EFFICIENT CARBON-CONTAINING LININGS FOR HIGH-TEMPERATURE EQUIPMENT IN NONFERROUS METALLURGY

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The influence of carbon materials on the physico-mechanical properties of refractories is studied, methods of impregnating refractories possessing a magnesian composition with carbon materials are developed, techniques of protecting carbon materials against oxidation are investigated, and zones of lining in which the use of carbon materials would be efficient are determined. Lining with the use of carbon materials are tested and introduced into plants in the nonferrous metallurgy industry. A technology for the fabrication of periclase-carbonaceous refractories and compound masonry and for impregnation of articles with pitch coke are developed from the results of the study. Carbon-containing refractories and coatings have undergone industrial testing at a number of enterprises and have been introduced in reverberatory, ore-smelting, and rotary kilns and in horizontal converters. The use of carbon-containing refractories and coatings in the lining of equipment in the nonferrous metallurgy industry will increase the operating period of the equipment by 30 to 200%.

Keywords: carbon-containing refractory, compound lining, sliding layer, periclase, periclase-chromite, rotary kiln, ore-smelting kiln

Carbon has long been the most important of all refractories as a consequence of fact that it exhibits the highest resistance to slag and metal as well as thermal stability at elevated service temperatures. In view of the fact that around 70% of existing refractories wear down as a result of slag corrosion, carbon-containing and carbon refractories have been developed to the greatest extent simply because they are the most abrasive resistant of all refractories. Oxygen is the basic reagent that corrodes refractories in the course of service. Prevention of oxidization of refractories through the development of anti-oxidant processes is the basis for increasing the wear resistance of the new generation of periclase-carbonaceous refractories. Carbonization of refractories constitutes a combination of two interrelated processes: carburization, or the introduction of carbon into refractories in the course of manufacture, and stabilization of carbon, or preventing the release of carbon from a refractory in the course of service. Therefore, processes of carburization and stabilization of carbon in magnesian refractories depend chiefly on the technological parameters of their manufacture, and next by the service conditions of the refractories.

Carbon is added to magnesian refractories basically in two forms, separately or in combination:

– in solid form, through the action of electrodes, in the form of coke, pitch, wastes from graphitization, carbides, graphite, phenol powder-forming binder, carbon fibers, etc. Phenol powder-forming binder and graphite are the best forms.

– in liquid form, as technical-grade liquid lignosulfonate, different resins (coal-tar, phenolic, furan, and synthetic resins), bitumen, tar, etc.

We carried out studies with the goal of developing a technology for the production of periclase-carbonaceous refractories that takes into account the service conditions of linings in equipment used in the nonferrous metallurgy industry. The influence of different additives, such as anti-oxidizing agents, chemical binders and glazes, on the physico-mechanical properties of the resulting periclase-carbonaceous refractories was studied. The dependence of the operating characteristics of periclase-carbonaceous refractories on the composition of the slag, technological parameters, and the type of atmosphere and temperature regime in which the equipment functions was considered.

In determining the dependence of the compressive strength σ_{com} on the content of carbon in the refractory, it was established that σ_{com} falls sharply if the quantity of graphite in the material is greater than 10% (Fig. 1). Periclase-carbonaceous refractories were fabricated from

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periclase of differing degrees of size reduction in order to reduce the unfavorable action of graphite on the value of σ_{com} of the articles. The optimal fractional composition of a charge for manufacture of periclase-carbonaceous refractories of sufficient strength, thermal stability, and resistance to slag comprises 30% periclase of fraction 3 – 1 mm and 15 – 20% of 1 – 0 mm fraction, 30% finely milled fraction ≤0.063 mm, and 10 – 12% natural graphite <0.1 mm.

The influence of different chemical binders, such as lignosulfonate (sulfite-yeast mash), sodium polyphosphate, and chromium-aluminophosphate binder, sodium-silicate solution, and bakelite and bakelite lacquer, on the physical and ceramic properties of periclase-carbonaceous refractories following drying and roasting was also investigated. The mineral binders that represent the greatest interest are sodium polyphosphate; its introduction tends to increase the strength and density of the article and serves as protection against oxidation.

As a result of our studies it was determined that the optimal ratio between the binder components of bakelite and sulfite-yeast mash was 2 : 1. Following drying the open porosity of the articles is 10 – 12% and the compressive strength 41 – 44 MPa.

Several additives that hinder burn-out of graphite are introduced into the composition of the charge in the course of fabricating the refractories, such as readily oxidizable metals (aluminum, magnesium), silicon carbide, chromite, and boron nitrite. It was found that an impermeable protective film of silicon dioxide that prevents oxidation is formed if silicon carbide is used as additive. If readily oxidized metals or silicon carbide are added to the refractories, their degree of oxidation at high temperatures (1200 – 1400°C) is reduced.

On the basis of the results of the studies, semi-industrial batches of periclase-carbonaceous refractories in 1 t lots were fabricated at OOO Kombinat Magnezit (Satka, Chelyabinsk District) and in 10 t lots at the refractory plant of OAO Lower Tagil Metallurgical Factory. The refractories were tested in the slag zone of the reverberatory kiln of the Central Ural Copper Smelting Factory (Revda). A 30 – 40% greater resistance was achieved with the use of periclase-carbonaceous refractories as compared to PKHS brand refractories. In terms of the level of physico-mechanical properties, the newly developed refractories of semi-industrial batches were close to the articles produced by the leading foreign firms.

We developed compound lining for an ore-smelting kiln in order to fabricate germanium at SP Angren Énergotsvetmet. The traditional lining of the kiln consists of chromomagnesite and chamotte articles and exhibits low resistance, with service life 2 – 3 months [2] due to the corrosive nature of the products produced in smelting of germanium-containing stock (cf. Table 1).

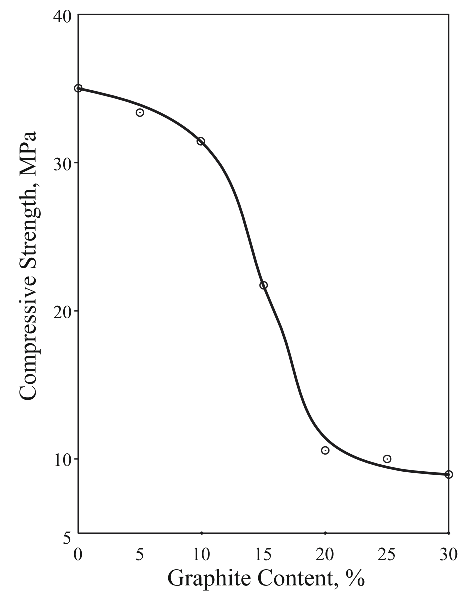

Fig. 1. Compressive strength of periclase-carbonaceous refractories as function of graphite content.

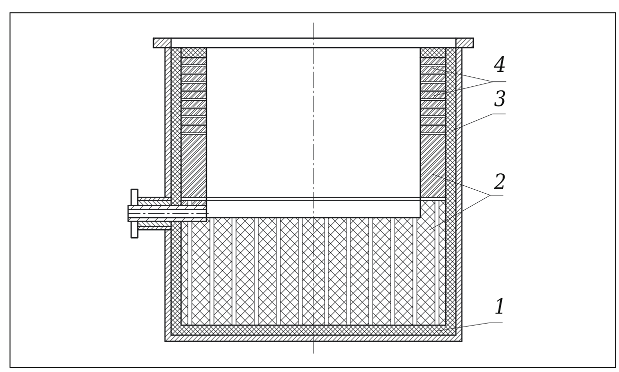

Fig. 2. Compound lining of ore-smelting kiln: *1* — carbon packing; *2* — carbon blocks; *3* — chromomagnesite fill; *4* — chamotte refractories.

Figure 2 presents a diagram of the improved lining of the kiln. The hearth is lined with blocks 1600 mm in height. The

TABLE 1. Chemical Composition of Products of Smelting* of Germanium-containing Stock, %, at SP Angren Energotsvetmet

Material	SiO_2	Fe_2O_3	Al_2O_3	CaO	S_{tot}	Zn	Pb	As
Sulfide-metal alloy (Regulus)	48.89	16.48	6.32	25.82	1.28	1.10	0.03	0.02
Slag	58.96	2.98	17.98	18.78	0.85	0.33	0.025	0.002

* Melting point 1350 – 1450°C.

height of the blocks is determined from a calculation of the range of the point at which solidification of the melt occurs, i.e., at a given height of the melt in the case where it penetrates through the seams and succeeds in congealing without slipping under the blocks.

The seams between the blocks are filled with a self-baking carbon paste. Impermeability of the hearth and prevention of penetration of melt beneath the blocks as well as emersion of the hearth are achieved by increasing the thickness of the lining of the hearth and by filling the seams with paste. The service life of the lining of an ore-smelting kiln during industrial testing amounts to 16 months, i.e., it increases 2.5-fold. Experience gained from the use of the improved lining may be extended to the electric furnaces used in nonferrous metallurgy, for example, the test lining design may be used in the hearths of the electric furnaces used in lead production.

Experience gained from the use of a graphite layer in the lining of the RKZ-4.5 furnace at OAO Pobuzh'ye Nickel Factory is worth noting. Studies were performed for the purpose of relieving the thermal stresses that arise between the linings of the hearth and walls at their contact site and that may lead to fracturing of the lining. A sliding layer makes it possible for the hearth to grow in the course of service without fracturing at the contact site (Fig. 3). No emergencies occurred during industrial tests in this component of the test lining.

Addition of carbon to standard refractory articles for the lining of equipment used in the nonferrous metallurgy industry was also considered. For this purpose, 60 t of standard chromite-periclase heat-resistant refractories were impregnated with carbon-containing pitch at OAO Novosibirsk Electrode Factory and sent to OAO Chelyabinsk Electrolytic Zinc Factory and OAO Ust'-Kamenogor Lead-Zinc Combine for the lining of rotary kilns. Compound "tape" lining produced from periclase-chromite refractories and chromite-periclase heat-resistant refractories that had been impregnated with carbon-containing pitch from the 25-th to the 40-th meter was created. The tests demonstrated that the test linings were 30 – 40% more heat resistant.

The useful life of the lining of metallurgical equipment is often achieved by periodic deposition of gunning body on the surface of the lining by the method of torch guniting and admission used in ferrous metallurgy. Attempts to transfer experience acquired in ferrous metallurgy to nonferrous metallurgy have not been successful, since the service temperature of the linings in this branch of industry is significantly less and not sufficient to enable sintering of the well-known gunning bodies to the surface of the masonry. A problem then arises, namely how to reduce the sintering temperature used with gunned coatings to enable their use for the heating equipment used in nonferrous metallurgy. An optimal composition of gunning bodies that differ from the known gunning bodies by the fact that these bodies contains quartzite with the following ratio between the components, wt.%, was developed as a result of studies carried out to learn how to reduce the sintering temperature of the gunned coating: pitch coke, 22; quartzite, 25, and chromite-periclase, 53.

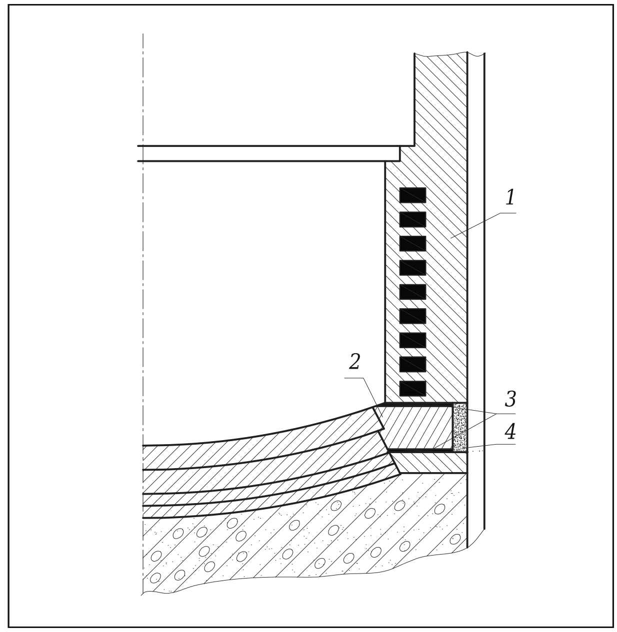

Fig. 3. Design of sliding layer of ore-smelting kiln at OAO Pobuzh'ye Nickel Factory. *1* — cooled lining; *2* — uncooled assembly; *3* — layer of graphite; *4* — compensation zone.

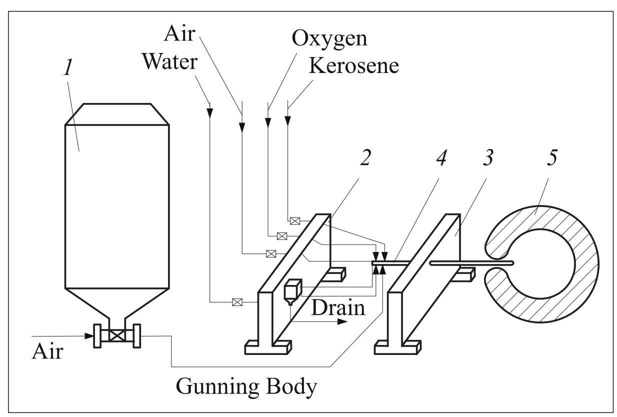

Fig. 4. Semi-industrial gunning plant: *1* — feed hopper; *2* — control unit; *3* — protective screen with mechanism for stirring the tuyere; *4* — tuyere gun; *5* — converter.

The gunning body is prepared in the following way: 20 – 25% pitch coke is mixed with 20 – 30% quartzite and 50 – 53% chromite – periclase. The milling grain size ≤80 μm. The gunning body is deposited in a chamber heated to 1400 – 1500°C on PKhS articles that had been heated by a torch having a temperature of 1700 – 1800°C. Deposition is stopped once the thickness of the gunned coating reaches 10 mm. Strength and resistance testing is then performed. The compressive strength of a gunned coating is 9.8 MPa with spalling resistance 4.1 MPa, which is twice the indicator of a gunned coating based on chromite-periclase. Porosity is 18 – 25%, apparent density 2.4 – 2.6 g/cm^3, compressive strength 30 – 40 MPa, and working temperature 1300 – 1400°C. A gunning body of this composition may be deposited in hot repairs of the lining of rotary kilns and horizontal copper-nickel converters by the method of torch guniting, with the operating period of the equipment lengthened by 30 – 40%. We developed a semi-industrial gunning plant with productivity 2 kg/min [4]. A diagram of the plant is presented in Fig. 4. As a result of our studies, it was established that the thickness of the gunned coating was from 10 to 70 mm. A gunning body containing a thermite mixture as special additive at a rate of 5 to 12% has also been developed and tested. Only a short period of time is needed to melt the particles as a consequence of an exothermic reaction between the aluminum and iron oxide. Since the particles of the gunning body are in the flame for only a brief period of time, some of the particles of the thermite mixture do not succeed in reacting in the flame and, once they have fallen into the lining, interact with it, forming refractory compounds, e.g., magnesioferrite and complex spinel. As a result of the formation of these compounds, both in the lining and in the gunned coating, strong adhesion of the gunned coating with the lining, in the form of a unified monolith, is achieved.

The characteristics of gunned lining based on chromite-periclase compound, thermite mixture, and coke breeze deposited by the method of torch guniting are as follows: open porosity 17 – 25%, apparent density 3.1 – 3.3 g/cm^3, compressive strength 25 MPa, and working temperature 1300 – 1500°C.

CONCLUSION

The use of carbon-containing refractories and coatings in the linings of high-temperature equipment used in the nonferrous metallurgy industry yields a 30 – 200% increase in the durability of this equipment, Carbon-containing refractories should be applied in equipment with a weakly oxidizing and reducing atmosphere, i.e., in reverberatory, rotary, and ore-smelting kilns. A sliding graphite layer at the joint between the linings of the walls and the hearth of ore-smelting kilns prevents emergency shut-downs in view of the fact that it is possible to achieve sufficient displacement of the lining of the hearth relative to the lining of the walls. Gunning bodies with the addition of coke breeze are an effective means of increasing the durability of the horizontal converters used in the copper-nickel industry.

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