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THEORETICAL ASPECTS OF THE CREATION OF HIGHLY EFFICIENT REFRACTORIES ON THE BASIS OF SHS TECHNOLOGY

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The theoretical principles behind the self-propagating high-temperature synthesis of refractory materials are established. The physico-chemical characteristics of these materials are studied and the technology for their production is optimized. The thermochemical and kinetic parameters of the solid-phase combustion of systems based on fireclay, chromite, magnesium sulfate, and aluminum are examined; the phase composition and thermodynamic and physico-mechanical characteristics of the combustion products are determined and formulations are developed for refractory concretes and gunites.

Keywords: self-propagating high-temperature synthesis; SHS-technology; refractory materials; chromium-oxide materials; chromium-corundum refractories; aluminothermy; heat resistance; mechanical strength at high temperatures.

Successful completion of the “Federal Program for Making Kazakhstan one of the Fifty Most Competitive Nations in the World” entails the introduction of innovative technologies to foster the growth of its industries. Speeding up production processes and finding innovative ways to promote growth of the metallurgical, chemical, petrochemical, and cement industries will be impossible without the creation of new materials with excellent service properties. Among these materials are the refractories used to line high-temperature process units such as furnaces. Increasing interest is being shown in the production of high-quality refractories with specified properties. In connection with this, exhaustive research should be undertaken to develop and introduce environmentally clean technologies that save energy and other resources while helping to improve the production of refractories based on the raw materials available in Kazakhstan.

The Republic of Kazakhstan currently imports alumosilicate and magnesian refractories from Russia, the Ukraine, China, Austria, and other countries. To supply its own refractories, the Republic needs to develop its own refractories industry to the point where it can offer a competitive product both to the internal market and to customers abroad. Such a development will in turn require the establishment of a scientific foundation for the industry, creation of the necessary technologies, and, in particular, realization of the production of unshaped and shaped refractories that can withstand substantial mechanical and thermal loads at high temperatures while providing the longest possible service for the linings of metallurgical equipment.

We analyzed general and specific issues that surround the subject of self-propagating high-temperature synthesis (SHS) as a method of producing alloys and composites. The theoretical principles of SHS and the laws and mechanisms of combustion in SHS systems were laid out and the thermochemical and kinetic aspects of the interactions between the components during the synthesis of new materials in the combustion regime were examined [1 – 4].

The rate of combustion was measured by the thermocouple method. The shear strength of the refractory products was determined along with the resistance of the refractory materials to the corrosive action of melts. The intermediate and end products of pyrolysis were identified through chemical and x-ray-phase analysis. Refractory specimens were tested for compressive strength on a special laboratory press and the breaking load was automatically recorded. Refractoriness was determined at 1100 – 1750°C in increments of 50°C, with the increments also being reduced to 20°C for a more accurate determination of this characteristic. The measurements were made with tungsten-rhenium thermocouples. The porosity of the specimens was determined on the basis of water absorption.

One of the main directions being taken in research on new refractories for metallurgical equipment is the creation of new high-durability materials that can be classified as

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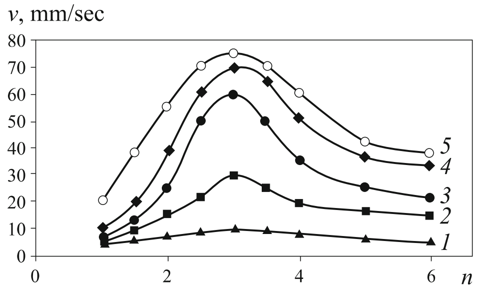

Fig. 1. Dependence of combustion rate *v* on the dispersity and amount of aluminum in the system Cr_2O_3–*n*Al. Particle size, μm: *1*) 10 – 15; *2*) 20 – 30; *3*) 30 – 50; *4*) 80 – 120; *5*) 150 – 250.

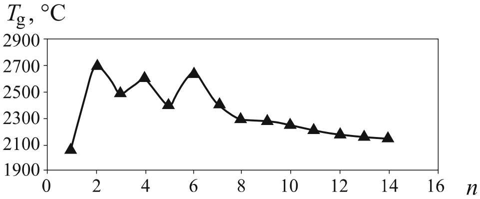

Fig. 2. Dependence of combustion temperature T_g on the amount of aluminum in the system Cr_2O_3–*n*Al.

multi-component oxide systems which contain chromium. The high refractoriness and chemical inertness of chromium oxide has served as the starting point for the creation of sintered chromium-oxide refractories which have a Cr_2O_3 content of up to 95% and possess extremely high corrosion resistance: when evaluated on the basis of this characteristic, chromium-oxide refractories are far superior to any well-known refractory currently in use.

Studies were made of the system Cr_2O_3–Al with different proportions of the reactants. To increase the concentration limits for combustion, the original specimens were heated to 750 – 800°C. The cylindrical specimens had a diameter of 2 cm and a height of 4.5 – 5.0 mm and were obtained by pressing at 10 MPa. Before the charge was pressed, it was moistened with water to a moisture content of 10%. The specimens were dried in a drying cabinet at 200°C and then were placed in a furnace with a temperature of 750°C. After the temperature of the specimens was equalized inside the furnace (which took roughly 10 min), combustion was initiated with a tablet of iron-aluminum thermite.

Figure 1 shows the dependence of the rate of combustion *v* on the coarseness of the Al powder. It is apparent that the effect of the dispersity of Al on the value of *v* is very small when the particles of the powder are smaller than 10 – 15 μm. This indicates that the kinetic mechanism is the operative mechanism of interaction under the given conditions. Powdered aluminum with a particle size of 10 – 15 μm was used in subsequent studies. The curve of T_c (Fig. 2) has three distinct maxima — at values of *n* equal to 2, 4, and 6. A thermodynamic calculation of the adiabatic combustion temperatures T_c was performed for different intervals with the assumption that one-stage reactions (1)-(3) take place and that one of the initial components undergoes complete transformation. When the proportions of the initial components Al:Cr_2O_3 are 70:30, 80:20, and 85:15, the adiabatic combustion temperatures are 2400, 2200, and 2100 K, respectively.

In other words, the relation $T_c(n)$ can be conditionally divided into three characteristic intervals and the following net reactions can be written for these intervals on the basis of the results obtained from x-ray phase analysis:

1. $[Al]/[Cr_2O_3]$ = 0,8 – 2,75; composition: Al_2O_3, Cr, Cr_2O_3;
elementary reaction $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$; (1)

2. $[Al]/[Cr_2O_3]$ = 2,75 – 4,75; composition: Al_2O_3, $AlCr_2$, Al_2Cr;
elementary reaction $Cr_2O_3 + 4Al \rightarrow Al_2O_3 + 2/3AlCr_2 + 2/3Al_2Cr$; (2)

3. $[Al]/[Cr_2O_3]$ = 4,75 – 14; composition: Al_2O_3, Al_2Cr;
elementary reaction $Cr_2O_3 + 6Al \rightarrow Al_2O_3 + 2Al_2Cr$. (3)

The maximum value of *v* corresponds to *n* = 3, which is wholly inconsistent with the positions of the peaks on the curve of $T_c(n)$. Thus, there is no unambiguous relation between T_c and *v* for the combustion of the system Al–Cr_2O_3 in the kinetic regime. The results obtained here make it possible to propose that a multi-stage mechanism is responsible for the reactions of the components in Al–Cr_2O_3. The reduction of chromium proceeds by the reaction

$$Cr^{3+} \rightarrow Cr^{2+} \rightarrow Cr^0. \tag{4}$$

The oxidation of aluminum also occurs in stages:

$$Al \rightarrow Al^{+} \rightarrow Al^{2+} \rightarrow Al^{3+}. \tag{5}$$

If we represent the chemical formula for an element of the crystalline lattice of a particle of CrO in the form $\langle Cr_2O_3 \rangle$, then the elementary stages of the oxidation-reduction reaction being examined here can be written in the form:

$$\langle Cr_2O_3 \rangle + 2\langle Al \rangle \rightarrow \langle Al_2O \rangle + 2\langle CrO \rangle, \tag{6}$$

$$\langle CrO \rangle + 2\langle Al \rangle \rightarrow \langle Al_2O \rangle + \langle Cr \rangle, \tag{7}$$

$$\langle CrO \rangle + \langle Al_2O \rangle \rightarrow \langle Al_2O2 \rangle + \langle Cr \rangle. \tag{8}$$

The elementary stages are stimulated by the reaction

$$\langle Cr_2O_3 \rangle + 3\langle Al \rangle \rightarrow 2\langle Cr \rangle + 1.5\langle Al_2O_2 \rangle. \tag{9}$$

Fast reactions (1) – (3) are followed by secondary combustion, which proceeds at a lower rate:

$$\langle Cr_2O_3 \rangle + \langle Al_2O_2 \rangle \rightarrow 2\langle CrO \rangle + \langle Al_2O_3 \rangle, \tag{10}$$

$$\langle CrO \rangle + \langle Al_2O_2 \rangle \rightarrow \langle Cr \rangle + \langle Al_2O_3 \rangle, \tag{11}$$

$$\langle Al_2O_2\rangle \rightarrow \langle Al\rangle + \langle Al_2O_3\rangle. \qquad (12)$$

The experimental data shows that the combustion of chromium-aluminum thermite takes place by a more complex mechanism and that the final product is formed as a result of the occurrence of several successive transformations.

For the SHS of chromium-corundum refractories, we chose the region of the ternary system Cr_2O_3–Al–SiO_2 that is bounded by the following concentrations, mass %: Cr_2O_3 5 – 85; Al 50 – 90; SiO_2 5 – 15. A glassy phase is obtained by adding small amounts of Na_2O to the refractories, the amount added being based on obtaining a value of 12:1 for the theoretical ratio SiO_2:Na_2O. A single crystalline corundum-like phase was found in the structure of synthesized chromium-corundum refractories subjected to x-ray diffraction analysis on a URS-50 IM unit in Cu K_α-radiation. The diffraction maxima of the reflections of the corundum-like phase were systematically shifted in the direction of larger interplanar spacings as the content of chromium oxide in the specimens increased, which is indicative of the formation of $(Cr,Al)_2O_3$ solid solutions in the structure of the materials. Eskolaite, mullite, and corundum were not detected in the form of separate phases.

Petrographic study of the specimens in reflected light on an MBI-6 microscope and in transmitted light on a POLAM R-112 microscope established that the structure of the refractories consists of one crystalline phase — a $(Cr, Al)_2O_3$ solid solution — and a glassy phase. The texture of the refractories is porous. Porosity ranges within 10 – 18%, depending on the composition of the material. The porosity typically decreases with an increase in the contents of the glassy phase and chromium oxide. The composition of the chromium-corundum refractory was optimized based on the results from a comprehensive investigation of the main physicomechanical and service properties of the materials that were synthesized.

The thermal expansion of these materials is quite uniform within the range 20 – 1500°C. Their heat resistance was determined by the method of thermal cycling: heating of 16-mm-diam., 50-mm-high cylindrical specimens to 1300°C – cooling of the specimens in air. It was found that the heat resistance of the synthesized materials decreases with an increase in their content of chromium oxide. All of the systems that were studied contain aluminum as part of their composition.

Aluminothermy is one of the most long-standing and widely used processes for obtaining pure metals. One by-product of this process is aluminum oxide, which is one of the most important components of refractory materials. It is known that magnesium sulfate can play a dual role in bulk refractories: it can serve as a binder that provides good adhesive ability, and it can act as an oxidizing agent. Magnesium sulfate crystallizes from hot water in the form $MgSO_4{\cdot}H_2O$ and from cold water in the form $MgSO_4{\cdot}7H_2O$. An aqueous solution of magnesium sulfate has a slightly acidic reaction (pH = 4 – 6, the exact value depending on the concentration). It should be pointed out that magnesium sulfate is a strong oxidizing agent and can therefore have a significant effect on the thermochemical and thermophysical properties of the charge. Analytically pure magnesium sulfate $MgSO_4$ was used for our experiments. The following reactions can occur when magnesium sulfate interacts with aluminum:

$$4Al + 2MgSO_4 \rightarrow 2MgO{\cdot}2Al_2O_3 + S_2, \qquad (13)$$

$$2Al + 3MgSO_4 \rightarrow 3MgO{\cdot}Al_2O_3 + 3SO^{2-}, \qquad (14)$$

$$8Al + 3MgSO_4 + 3H_2O \rightarrow 3MgO{\cdot}4Al_2O_3 + 3H_2S. \qquad (15)$$

The thermal effects from these reactions are equal to –996.8, –531.4, and –400.2 kJ/mole, respectively. All of these reactions are appreciably exothermic, which can ensure that the process being discussed takes place in the combustion regime. Reaction (13) is the reaction that is most likely to occur. An analysis of the combustion products shows that elemental sulfur is formed in the course of the process. Thus, further calculations were performed with allowance for the occurrence of reaction (13). Table 1 shows results obtained from calculation of the adiabatic combustion temperatures T_c and the yield of magnesium oxide η_{MgO} in relation to the proportions of the initial components. The parameters indicated above are determined from the relation

$$\eta = Q_k / Q_{ini}, \qquad (16)$$

where Q_k is the content of the reductive target element in the combustion products when they are in the condensed state ; Q_{ini} is the content of the reductive element in the initial compounds.

The theoretical combustion temperatures are fairly high for the system being examined. Thus, it can be proposed that it is possible for synthesis to take place in the combustion regime. Judging from the results of thermomechanical calculations, it can also be suggested that the specific system being discussed can undergo combustion and that the conditions for SHS can be optimized. One method that is widely used to study heterogeneous processes in condensed media is thermal analysis. Simultaneous recording of thermogravimetric (TG), derivative thermogravimetric (DTG), and differential thermoanalytical (DTA) curves with identification of the in-

TABLE 1. Adiabatic Combustion Temperature T_g and Yield of Magnesium Oxide η_{MgO} for the Al–$MgSO_4$ System with Different Proportions of the Initial Components

Proportions of the initial components Al:$MgSO_4$	T_g, °C	η_{MgO}, %
0.50:0.50	1700	63.7
0.55:0.45	1677	70.2
0.60:0.40	1727	81.4
0.70:0.30	1627	97.3
0.80:0.20	1387	100.0

termediate and end products makes it possible to completely describe the processes that take place. Several processes that are accompanied by thermal effects and a change in the mass of the specimen can be seen on the thermogram of the system Al–$MgSO_4$.

The first endothermic effects to take place within the range 117 – 207°C are accompanied by a decrease in mass, this occurrence corresponding to the process of the removal of water of crystallization. The exothermic effect seen at 227°C may be due to the interaction of aluminum with chemically bound water in an acid medium:

$$4Al + 3H_2SO_4 + 3H_2O \rightarrow Al_2O_3 + Al_2(SO_4)_3 + 6H_2. \quad (17)$$

An increase in the content of aluminum reinforces the exothermic effect. In addition, the specimen is seen to expand as a result of the release of hydrogen.

An endothermic effect caused by melting of the aluminum is seen at 680°C. As it melts, the aluminum is oxidized by oxygen and forms a secondary oxide film that delays ignition of the charge. A large amount of energy is needed to destroy this strong film. Accordingly, the charge ignites at a higher temperature, as confirmed by the effect seen at 817°C. Magnesium sulfate melts at 1137°C. According to calculations, the combustion temperature of the Al–$MgSO_4$ system is within the range 1627 – 1727°C. It can be assumed that the reaction is homogeneous and takes place in the kinetic regime and that its rate is independent of the rate of diffusion. The statement that the reaction occurs in the kinetic regime is substantiated by the fact that the combustion rate is independent of the dispersity of the particles of Al and $MgSO_4$. Diffusion mixes the components ahead of the reaction zone. The MgO and Al_2O_3 formed as a result of reactions (13) – (15) may interact to form a noble spinel, as was confirmed by the results from x-ray phase analysis. These results show that the combustion products are $MgAl_2O_4$ and elemental sulfur.

The results obtained from the above analysis and the experiences of foreign researchers show that materials of the system MgO–Al_2O_3–Cr_2O_3 are promising materials for the production of high-durability refractories. Their use ensures stable service properties for the refractory products, and they are distinguished by their good heat resistance and their strength at high temperatures. Studies were performed by using magnesium aluminate and magnesium chromite obtained by chemical synthesis. The studies entailed investigation of the materials' crystallographic, structural, and phase characteristics. The roentgenographic characteristics that are the most important for diagnosing compounds are the parameters of the unit cell: the principal interplanar spacings *d/n* and their crystalline indices, as well as the relative values of the diffraction maxima *I* (Table 2).

TABLE 2. Interplanar Spacings *d/n* of the Crystalline Lattice and Intensity of Radiation *I* of the Initial Powders of $MgAl_2O_4$ and $MgCr_2O_4$ and the Standards*

Indices of the standards				Indices of the experimental specimens			
$MgAl_2O_4$		$MgCr_2O_4$		$MgAl_2O_4$		$MgCr_2O_4$	
d/*n*	*I*	*d*/*n*	*I*	*d*/*n*	*I*	*d*/*n*	*I*
4.660	35	4.813	65	3.807	10	3.622	30
2.858	40	2.945	25	3.174	15	2.940	25
2.437	100	2.512	100	2.811	15	2.548	30
2.020	65	2.406	25	2.210	30	2.505	60
1.650	45	2.083	55	1.708	10	2.097	20
1.555	55	1.603	40	1.525	15	2.041	25

* Based on ASTM standards.

Magnesium aluminate can turn out to be roentgenographically amorphous when the synthesis process is not completed and the crystalline structure of the given substance is not sufficiently formed. In this case, the material may be composed of such compounds as hydro-spinels $MgAl_2O_4 \cdot nH_2O$, $Mg(OH)_2 \cdot Al_2O_3$, and $Mg(OH)_2 \cdot Al(OH)_3$, as well as $MgAl_2O_4 \cdot nH_2O$ + hydrargillite $Al(OH)_3$, $MgAl_2O_4 \cdot nH_2O$ + diaspore AlO(OH), and $MgAl_2O_4 \cdot nH_2O$ + boehmite $Al_2O_3 \cdot nH_2O$. To refine the results, we determined the phase composition of the powders that were studied. It was determined that the main phase in magnesium chromite is $MgCr_2O_4$. In addition to $MgAl_2O_4$, magnesium aluminate also contains the hydro-spinel $MgAl_2O_4 \cdot nH_2O$. After heat treatment and x-ray phase analysis, the following main phases were identified in the specimens: $MgAl_2O_4$ in magnesium aluminate and $MgCr_2O_4$ in magnesium chromite.

Thermodynamic analysis of $MgCr_2O_4$ revealed two endothermic effects on its DTA curve. The first such effect (at 110°C) is related to the loss of 4 wt.% of the adsorbed water, while the second effect (at 420°C) may be due to the decomposition of $Mg(OH)_2$ into MgO and H_2O. A thorough thermal analysis showed that, in addition to $MgCr_2O_4$, the samples of magnesium chromite contain $Mg(OH)_2$ and magnesium aluminate; the content of $Mg(OH)_2$ is very small. The hydro-spinel $MgAl_2O_4 \cdot nH_2O$ has a value of n equal to 3. The occurrence of endothermic effects due to dehydration and the fact that the exothermic effects usually associated with the solid-phase synthesis of compounds do not occur shows that the synthesis process is almost complete. However, the end products of chemical synthesis (especially $MgAl_2O_4$) are insufficiently calcined.

The completed studies made it possible to determine the phase composition of the initial magnesium aluminate and magnesium chromite. However, in order to be able to find efficient regimes for refractories production, it is also necessary to determine the calcination temperature that is needed for the material to acquire a crystalline structure while preserving a certain level of activity for sintering. To do this, we followed the thermal analysis with an x-ray phase analysis. The phase analysis revealed the presence of $MgAl_2O_4$ and MgO in the magnesium aluminate specimen and $MgCr_2O_4$ and MgO in the magnesium chromite specimen. Thus, the processes of synthesis and crystallization are completed after heating to 1500°C. In order to be able to more accurately describe the structural features of the powders and determine the temperature at which a crystalline lattice is formed, a high-temperature x-ray phase analysis was performed on diffractometer URS-50 IM with heating of the specimens at a rate of 5°C/min.

The use of an extension piece to conduct the high-temperature x-ray phase analysis made it possible to track the change in the phase composition of the specimen from room temperature to 1500°C. The diffractogram of the magnesium aluminate specimen does not contain any of the lines characteristic of crystalline phases. Diffuse lines of $MgAl_2O_4$ and MgO appear on the diffractogram when the specimen is heated to 500 – 600°C. The appearance of the diffractogram changes sharply when the specimen is heated to temperatures within the range from 900 to 1200°C. The lines become distinct and increase in intensity, and a 1500°C the diffractogram clearly shows the presence of two phases: $MgAl_2O_4$ and MgO, both of which are present in small amounts. Thus, the completed studies have made it possible to determine that the transition of magnesium aluminate from the roentgenographically amorphous state to crystalline forms occurs within the range 900 – 1200°C.

Magnesium chromite was not subjected to high-temperature x-ray phase analysis because the temperature at which the same transition takes place can easily be determined from data obtained by high-temperature thermal analysis. That temperature is within the range 500 – 600°C.

To ascertain that solid solutions are formed in the systems $MgAl_2O_4$–MgO and $MgCr_2O_4$–MgO and to determine the temperature thresholds at which this takes place, studies were performed in the high-temperature (20 – 2000°C) region in a medium of argon. No abrupt thermal effects are seen during the heating of specimens of $MgAl_2O_4$ and $MgCr_2O_4$ that were previously calcined at 700°C. However, a smooth exothermic effect is seen in the range 970 – 1700°C for $MgAl_2O_4$ and in the range 1270 – 1735°C for $MgCr_2O_4$. To determine the phase composition of the powders, an x-ray phase analysis was performed after high-temperature (2000°C) thermography. The diffractogram of $MgAl_2O_4$ shows the presence of an $MgAl_2O_4$–MgO solid solution based on the lattice of $MgAl_2O_4$, while the diffractogram of $MgCr_2O_4$ shows the presence of an $MgCr_2O_4$–MgO solid solution based on the lattice of $MgCr_2O_4$.

Thus, a group of accurate instrument-based methods has been used to study synthesized magnesium aluminate and magnesium chromite and has established that these compounds are roentgenographically amorphous powders whose crystallochemical features cannot be determined by x-ray structural or x-ray phase analysis. High-temperature thermographic analysis of the initial powders revealed the presence of hydroxides: $Mg(OH)_2$ in magnesium chromite, $Mg(OH)_2$ in magnesium aluminate, and $MgAl_2O \cdot 3H_2O$ in hydro-spinel. Phase transformations involving the formation of solid solutions $MgAl_2O_4$–MgO and $MgCr_2O_4$–MgO were observed in the initial materials within the range 20 – 2000°C. Here, the degree of perfection of the crystalline structure began to improve beginning at 900 – 1000°C in $MgAl_2O_4$ and at 500 – 600°C in $MgCr_2O_4$. The phase transformations just alluded to are irreversible. The completed studies make it possible to determine the heat-treatment regime for the initial powders that is optimum from the standpoint of preserving a certain level of activity for sintering during the formation of the crystalline structure. The thermodynamic and kinetic parameters reported here for combustion processes in the system Al–$MgSO_4$ show that this system is a promising starting point for the creation of new refractory materials by SHS technology.

Experiments were conducted using analytically pure aluminum of grade PA-4. This aluminum has the following characteristics: particle size 80 – 120 μm; content of the main component no lower than 98%; moisture content no higher than 0.5%; analytically pure barium sulfate no coarser than 100 μm. This system is close to the aluminum-magnesium-sulfate system studied earlier in terms of its properties. The main difference is that the melting point of $BaSO_4$, which is 1680°C, is 500°C higher than the melting point of $MgSO_4$. In connection with this, depending on the temperature in the molten state, only aluminum may be participating in the combustion process and the reaction may take place in the diffusion regime. The following reactions can occur when aluminum interacts with barium sulfate:

$$4Al + 2BaSO_4 \rightarrow 2BaO \cdot 2Al_2O_3 + 3S, \qquad (18)$$

$$\Delta H = -603{,}3 \text{ kJ/mole};$$

$$6Al + 3BaSO_4 \rightarrow 3BaO \cdot 3Al_2O_3 + 3S_2, \qquad (19)$$

$$\Delta H = -415{,}6 \text{ kJ/mole};$$

$$8Al + 3BaSO_4 + 3H_2O \rightarrow 3BaO \cdot 4Al_2O_3 + 3H_2S, \quad (20)$$

$$\Delta H = -332{,}5 \text{ kJ/mole}.$$

Reaction (18) is the reaction that is most likely to occur.

Table 3 shows results from calculations of the adiabatic combustion temperatures T_c and the yield of barium oxide

TABLE 3. Adiabatic Combustion Temperature and Barium Oxide Yield for the Al–$BaSO_4$ System with Different Proportions of the Initial Components

Proportions of the initial components Al:$BaSO_4$	T_g, °C	η_{BaO}, %
0.40:0.60	1600	50.0
0.50:0.50	1650	57.2
0.60:0.40	1680	60.8
0.70:0.30	1700	98.4
0.80:0.20	1550	100.0

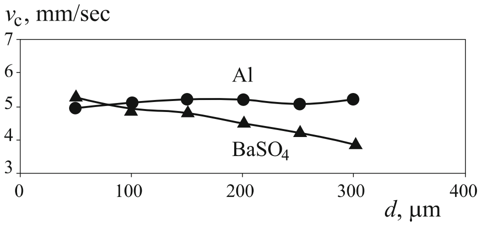

Fig. 3. Dependence of combustion rate v_c on average particle size d in the system Al–BaSO$_4$.

η_{BaO} in relation to the proportioning of the initial components. The calculations showed that the reaction nearly proceeds to completion under the given conditions when the aluminum content of the charge ≥70%. The maximum combustion temperature is 1700°C, which is 200°C higher than for the system Al–MgSO$_4$. As is known, the existence of values of T_c within the range 1500 – 2500°C does not unambiguously prove that synthesis can take place in the combustion regime. The occurrence of self-propagating high-temperature processes will depend on the specific thermophysical conditions under which the experiment is conducted. An experimental study of the combustion parameters as a function of the molar ratio of the initial components showed that the maximum of T_g is 200°C lower than the calculated value. Thus, in the given case $T_g < T_{\text{ml BaSO}}$. A heterogeneous reaction takes place in the system, the rate of this reaction being determined by the rate of diffusion of liquid aluminum to the surface of solid particles of barium sulfate. Further proof of this is the nature of the dependence of combustion rate on the dispersity of Al and BaSO$_4$. The rate of the reaction is nearly independent of the size of the aluminum particles (Fig. 3).

An increase in the size of the BaSO$_4$ particles from 100 to 300 μm decreases the rate of combustion from 5.2 to 3.8 mm/sec, which is probably an indication that within the combustion front the components interact as a result of dissolution in liquid aluminum. The activation energy of the overall reaction between aluminum and barium sulfate was found graphically and is 96 kJ/mole, which is appreciably lower than the activation energy for the system Al–MgSO$_4$. This is obviously related to the diffusional nature of the process by which aluminum and barium sulfate interact with one another. Their reaction results in the formation of two oxides with high melting points ($T_{\text{ml Al}_2\text{O}_3} = 2050$°C, $T_{\text{ml BaO}} = 2020$°C), which can serve as a foundation for the creation of new refractory products [5].

The results obtained here have made it possible to optimize the processes used to produce refractory materials, optimize their physicomechanical characteristics, determine the main laws that govern their production, and establish the main elements of the scientific-technological approach that should be used to make refractory products with the specified properties. The completion of full-scale commercial trials and the introduction of refractories made by the given technology (for use as lining solutions, coatings, gunites, and ramming mixes) at metallurgical plants has made it possible to increase the service life of linings by increasing their mechanical strength (the bricks are now welded into monoliths), their refractoriness, and their resistance to slag, metal, and heat.

Use of the new refractories at factories in the Republic of Kazakhstan has significantly increased the service life of the linings of metallurgical equipment that operates at high temperatures, and this improved durability has been accompanied by a substantial monetary savings as well.

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