Combination of the Sol-Gel and SHS-Technologies for Obtaining the Carbonauces Refractories

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Abstract

The present paper contains the results of the carbonaceous refractories SHS-synthesis carried out in the presence of nanodispersed silica added to the system by means of sol heterocoagulation. The SHS-refractory compositions have been optimized based on periclase-chromite and alumino-silicate mortars and their physical and technical properties have been determined. This material has been successfully used for lining of the induction melting furnace at one of the machinery plants.

Introduction

Conventional technologies of obtaining carbonaceous refractories, as a rule, include high temperature roasting and smelting in reducing or inert atmosphere. They are quite power consuming and require complex equipment. In this connection, the technology of self propagating high temperature synthesis (SHS) of refractory material and products from them is very prospective. [1-3]. Earlier, a highly carbonaceous refractory material obtained on the basis of principles of SHS – and sol-gel technologies was used for lining of a melting crucible of the induction furnace which showed exclusively high technical-economic characteristics when melting aluminium.

The goals of the present study are to develop a high-carbon lining paste-like substance (mass) with minimum refractory quality 1850°C based on the SHS- and sol-gel-technologies for the application instead of the graphite crucibles in the induction furnaces for melting nonferrous metal such as aluminum and its alloys, copper, brass, bronze etc. In this work, the properties of carbon containing SHS-refractories, which are prospective when melting bronze copper and others in induction furnaces, have been studied.

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Experimental

The general approach to synthesis of carbon containing refractory materials is carrying out of aluminothermal solid phase combustion of metal oxides under the conditions of SHS in the presence of carbon. Usually, carbon in the form of graphite is introduced into the system in amounts exceeding stoichiometric ratios of initial materials. At high temperatures of synthesis – 1500°C the reduced metal may interact with excess carbon forming carbides. As SHS product is a composition material from refractory compounds – aluminium oxide, metal carbide, carbon, etc.

In this work, mixtures of chromite are with periclase powder and alumosilicate mortar MSH-39 was used as oxidants in SHS-systems, aluminium powder of the brand PA-4 was used as a reducer. The content of graphite and the ratio of oxidant/reducer were varied in exothermal mixture. Optimum composition of exothermal mixtures are presented in Table 1.

Dry exothermal mixtures were tempered by silica sol or magnesium sulphate solution to obtain semi-moisturized mass with a high content of graphite. The use of silica sol as a binder has a new effect – heterocoagulation of sol [4]. The authors studied silica sol obtained by different methods: the ion – exchange method from sodium silicate solution, by hydrolysis of tetraetoxysilane and silicic acid ether – ethylsilicat.

Table 1
Optimum dry carbon containing exothermal mixtures

Component	The content of components, % mass.	
	Periclase-Chromite Oxidant	Aluminosilicate Oxidant
Aluminium	16 – 18	16 – 18
Chromite	30 – 34	–
Periclase	18 – 20	–
Mortar MSH-39	–	30 – 40
Calcium fluoride	2	2
Electrode graphite	30 – 40	30 – 40

Results

Electron microscopic pictures (Fig.1) present patterns of heterocoagulation of silica sol on aluminium and chromite powders which are also typical for other heterogeneous systems. The phenomenon of sol heterocoagulation provides formation of ultradisperse silica with the sizes of particles 20-30 nm and less the system.

An important cause of sol heterocoagulation is the fact that, on account of blocking the surface of aluminium particles by nanodisperse silica, its activity is inhibited both in an alkaline medium with pH 10-11 and in an acid medium with pH 1-2.

An immediate release of hydrogen is observed in the absence of sol. In the further work, silica sol obtained at weak acid hydrolysis of Ethyl silicate was used.

The optimal conditions for production of sol silica by hydrolysis ethyl silicate present in Fig. 2.

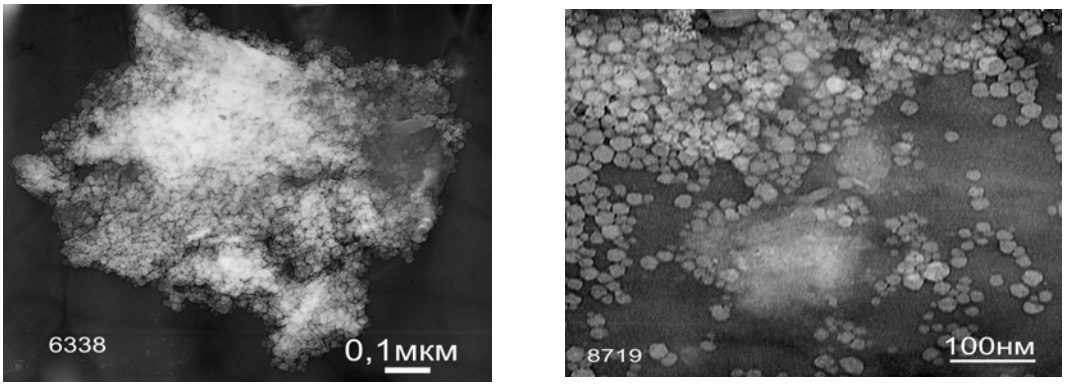
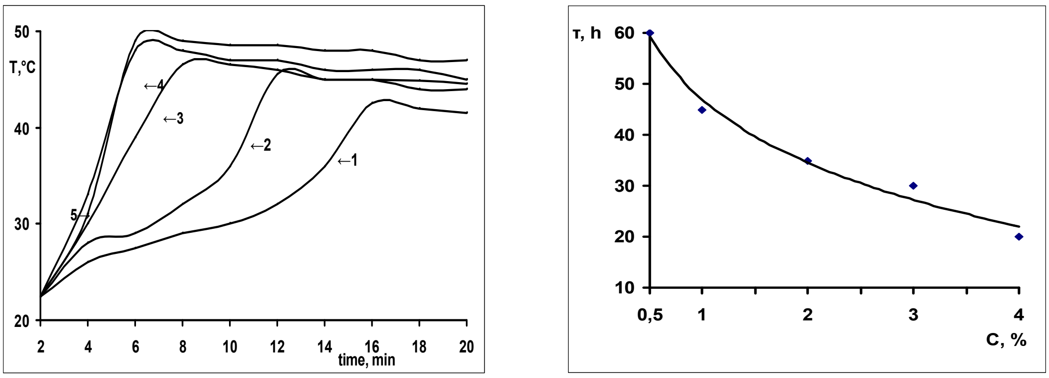


Fig. 1. Heterocoagulation of silica sols on aluminium particles (left) and chromite particles (right)

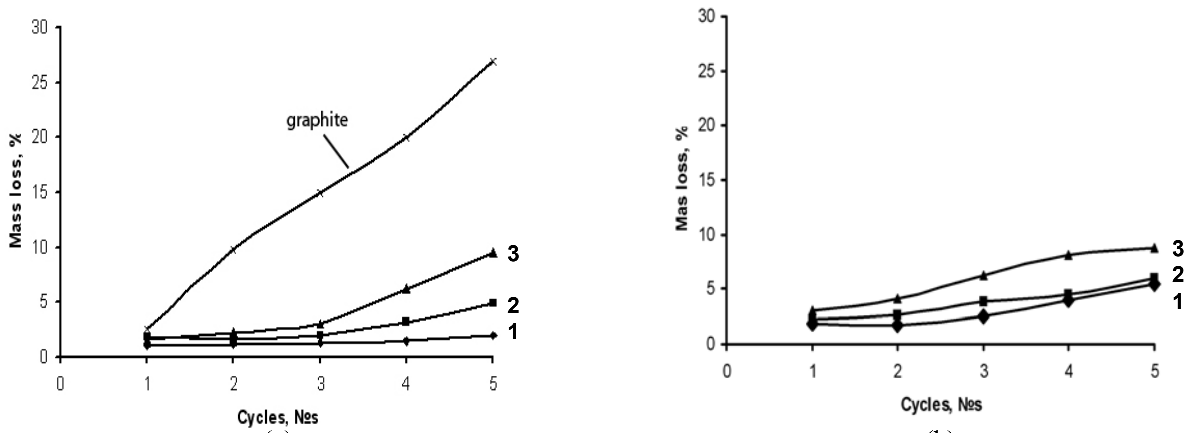


(a) (b)

Fig. 2. The optimal conditions for production of sol silica by hydrolysis ethyl silicate:
a) – the temperatures of hydrolysis with present of H_2SO_4: 1 - 0,5 %; 2 - 1,0 %; 3 - 2,0 %; 4 - 3,0 %; 5 - 4,0 %; b) – the time stability of sol silica

An optimum composition of hydrolusate having a sufficient resistance to sol coagulation was determined: ethylsilicate ES – 40 – 55 %, 0.5 % sulphuric acid solution – 45 %.

The presence of nanodisperse silica contributes to initiation of SHS at relatively low temperatures of system heating up to 850 – 900°C. For cubic specimen with the sizes $2\times2\times2$ cm, and cylindric specimen with the diameter of 2 cm and height of 4 cm pressed from exothermic mixtures moisturized by silica sol, after carrying out SHS, burning off of the products in air was determined. For this, the specimens were subjected to cyclic thermal treatment at 950°C with 30-minute exposure in each cycle. The character of the change in the mass of specimen at cyclic thermal treatment is shown in Fig. 3a. In all specimen, a periclase-chromite mixture with different ratios of chromite and magnesium oxide was used as an oxidant, the content of carbon in the initial systems made up 30 % and 40 % mass, the figure also present for comparison the relative change in the mass of crucible graphite which shown the greatest burning of ability in air. The burning off ability of carbon containing SHS refractory materials is 3-5 times lower than that of graphite. Similar results were obtained for carbonaceous SHS-refractories in which aluninosilicate mortal MSH-39 was used as an oxidant. These results are presented in Fig. 3b. Physico-mechanical properties of synthesized refractories are present in Table 1. Tables 2 and 3 present the changes in compressive strength of carbonaceous SHS-refractories as a result of cyclic thermal treatment and thermal treatment at 1400°C.



(a) (b)

Fig. 3. Profile of SHS-refractories burn-off at cyclic heating in the air: with periclase-chromite oxidizer; (a) and alumino-silicate oxidizer (b). Content of Carbon: 1 - 30 %, 2 - 40 %, 3 - 50 %

Table 2

Compressive strength of carbonaceous SHS refractories before and after cyclic thermal treatment

Specimen, No,	1	2	3	4	5	6	Graphite	Graphite-fireclay refractory
C, %	30	40	50	30	40	50		
σ_1, MPa	4,0	6,4	12,0	7,2	3,2	6,4	11,2	3 – 5
σ_2, MPa	4,4	6,8	12,4	6,4	6,4	7,2	6,0	-

σ_1, σ_2 – compression strength directly after SHS and after 5 cyclic thermal treatment.

Multiple thermal effect strengthens the material, unlike graphite and graphite containing convention refractories. It is seen in Table 2 that as a result of thermal treatment strength of SHS refractories increases, as a rule, while crucible graphite shows almost twofold decrease in compressive strength. Detections of refractories were made by the method of measuring the temperature of fall of standard conuses made of carbon containing compositions. A graphite conus was used as a reference. The temperatures were measured by a pyrometric thermometer “Ircon Ultimax Plus UX10P”.

The measurements showed that softening and fall of conuses is not observed even at maximum heating of Tamman furnace up to temperatures 1850-1900°C. These results indicate high refractoriness of carbon containing material after SHS – not less than 1850°C

Table 3
The effect of the content of graphite in the initial exothermal mixture on the strength of specimen

Compressive strength after SHS, MPa			Comprehensive strength after thermal treatment at 1400°C, MPa	
The content of carbon in the mixture	A binder sol $MgSO_4$ solution	A binder silica sol	A binder $MgSO_4$ solution	A binder silica sol
20	5,1	3,1	12,0	18,2
30	6,2	4,8	10,9	13,9
40	4,8	4,2	7,5	8,9
50	3,5	3,4	5,1	8,6

The results of X-ray phase analysis presented in table 4 show that high refractories of the material after SHS is conditioned by a high content of refractory compounds: aluminium oxides, chromium carbides, silicon, spinel, carbon.

Table 4
The phase composition of SHS products

Compounds	Periclase-chromite oxidizer % mass .	Aluminosilicate oxidizer % mass
$MgAl_2O_4$ (spinel) , %	44 – 66	–-
Cr_3C_2, %	3 – 9	–
Cr_7C_3, %	5 – 10	–
Carbon , %	23 – 32	43 – 50
Al_2O_3, %	–	21 – 44
Si, %	–	Less than 2

The main refractory phases – aluminium oxide, graphite, chromium, silicon, spinel, carbides – provide refractoriness of specimen higher than 1850°C.

Resistance of the synthesized specimen of carbon containing SHS refractories to metal melts was determined. For this, the specimen were exposed to the action of bronze during 15 minutes at the temperature 1450°C. Resistance to the melt was determined by the change in the mass of refractories on account of dissolution or chemical interaction with the liquid phase.

Table 5 illustrates the character of the change in the mass of the specimen being studied under the high temperature effect of liquid metal depending on the content of carbon in the initial mixture and the binder.

Table 5
Corrosion resistance of SHS refractories to the melt of bronze

Number of examples	The content of carbon in the initial mixture, %	The binder– $MgSO_4$ solution	The binder- silica sol
1	20	1,3	2,0
2	30	3,4	0
3	40	0	2,3
4	50	0	4,0

Wettability of specimen surface by liquid metal is absent, the specimen show high corrosion resistance to liquid metals. Refractory products in the form of cylinders with the height 80 mm, external diameter 50 mm, the thickness of walls 7 mm, the thickness of bottom 15 mm were made from the developed materials by the method of semi-dry pressing followed by SHS. In these cylindrical crucibles in Tamman furnace melting of duraluminium out at 950°C, that of copper and bronze – at 1400-1450°C, cast iron – at 1600°C. The pictures of the obtained bars of metals are shown in Fig. 4.

Fig. 4. Bars of metals melted in cylindric glasses:
1 - duraluminium, 2 - bronze, 3 - copper, 4 - cast iron

Only on the cast iron bar one can see drops of metal – the product of interaction of the melt with the surface of crucible, the rest melts do not interact with the material of glasses.

In order to carry out tests in the induction furnace at the JSC "The Kirov Mashine-Building Plant" (Almaty), 500 kg of dry carbon containing mixture were prepared from which a lining mass was obtained at tempering by hydrolyzed solution of ethylsilicate and mixing. The lining mass was used for production of a melting crucible by packing directly in the furnace.

Fig. 5 presents these operations. Synthesis of carbon containing materials proceeded as a result of heating in the produced crucible of a graphite cylinder up to 1000°C on account of induction currents of the put on furnace. Fig. 6 presents the procedure of initiation of SHS in the material. As a result of SHS, the filled crucible acquired the necessary quality for carrying out melting of non-ferrous metals. Experimental meltings of bronze in the produced crucible were carried out. The crucible was in good condition after 15 meltings.

Fig. 5. The lining works on the induction furnace

a b

Fig. 5. a) Initiation of SHS in the crucible, b) Crucible after melting

The results of test of high-carbon SHS-material are compared with regular material when melting aluminium. The results present in Table 6.

So there is increasing of fusions quantity in 5-6 times in comparison with graphite crucible it would save a lot of materials

Table 6
The results of test of induction furnace IST-016 at the JSC "The Kirov Machine-Building Plant" (Almaty, Kazakhstan)

Parameters	Furnace lining is made of high-carbon SYS-material			
Quantity of fusions	1 – 25	26 – 45	46 – 50	51 – 280
Furnace lining conditions	90- 120 min to get the operational temperature. Surface is not damaged	40-60 min to get the operational temperature. Surface is not damaged	40-60 min to get the operational temperature. Surface is not damaged. There is lining slag	40-60 min to get the operational temperature. Surface is not damaged. Surface is clean and not damaged, lining slag can be easily removed
Parameters	Conventional graphite crucible			
Quantity of fusions	1 – 25	26 – 45	46 – 50	–
Furnace lining conditions	60- 90 min to get the operatio-nal temperature. Surface is not damaged. Small damade of surface	60- 90 min to get the operational temperature. Deep damage of surface	60- 90 min to get the operational temperature. Deep damage and destruction of furnace lining	–

Conclusion

Highly carbonaceous materials worked out in this work on the basis of SHS- and sol-gel-technologies surpass conventional carbonaceous and carbongraphite refractory materials by their main characteristics.

These materials can be used not only as a lining material when repairing induction furnaces for melting non-ferrous metals but also for production of small highly refractory products: moulds, crucibles, glasses, metal wire, by the method of pressing followed by SHS.

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