NEW TECHNOLOGY FOR REFRACTORY MATERIAL PREPARATION

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Translated from *Novye Ogneupory*, No. 3, pp. 119 – 122, March, 2014.

Original article submitted February 12, 2013.

Use of cheap local raw material resources (barite and witherite concentrates of the Karagailinsk deposit, Arkalyk clay, chromite-magnesite scrap objects, copper production dump slag, chromite ore, etc.) makes it possible to create new import-substitution refractory materials. Non-traditional technology is created for obtaining moldable import-substitution refractory materials from cheap local raw material resources based on occurrence of self-propagating high-temperature synthesis (SHS). A number of new compositions are proposed for self-sintering refractory mixes, whose objects have good technical and economic indices.

Keywords: local mineral raw material, self-propagating high-temperature synthesis (SHS), SHS-technology, self-sintering refractory mix.

Over the extent of all human history creation of new materials and various objects and structures based upon them has always determined a breakthrough in different fields of science and technology, and as a rule comprised a whole era in the world of technology. The scientific base, created by work of Soviet scientists of the Academy of Sciences in the period 1970 – 1980 made it possible to discover new phenomena in the field of condensed system combustion physics.

The era of self-propagating high-temperature synthesis (SHS) started from the instant of discovery by professor A. G. Merzhanov of a new class of heterogeneous combustion processes in a condensed phase, proceeding at a phase boundary, and what is particularly important, without participation of gaseous oxygen [1, 2].

Self-propagating high-temperature synthesis is a promising resource saving and highly productive method for preparing refractory inorganic compounds, hard alloys, and refractory materials. It is used in order to prepare refractory inorganic ingots, objects, and coatings, using as raw material mixtures of metal oxides with metal reducing agents and non-metals. A wide range of cast carbides and other hard alloys based on them, a number of borides, and also some silicides and intermetallics have been prepared by this method. Materials have been obtained mainly from chemically pure reagents, whose use increases the cost of synthesized materials. In view of this it is necessary to carry out research aimed at using available raw material.

Intensification of production processes and innovative ways of developing different branches of industry impose even more stringent requirements for refractory objects used for lining high-temperature units. On the basis of results of previous studies, concerning development of scientific and theoretical bases of refractory material controlled synthesis and establishment of physicochemical phase equilibria, a number of new compositions have been proposed for self-sintering refractory mixes, whose objects have good technical and economic indices. Non-traditional technology has been created for preparing moldable refractories, based on occurrence of a process in a SHS regime [3 – 6].

On the whole creation of technology for preparing refractory materials from local mineral raw material by SH-technology is a contribution of science to solving the task of adding currency resources to the country as a result of import substitution of high-tech products. Use of cheap local raw material resources (barite and witherite concentrates of the Karagailinsk deposit, Arkalyk clay, chromite-magnesite object scrap, copper production dump slag, chromite ore, etc.), makes it possible to create new import-substitution refractory materials, whose testing under laboratory and semi-industrial conditions points to an increase in service life of Waelz kiln linings on average by 60%. An advantage of the compositions developed is use of production waste, for example copper production dump slag not of ecological value and cheap local natural raw material, which markedly

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cheapen preparation of refractory objects with good operating properties.

Composition No. 1. Self-sintering refractory mix No. 1 for objects includes chamotte, barite concentrate, aluminum, copper production dump slag, and water as a binder (Table 1). The self-sintering reaction occurs with interaction of barite concentrate oxidizing agent with a reducing agent, i.e., aluminum:

$$2BaSO_4 + 4Al \rightarrow 2BaO{\cdot}Al_2O_3 + S_2. \qquad (1)$$

The self-sintering of exothermic mix occurs with considerable heat release, reaction products are obtained in a molten condition, and therefore copper production dump slag and chamotte are added to the mix in the form of filler. The self-sintering temperature for the exothermic mix varies within the range 850 – 1850°C.

As results of x-ray structural and phases analyses show, the aluminum oxide content in refractory objects from this mix increases by more than a factor of two compared with its original content in the mix. Consequently, refractoriness of these objects increases. In particular, their ultimate strength in compression at 500°C was 45 – 75 MPa, and at 1100°C it was 40 – 70 MPa. It is important to note that use in the refractory mix proposed of copper production dump slag, not of economic value, and cheap Kazakhstan natural raw material in the form of barite concentrate cheapens the process for refractory object preparation. Barite concentrate from the Karagailinsk deposit was used of the following composition, wt.%: $BaSO_4$ 80, SiO_2 7.5, Pb 0.15, Zn 0.1, concentrate fineness less than 20 μm.

Composition No. *2*. Self-sintering mix composition No. 2 includes aluminum, chromite-magnesite object scrap finer than 15 mm, chromite ore, barite concentrate, and water as a binder (Table 2). Introduction of barite concentrate combined with chromite-magnesite object scrap finer than 15 mm within the composition of the self-sintering mix, and presence within it of chromite ore and water in the form of a binder reduces refractory object open porosity.

The water content in refractory mix is less than 4 wt.%, and makes it friable; consequently, conditions are absent for developing binder properties for components within the refractory mix. With a water content of more than 7 wt.% the exothermic mix on heating cracks up; refractory object open porosity increases. The content of filler in refractory mix is dictated by a requirement for stable self-sintering of an exothermic mix, which promotes preparation of objects without pores and cracks. The composition is recommended for manufacturing refractory objects in the form of bricks and plates.

Composition No. *3*. In order to give mix No. 3 binder properties it was mixed with a barite-containing component (barite or witherite concentrate) with silica and water (65 – 70 wt.% of the total amount), and it was mixed for 80 – 90 sec (Table 3). Aluminum was added to the mix obtained, giving it plasticity and uniformity, creating thereby production conditions for charging chamotte grains finer than 10 mm. The mix absorbed and enveloped chamotte grains during mixing for 80 – 90 sec, excluding thereby sub-

TABLE 1. Self-Sintering Refractory Mix No. 1 Properties

Composition number	Content, wt.%					Ultimate strength in compression, MPa, at temperature, °C	
	barite concentrate	aluminum	copper production dump slag	chamotte	water	500	1100
1	17.5	7.5	25	40	10	75	70
2	20	10	20	42	8	70	67
3	15	8	30	40	7	67	62
4	25	5	22	38	10	60	54
5	23	7	20	37	13	45	40

TABLE 2. Self-Sintering Mix No. 2 Properties

Composition number	Content, wt.%					
	barite concentrate	aluminum	chromium-magnesite fraction	water	chromite ore	object open porosity, %
1	14	7	50	7	22	8
2	12	6	50	6	26	8
3	8	5	49	5	33	9
4	5	3	49	7	36	10
5	3	2	48	4	43	10

TABLE 3. Self-Sintering Refractory Mix No. 3 Properties

Composition number	Content, wt.%						Object refractoriness, °C
	barite concentrate	silica	aluminum	chamotte fraction, mm		water	
				<10	10 – 20		
1	17	27	7	17	17	15	1870
2	24*	27	8	13	13	15	1870
3	8	42	5	13	13	19	1870
4	24	25	2	17	17	15	1840
5	14	29	5	17	17	18	1850
6	21	29	8	13	14	15	1870
7	8	39	12	13	13	15	1870
8	30	25	3	13	14	15	1840
9	17*	25	7	18	18	15	1870

* Witherite concentrate weight fraction is shown, %.

sequent crack formation during heat treatment and promoting an increase in refractoriness and consequently refractory wear resistance. The next chamotte fraction of 10 – 20 mm with the rest of the water was added during mixing for 80 – 90 sec in order to increase mix strength before heat treatment, providing easier molding, and also in order to give a finished (face) surface during laying in a mold and subsequent heat treatment at 850 – 900°C for 15 – 20 min.

This sequence of operations in preparing refractories and use of additional barite-containing component, silica, aluminum, and also chamotte fraction finer than 10 and 10 – 20 mm, makes it possible during heat treatment at 850 – 900°C for 15 – 20 min and a specific weight ratio of reagents in self-sintering refractory mix to prepare objects with increased refractoriness (1840 – 1870°C), strength, and to simplify and cheapen the process excluding labor-intensive operations, reducing electric power consumption, and heat treatment duration, and also the duration of the production process as a whole. Self-sintering refractory mix for preparing objects is self-ignited at 850 – 900°C. Mix self-sintering occurs due to exothermic reaction between oxidizing agents, barite-containing component, silica and reducing agent, i.e., aluminum for 15 – 20 min. The fillers used are chamotte and silica. Combustion products are obtained in a molten condition, and therefore chamotte filler is added to the refractory mix composition, which apart from giving it strength during molding and a finished surface, plays the role of a reagent diluent reducing mix sintering temperature to the sintering temperature for solid products. A strong refractory brick is obtained.

Industrial tests of new highly effective refractory materials were performed in TOO Kazakhmys Corporation, TOO Kaztsink, AO Mittal Stil Temirtau, AO TsentralAziyaTsement, a branch of AO Transnational Company Kazkhrom – Aksusk Ferroalloy Plant, TOO Ferrum-Vtor, OAO Staro-oskol'sk Metallurgical Combine, and other enterprises oft eh Kazakhstan Republic and Russian Federation. Results of tests showed that the new materials are no worse with respect to quality, and for some indices they surpass refractory materials produced by DiDier (Austria) and Betkerov (Finland), currently supplied to Kazakhstan metallurgical enterprises. Use of the new refractories provides improvement of layer sealing between highly refractory objects and a protective lining layer of heating units due to an increase in mechanical strength (bricks are bonded into a monolith), slag and metal resistance, thermal shock resistance, and refractoriness. Use of them in Kazakhstan Republic enterprises markedly improves the service life of the lining of high-temperature metallurgical units with acquisition of a significant economic effect.

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