Refractory and heat-insulating materials based on aluminosilicate SHS compositions

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Abstract. The phase composition, structure, and physical and mechanical characteristics of refractory aluminosilicate SHS materials (AS materials) were investigated taking into account the properties of initial components and the production method. Computational methods were used to reveal macrokinetics of processes and determine the possible formation of mullite structures and corundum in aluminosilicate refractory SHS materials during the synthesis reactions. Heat losses caused by the small thickness of a coating or the walls of the material between pores were found to have a significant effect on the synthesis reaction in thin coatings and porous AS materials, as well as the on the formation of various chemical compounds.

1. Introduction

In industrial processes the refractory lining of thermal generating units is often exposed not only to high temperatures, but also to abrasive wear or corrosive media. The combined effect of destructive factors on refractory lining leads to fast damage to the material of refractory lining and requires significant repair costs.

A review of research and developments of new refractory materials and products used in modern heat generating units for metallurgy and engineering demonstrates a worldwide increasing interest to unmolded refractories and their mechanical characteristics and high temperature resistance. Refractory and heat-insulating materials are more often required due to the ability to operate for a long period of time at extremely high temperatures (up to 1700ºC and above), as well as due to high wear resistance and resistance to corrosive media and flue gases.

Aluminosilicate materials are of the greatest interest caused by chemical and mineral composition, since their proportion in the refractory linings of heat generating units exceeds 80% of all types of refractories used, in particular, in the engineering industry.

Among the modern methods for producing and using unmolded refractory materials, self-propagating high-temperature synthesis (SHS) is one of the most attractive methods, since it can significantly reduce the energy consumption in the production of refractory products. In most cases, the refractory lining acquires final refractory and operational properties in the first hours of operation of heat generating units that uses SHS refractories.

SHS can be used to obtain various high-purity and lightweight refractories. SHS allows materials to be obtained with high physical and mechanical characteristics, such as strength, wear resistance, corrosion resistance, as well as high stability of properties, shapes and sizes when exposed to high temperatures. In recent years, various refractory AS materials on various bases have been developed.

In 2000 a Malaysian-American team of scientists conducted much experimental and theoretical work to obtain magnesium-aluminum refractory spinel MgAl$_2$O$_4$ [5]. The researchers used the SHS
method for obtaining magnesium aluminate powder with very high phase purity. Low-temperature melting of aluminum followed by an exothermic reaction between molten aluminum and magnesium oxide allowed a powder to be obtained with a very high proportion of spinel phase, small particle size and narrow particle size distribution. Compacts with a density of up to 92% were obtained from this powder during sintering for 4 h at 1600°C. The addition of a small amount of aluminum oxide was found to have a favorable effect on the sintering characteristics and density of the material.

Studies concerning the use of mineral and secondary raw materials for the production of AS refractories were conducted by the Kazakh Interbranch Scientific and Technical SHS Center. Alumothermite refractories “Furnon” and “Thermok” [1] were developed. The Combustion Problems Institute (Kazakhstan) also investigated the systems TiB₂–Al₂O₃, CrB₂–Al₂O₃ and ZrB₂–Al₂O₃ which were subjected to SHS with preliminary mechanical activation. The products of exothermic interaction under constant pressure in an argon atmosphere were found to be refractory compounds of metal borides and corundum which formed a dispersed phase and a ceramic binder in a ceramic composite material [4].

In the early 2000s, much work has been done at Samara State University of Architecture and Civil Engineering to study the conditions for the production of refractory composite materials from AS refractories using various industrial wastes in AS mixtures [2]. The dispersed materials, such as a spent aluminoborate AM 2201 catalyst, fireclay dust, and dusty metal processing waste can be used as ballast in AS mixtures for the production of aluminothermic composite materials. A production process was also developed to obtain products from aluminothermic composite materials.

The possible obtaining heat-resistant coatings on fireclay refractories by the method of self-propagating high-temperature synthesis in the MgO–SiO₂–Al system using liquid sodium glass as a binder with the addition of sodium tripolyphosphate and titanium dioxide activating the SHS process was studied at the Physical-Technical Institute of the National Academy of Sciences of Belarus [3]. The optimal composition was determined, and the physical and mechanical properties, macro- and microstructure of the coatings were investigated.

A large number of refractory AS materials was developed at the Scientific and Production Commercial Company “MaVR”, Zhukovsky [6, 7]. Synthesis of ceramic structures (corundum, sillimanite, mullite, etc.) in most of these materials is conducted after heating up to a temperature of 850–900°C and initiating self-propagating high-temperature synthesis. The synthesized ceramics is a mullite structure with the formula mAl₂O₃ nSiO₂.

Despite a significant number of studies, the practical application of such materials is limited due to insufficient studying the processes that take place in the materials during the SHS process, which does not allow their physical and mechanical and operational properties to be predicted with sufficient accuracy.

The purpose of this work is to find the phase composition, structure and physical and mechanical characteristics of refractory aluminosilicate SHS materials, taking into account the properties of initial components and the production method, as well as to improve the production process and use of AS materials and products from them to protect the heat generating units against high temperatures.

2. Materials and Methods

In the work the parameters were calculated and the composition of final products was determined for all AS materials studied. The computation of the combustion parameters for the AS material (M-1 grade) and the composition of the products obtained, depending on the initial temperature for the initiation of the synthesis reaction, is given as an example.

The computation was performed in the «Combustion Regime \( P = \text{Const} \)» mode. Table 1 provides the input data for the mass ratio of the initial components in the mixture (M-1 grade). The computation temperature varied from 800 to 1500°C with a step of 100°C. When the initiation temperature exceeds the melting point of metallic aluminum \( T_m = 660°C \) means that aluminum starts reacting in the molten state. The formation of the melt indicates the occurrence of synthesis reactions on the surface of solid SiO₂ particles with the melt in the mode of capillary spreading.
The experimental procedure involved the annealing of samples in the step heating mode in a laboratory electric chamber furnace, followed by an investigation of phase composition, microstructure, and material properties. The maximum annealing temperature of samples varied from 900 to 1600°C with a step of 100°C [8].

### Table 1. Chemical composition of the AS material (M-1 grade) during the reaction

| Mass, g | Amount of substance in the composition, mol | aggregative state |
|---------|------------------------------------------|-------------------|
| Al      | 135                                      | 5.0000            | Liquid            |
| Al₂O₃   | 6                                        | 0.0590            | Solid             |
| SiO₂    | 989                                      | 16.5000           | Solid             |
| Fe₂O₃   | 0.7                                      | 0.0044            | Solid             |
| N₂      | 77.8                                     | 2.7990            | Gas               |
| Mixture | 1200                                     | 24.3534           | -                 |

### 3. Results and Discussion

The calculated adiabatic temperature of combustion of the AS material is 1727°C. The enthalpy of products ranges from minus 13,000 kJ to minus 14,000 kJ. All computations of the thermodynamic parameters for the synthesis process, as well as the composition of the final products obtained from the mixture (M-1 grade), depending on the initiation temperature, are given in table 2.

### Table 2. Thermodynamic synthesis parameters and the composition of the final reaction products in the AS material (M-1 grade), and computations performed using the code ISMAN-THERMO

| Initiation temperature, °C | 800  | 900  | 1000 | 1100 | 1200 | 1300 | 1400 | 1500 |
|----------------------------|------|------|------|------|------|------|------|------|
| Gas pressure, atm          | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    |
| Volume of gaseous products, liter | 355  | 394  | 434  | 474  | 513  | 554  | 595  | 637  |
| Adiabatic temperature, °C  | 1727 | 1727 | 1727 | 1727 | 1727 | 1727 | 1727 | 1727 |
| Moles of the gas phase     | 2.094| 2.326| 2.558| 2.793| 3.028| 3.267| 3.508| 3.758|
| Heat capacity (Cp) of products in the mixture, J/K | 1739 | 1720 | 1700 | 1680 | 1660 | 1639 | 1619 | 1598 |
| Entropy of products, J/K   | 4144 | 4147 | 4148 | 4151 | 4153 | 4156 | 4158 | 4161 |
| Enthalpy of products, kJ   | −13980| −13839| −13697| −13554| −13410| −13265| −13118| −12967|
| Jump in enthalpy, kJ       | 2413 | 2412 | 2411 | 2412 | 2410 | 2411 | 2410 | 2412 |
| Mass of the system, kg     | 1.2  | 1.2  | 1.2  | 1.2  | 1.2  | 1.2  | 1.2  | 1.2  |
| Mass of the product Al₂SiO₃, kg | 0.3165| 0.2768| 0.2369| 0.1977| 0.1572| 0.1173| 0.0757| 0.0342|
| Mass of the product Al₂Si₃O₁₁, kg | 0.1584| 0.1762| 0.1941| 0.2116| 0.2297| 0.2476| 0.2662| 0.2847|
| Mass of the product SiO₂, kg | 0.2741| 0.3049| 0.3358| 0.3661| 0.3975| 0.4284| 0.4607| 0.4927|
| Mass of the product Al₂O₃, kg | -    | -    | -    | -    | -    | -    | -    | -    |
| Mass of the product Si, kg  | 0.1174| 0.1119| 0.1063| 0.1008| 0.0951| 0.0895| 0.0837| 0.0778|

Experimental annealed samples were analyzed using X-ray diffraction by DRON-3M diffractometer that showed that after heating to 900°C, the structure consisted of Al₂O₃, SiO₂ and Si, which is related to the nonadiabaticity of synthesis in thin coatings due to the significant heat removal to the environment and the fireclay base material. In this regard, the elements obtained in the coating at 900°C interacted during the annealing of the samples in the temperature range from 1300 to 1600°C and formed the mullite structure (sillimanite) with the chemical formula Al₂SiO₅.
This fact is confirmed by studies of the microstructure of the coating using a scanning electron microscope. The photograph of the microstructure of the coating, which is presented in figure 1a (heat treatment at 1100°C), clearly shows corundum in the form of spherical boulders, while figure 1b (heat treatment at 1600°C) shows a monolithic mullite structure.

![Figure 1. Microstructure of the AS material (M-1) after heating at: (a) 1100°C and (b) 1500°C](image)

Experimental studies of AS materials (VBF grade) in the form of bulk cellular samples showed that a synthesis process was initiated in the material after heating to 1100°C, and as a result, such compounds as Al₂O₃, SiO₂ (christabolite) and SiO₂ (quartz) became the main components in the structure of materials (VBF grade). Mullite structures (as well as in thin coatings) were not formed due to the high porosity of porous materials, the small thickness of the walls between pores, and significant heat losses.

![Figure 2. Structure of porous AS material (VBF grade) after annealing at the temperature of 1100°C](image)

Thus, the following conclusions can be drawn from this study:

- macrokinetics of processes was established and the formation of mullite structures and corundum in aluminosilicate refractory SHS materials subjected to heating to different temperatures was determined during the synthesis reaction using computational methods and the specialized code ISMAN-THERMO.
- composition of compounds obtained in the material was experimentally studied to develop the application technique and evaluate structural changes in various modes of operation of refractory products based on AS materials. The computations were in good agreement with experimental data.
- heat losses caused by the small thickness of a coating or material walls between pores have a significant effect on the development of the synthesis reaction in thin coatings and porous AS materials, as well as the on the formation of various chemical compounds.

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