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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Regularities Governing the Two-Stage Synthesis of Cast Cr_2O_3/Al_2O_3 under Conditions of the Autowave Synthesis

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Abstract—The study of the chemical, roentgen phase and structural properties of the products of combustion of system Cr_2O_3–Al–Fe_2O_3 was carried out. The analysis of the results shows the presence in the system of a set of solid solutions. The results of the study make it possible to establish the optimum regime of the heat treatment of the studied system for creating the new refractory material according to self-propagating high-temperature synthesis (SHS).

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The contemporary concept of the development of fireproof industry consists in a use of the production of the resource saving fireproof materials of new generation which are characterized by the increased environmental safety and wear resistance. At present the intensification of technological processes and the innovation ways of the development of the acting branches of the metallurgical, chemical, petroleum refining industry, power engineering and other fields impose ever more stringent requirements to the fireproof articles utilized for the brick lining of high-temperature aggregates (fire-bricks, printed masses, masonry mortar, etc). The application to these purposes of a method of the self-propagating high-temperature synthesis characterized by high temperatures and speeds of chemical transformations (autowave synthesis) makes it possible to synthesize the materials of the specific phase composition and structure that govern chemical and mechanical properties [1, 2].

The chromium oxide Cr_2O_3 is a very promising effective fireproof compound for the production of different special fireproof material. The wide application of the chromium oxide fireproof materials in the metallurgical furnaces is limited by their high cost and complexity of the technology of their synthesis. In view of this the chromium oxide fireproof materials are used in the limited amounts [1–3].

In this paper we presented the results of studies of the fireproof materials synthesized by SHS from the charge which consists of chromite ore and aluminum with a change in the weight fraction (%) of the chromium(III) oxide and aluminum content from 15 to 24%. For the synthesis we used Al of a grade ASD-1 of 99.8% purity. Chrome ore (a concentrate of the Kempirsaysk deposit) according to the chemical analysis data had the following composition: Cr_2O_3 51.3%, Al_2O_3 8.3%, MgO 15.0%, FeO 17.8%, Fe_2O_3 2.0%, SiO_2 4.2%, CaO 0.14%, S 0.1%. Also in the experiments the powders of oxides (Al_2O_3, Cr_2O_3, Fe_2O_3) were used as the initial reagents.

Combustion in such systems has two principally different stages: reduction of elements from the oxides and futher interaction of the elements with each other and with the additives. The finely dispersed dry mixtures Cr_2O_3 + Al + Fe_2O_3 + MgO, SiO_2 + Al, and others can serve as the typical examples of such systems. However, use along with SHS of energy of the redox reactions between aluminum and iron(III) oxide assumes the presence in the products of the synthesis of the inclusions of metallic iron which reduce the acid resistance of the material. The presence of vitreous phase decreases its mechanical properties.

The basis of the concentrate comprises chromite (Fe, MgO)O·(Cr, Al, Fe)$_2O_3$ [3] according to the results of RFA

having parameter of crystal lattice $a = 8.312 \pm 0.005$ Å. Also small amount of serpentine was found in this concentrate. We studied the influence of the conditions for the preparation of samples and for conducting synthesis, of the heating and cooling rates on the phase composition, the structure and the properties of the end product of the reaction.

Conditions for preparation of the charge: the samples of the studied composition (85% of chrome ore, 15% of aluminum) were made in the form of pressed tablets of a diameter 20 mm and a height 20 mm from the dry mixture also with the addition 8% water. A part of the samples was dried for 3 hours, and other part, for 20 hours in air. After drying and mixing the finished charge was loaded into the refractory reaction forms and was placed into the reactor and synthesis under the pressure of gas (nitrogen, argon) 4.0–8.0 MPa was conducted.

The chemical analysis, RFA, local X-ray spectral and metallographic methods were used for investigating the products of synthesis in the course of the synthesis. In the experiments we determined: the average linear rate of combustion, the fullness of the output of oxide and metallic phases, the depth of the spread of product in the course of combustion. The dynamics of a change in the temperature with the heating and in the process of combustion were determined on the setup that consisted of a chamotte body, silicon-carbide heating elements, system of the registration of combustion which included two tungsten thermocouples VR-5/20 and loop oscillograph NO71-6M. Petrographical studies of samples were performed with the aid of the microscope MW -71V4.2 with 50- and a 500- multiple increase. RFA was carried out on the diffractometer DRON-3M, CoK_α radiation. The compressive strength of the samples was determined on the hydraulic press PSU-10.

The analysis of the results evidences the presence in the system of the set of solid solutions, the content of Cr_2O_3 in some of them changes from 0 to 17%. The visual inspection of the combustion products showed that with the low values of the weight part of the chromium oxide the combustion products took the form of two clearly divided cast layers (upper was oxide, lower, metallic). The presence of the solid solutions became possible because of the oxidation of aluminum with the formation of Al_2O_3. Certain formed surplus of Al_2O_3 contributes to the dissolution of Cr_2O_3, and its different content in the solution is determined by the gradient of crystallization temperature after the combustion reaction.

The analogous phase composition of the products of the aluminothermic reaction of the reduction of metallic chromium from the chromium concentrate is given in the work [4] and testifies about the dissolution into Al_2O_3 to 3.9% of Cr_2O_3. This material is classified as ruby and is characterized by high hardness [5]. As experiments showed reaching 100%-fullness of the chemical reactions under the given conditions is not possible. Depending on the efficiency of the phase separation the products are the cermet, in which metallic component is distributed in the form of particles in an oxide matrix, or a gradient material (divided) in which the part of the metallic phase is devided into the layers, and other part is distributed in the oxide matrix.

With an increase in the weight part (b) of Cr_2O_3 in the initial mixture (to 35–40%) the rate of combustion and the fullness of dispersion decrease and the limit of combustion is attained. Upon approaching to the limit the combustion of the mixtures becomes nonstationary, the front of the combustion is bent. With the large b the product takes the form of the cake in which oxide and metallic phases are mixed between themselves. With the growth b the weight of the oxide layer increases. At the analysis of the products the primary attention was paid to the region b in which occurs the clear separation of oxide and metallic phases.

On the basis of the data of chemical and metallographic analyses and of RFA of the synthesized products it was established that at the presence of Cr_2O_3 in the composition of the starting material the oxide layer contains 2 phases: (1) $Al_2O_3/Cr_2O_3/Fe_2O_3$ spinel and (2) Al_2O_3/Cr_2O_3 solid solution.

The chemical analysis of metallic and oxide phases showed that in the mixtures $(Fe_2O_3+2Al) + bCr_2O_3$ with scarce Al at the combustion occur competing chemical transformations. The first appears as a result of the reaction of aluminum with iron(III) oxide

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3.$$

This process increases the temperature in the combustion zone to 1200°C initiating further oxidation of aluminum in the reactions with the chromium oxides and partially silicon oxide resulting in a temperature growth to 2000°C.

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

$$3SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3$$

The high temperature developed in the combustion zone contributes to the separation of metallic and slag fractions. Chromium drops into the lower layers of the sample while in the slag part near the metal is located corundum, and already behind it follow solid solutions with the maximum concentration of Cr_2O_3 in the outer surface layer. This is completely confirmed by the results of RFA of different sections of the sample.

At a decrease in amount of aluminum in the charge to 24%, the pure corundum is absent in the phase composition of the reaction product but two solid solutions on the basis of Al_2O_3 are fixed even more clearly. According to the dependence of a change in the lattice parameters of solid solutions on the concentration of the components obtained for the hardened samples [6, 7] the concentrations of the above-mentioned solid solutions of Cr_2O_3 are 30 and 15%, respectively. The X-ray reflections in this case overlap; moreover the first of them is widened that indicates larger dispersiveness and nonequilibrium of this phase.

At a decrease in the content of aluminum in the charge to 21% in the course of the synthesis already not two but one solid solution which contain about 57% of Cr_2O_3 is formed, and metallic chromium is separated. In the samples with 18 and 15% of aluminum after the synthesis also two solid solutions are detected, but now on the basis of Cr_2O_3. The content of Cr_2O_3 in these solid solutions comprises respectively 53 and 66%, and 55 and 73%.

This regularity in the change in the phase composition with a decrease in amount of the reacting aluminum is reasonable if we evaluate the state of material at high temperatures by the diagrams of states $Cr–Cr_2O_3$ and $Al_2O_3–Cr_2O_3$ [6],as we have done earlier. Formation of two solid solutions with the large difference in the lattice parameters can be caused by the presence of stratification in the system $Cr–Cr_2O_3$ and dissolution in these two phases of different amounts of Al_2O_3. At the content in the charge of 18% aluminum the temperature of the warming-up of the sample as a result of the combustion will be higher than at 15%, and the state of the material will correspond to the upper peak of stratification. Only one solid solution in the sample can be synthesized when the composition of the charge is such that in the process of the synthesis of the material, it, according to the diagram, corresponds to the area of eutectic from the side of chromium, and its crystallization occurs at one temperature, i.e., in the absence the gradient of temperatures and concentrations.

Thus, RFA analysis of the materials synthesized on the basis of the aluminothermic reaction of Cr_2O_3 with aluminum at different content in the charge of the latter showed that in the product, besides the metallic chromium are formed the solid solutions of Cr_2O_3 and Al_2O_3 of different concentrations and consequently, with different melting points varied within the limits of the melting points of Cr_2O_3 and Al_2O_3 [6]. As it is known [5] the hardness of the composing components of these solid solutions are equal to 8.5 and 9.0 units, respectively, according to Mohs scale. An increase in the hardness number is possible with the formation of the solid solutions [7]. The obtained results on the hardness of the studied materials agree with literature data [8].

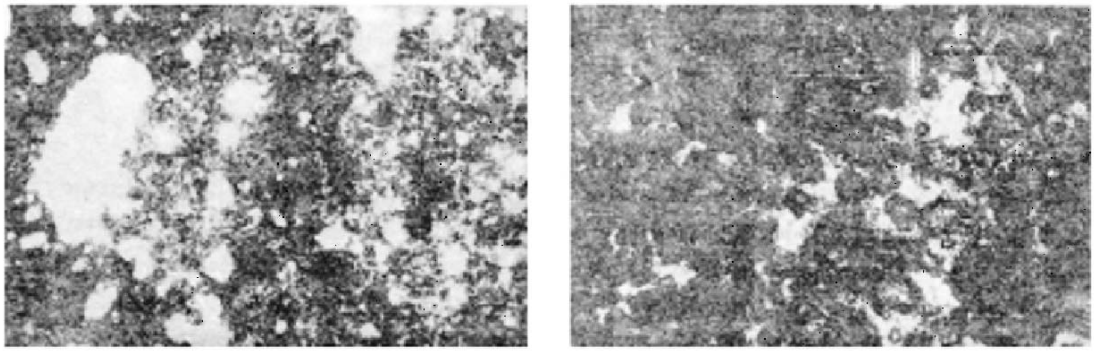
In this stage of the studies of aluminum the composition with 15% of aluminum which is a basis for preparing refractory material utilized in practice is of the greatest interest. Some of its properties were studied. It is known [6] that the density of the solid solutions of $Cr_2O_3–Al_2O_3$ determined according to X-ray and a bottle method data varies from 4.00 g cm^{-3} for Al_2O_3 to 5.25 g cm^{-3} for Cr_2O_3.

A density value of the studied composition get by the bottle method equals to 4.75 g cm^{-3}, and for the initial charge, 4.05 g cm^{-3}. Thus, we synthesized a material whose density grows by 17.5% in comparison with the initial material. Compaction of the material as a result of the synthesis leads to the appearance of a large amount of the pores which merge inside the sample to form significant cavities. We carried out an evaluation of their apparent porosity and density, water absorption and of bulk density. The results of measurement for five samples are presented in the table.

The scattering of the indices given in the table taking into account identical conditions of the synthesis

Experimental data on the samples with 15% content of aluminum

Sample number	Apparent density, %	Apparent density, g cm^{-3}	Water absorption, %	Bulk density
1	34.3	4.5	11.6	2.95
2	28.8	4.9	8.3	3.47
3	11.3	3.0	4.2	2.68
4	39.4	4.3	14.9	2.64
5	2.3	4.0	0.6	3.88



(a) (b)

Microstructure of the (a) upper and (b) top sections of the samples resulted in the charge combustion with 15% content of aluminum under the different conditions of the heat removal.

is explained by a form of the samples rather then by a difference in the characteristics of the product. The material of the samples is sufficiently dense (the bulk density reaches 3.88), poorly porous (the apparent porosity can be about 2.3%), and weakly absorbs water (~0.6%). At the same time the apparent porosity can be 40% which indicates the presence inside the samples of extensive cavity that is connected with the environment by means of thin cracks or small t number of capillary channels. Such samples have higher apparent porosity, and higher water absorption. If the internal cavity is completely closed the apparent porosity can be small thereby the apparent density and the water absorption, for example, for the sample no. 3, decrease. The significant porosity (discontinuity) of the samples in spite of the high hardness of material leads to the low strength indices (σ-compression about 6 MPa).

Thus, the material synthesized in the course of the combustion of the charge with 15% content of aluminum whose a phase composition is characterized by the presence of two solid solutions with the high content of Cr_2O_3, has the high density (4.75 g cm^{-3}) but in the samples in this case the significant porosity is formed.

It is necessary to note that the combustion temperature is effected by an influence of the heat losses caused by the specific conditions of heat withdrawal, and exerts an essential effect on the properties of the studied samples. The experiments with the cylindrical sample prepared from the charge with 15% content of aluminum placed into a furnace and heated to 1000°C in such a way that the heat withdrawal of an upper and lower surfaces essentially differs causing the gradient of temperature, leading to the same results.

Petrographic analysis and RFA showed a difference in the micro-compositions on the external end surface and the internal part of the samples. In the area of lower temperature the chromium isolations are more dispersed, and the solid solutions form the light and dark sections of different hardness. Thus, from the charge of one composition it is possible to form different materials changing only the reaction temperature. The phase composition in this case can be forecasted according to the diagram of state. The dark sections are crumbled in the course of the surface grinding (see the figure).

CONCLUSIONS

According to RFA data the parameters of these solid solutions are: $a = 4.841 \pm 0.005$ E, $c = 13.390 \pm 0.005$E; $c = 13.807 \pm 0.005$ E, i.e., somewhat greater than at a higher temperature of the synthesis. Thus, on the basis of the results of the conducted investigation it is possible to make the following conclusions:

(1) It is shown a possibility of using the SHS method for producing the refractory material from the charge which consisting of chrome ore and aluminum at a change in the content of the aluminum from 15% to the stoichiometric one with intermediate values 18, 21, and 24 wt %.

(2) It is shown that the studied mixtures have a wide range of combustion, melting and phase separation. The chemical composition of oxide solid solutions can be changed over wide ranges varying the ratio of reagents in the initial mixture, the temperature of initial mixture, and the gas pressure.

(3) The chemical analysis of the metallic and oxide phases shows that in the mixtures poor in Al proceed competing chemical transformations: reduction of iron oxides and of chromium by aluminum.

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