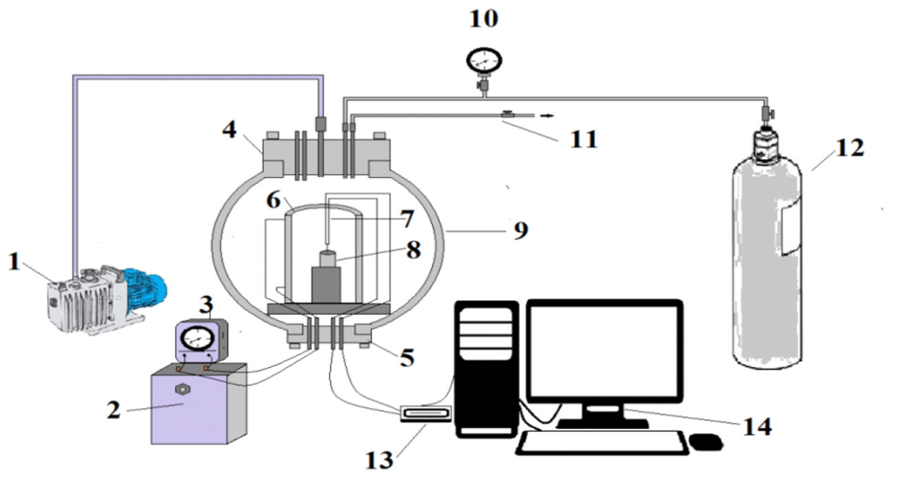

Fig. 1. SHS-reactor of high pressure: 1 – vacuum pump; 2 – transformer; 3 – ammeter; 4 – upper reactor cover; 5 – lower reactor cover; 6 – tube heating furnace; 7 – thermocouple; 8 – sample; 9 – reactor vessel; 10 – manometer; 11 – inlet and outlet valves; 12 – argon balloon; 13 – LTR-U-1 data acquisition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

Table 2
Combustion products of the Mg-C-B_4C-B_2O_3 (ore) system in an inert medium (1 MPa.)

Composition of the initial charge	Time MA, min	Products of SHS,%					
		MgO	$Mg_3(BO_3)_2$	SiO_2	$Mg(BO_2)_2$	$B_{13}C_2$	B_4C
Mg + B_2O_3 + C (C – CRH) (Mg 25%)	-	31.6	10.9	2.2	-	55.1	0.2
Mg + B_2O_3 + C (C – graphite) (Mg 25%)	-	-	-	3.7	23.3	73.0	-
Mg + B_2O_3 + B + C (CRH) (Mg 30%)	-	35.7	11.2	4.7	-	48.5	-
Mg + B_2O_3 + B + C (C – graphite) (Mg 30%)	-	29.7	-	0.9	3.8	65.2	0.4
Mg + B_2O_3 + C(C – CRH) (Mg 35%)	5	41.2	9.5	1.4	-	47.8	0.1
Mg + B_2O_3 + C (C – graphite) (Mg 35%)	5	-	-	13.2	3.1	83.7	-
Mg + B_2O_3 + B + C (C – CRH) (Mg 40%)	10	29.7	7.7	0.9	2.6	59.1	-

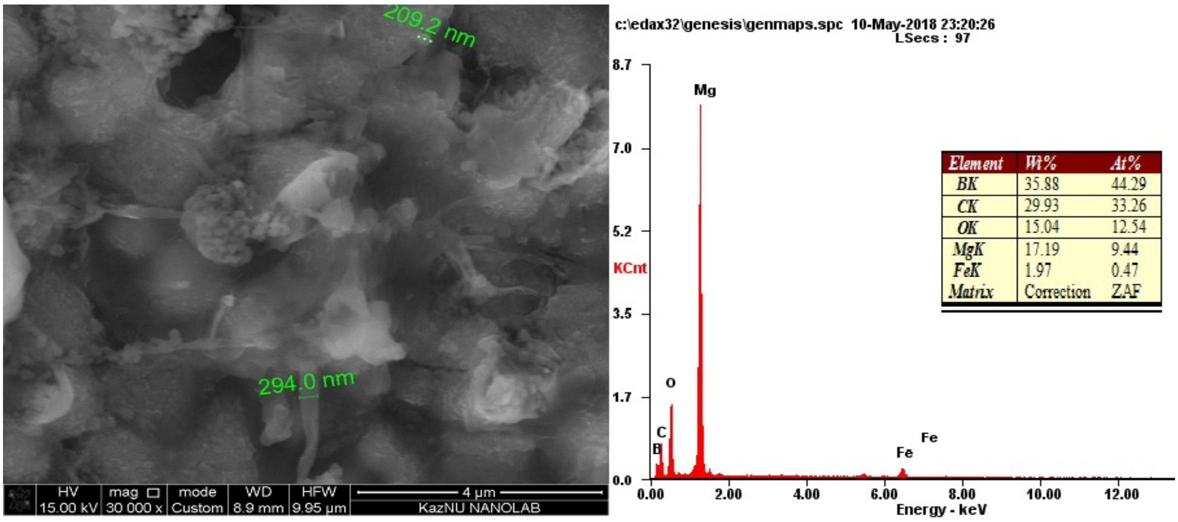

Fig. 2. The microstructure and energy-dispersive X-ray spectroscopy analysis of SHS products of the system Mg – B_2O_3 – C (C – CRH).

It has been established that the greatest amount of borides in SHS products is formed in an inert medium (argon). The possibility of obtaining boron carbide-B_4C in the B_2O_3-Mg-MeO-C system, where C-carbonized rice husk, graphite, is shown.

Investigation of the microstructure of the compositions revealed the formation of submicron refractory powders boron carbide (Fig. 2). It has been stated that the complex use of MA, SHS and subsequent processing of the obtained intermediate of SHS makes it possible to obtain submicron powders.

Conclusions

The possibility of using borate ore of Inder deposit of the Republic of Kazakhstan for production of boron carbide containing nanosized refractory powders by SHS method is shown.

The influence of MA, the composition of the charge, the SHS medium on the yield of the target products was determined It has been stated that the use of magnesium as a reducing agent in the initial charge is preferable to the use of aluminum in the synthesis of refractory boron carbide powders.

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Самораспространяющийся высокотемпературный синтез композиционных материалов на основе карбида бора

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Аннотация

Представлены экспериментальные результаты по получению композитов при широком варьировании концентрационных соотношений компонентов в исходных смесях и продукты СВ-синтеза механоактивированных систем. Показано, что продуктами экзотермического взаимодействия являются тугоплавкие соединения карбида бора и оксида магния, которые в керамическом композите образуют дисперсную фазу и керамическую связку. Изучено влияние длительности активированного смешения на морфологию реакционной смеси и формирование микроструктуры керамического композита.

Целью данного исследования является исследование возможности получения и композиционных материалов на основе корбида бора используя руды Индерского месторождения методом СВС.

Продукты СВС были исследованы методом рентгенофазового анализа и сканирующего электронного микроскопа.

Ключевые слова: карбид бора, самораспространяющийся высокотемпературный синтез механическая активация, минеральное сырье.

Бор карбиді негізіндегі композитті материлдардың өздігінен таралған жоғары температуралы синтезі

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Аңдатпа

Бастапқы қоспалардағы компоненттердің концентрациясия мен механикалық активтеу жүйелердің ӨЖ-синтезі өнімдерінкомпозитті материалдар алудағы тәжірбелік нәтижелер көрсетілген. Экзотермиялық өзара әрекеттесу өнімдері ретінде бор карбид және магний оксиді көрсетілген жәнеде олар керамикалық композитті дисперсті фазаны және керамикалық байланыстырғаштарды құрайды. Бор карбиді және магний оксиді қыйын балқыйтын қосылыстар болып табылады. Реакциялық қоспаның морфологиясына мен керамикалық композиттің микроқұрылымын қалыптасуына белсендірілген араластырудың әсері зерттелді. Зерттеудің мақсаты - Индер борат кені қолданып бор карбиді негізінде композиттік материалдарды ӨЖС әдісі арқылы алу мүмкіндігін зерттеу. ӨЖС өнімдері рентгенфазалық талдау және сканирлеуші электрондық микроскоп арқылы зерттелді.

Түйін сөздер: бор карбиді, өздігінен таралатын жоғары температуралы синтез, мехникалық активтеу, минералды шикізат.