SILICON CARBIDE REFRACTORIES FOR BLAST FURNACES

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The most important task facing the refractories industry is to save energy, material, and labor resources. Its solution to a large extent depends on the creation and introduction of effective resistant refractories and their rational use in service.

In the blast furnace the resistance of refractories in the various sections varies widely. For example, in the bottom and the hearth the life is mainly 15-18 years, while in the shaft, bosh, and shoulders it varies from 2 to 12 years. Analysis of the service of refractories shows that their life in these parts depends on the design of the structure, its cooling, the quality of the refractories, the operating schedule, the running of the furnace, and other factors.

At the present time the commonest refractories are those made from pure kaolinitic clays with weight proportions of Al_2O_3 of 41-42% and with a porosity of 8-12%. Apparently, dense chamotte refractories, up to the end of the current century, will prevail over the others. However, in economically developed countries, in parallel with improvements in dense chamotte articles, intensive research is going on into the development of new types of refractories.

In the shaft, bottom, and shoulders of blast furnaces the bricks are subjected to the action of alkalis and slags, thermal stresses, abrasion from the batch, and other factors. Since chamotte refractories do not possess sufficient resistance in these conditions, in the shaft, in addition to dense chamotte (41-44%* Al_2O_3) refractories, a start has been made with the use of other types: electrofused corundum and mullite, graphite and semigraphite, silicon–carbide–graphite, and also self-bonded silicon carbide and nitride-bonded silicon carbide or oxynitride bonded forms [1-4]. Recently authors [5] have recommended the use of corundum–chromite and spinel refractories.

All these researches have so far failed to produce a single answer to the question about the use of the optimum refractories. Studies were therefore carried out into the resistance of sintered and fused mullite, corundum, silicon carbide with oxynitride and nitride bonds, to the action of destructive factors. It is shown that the highest resistance is possessed by refractories based on self-bonded silicon carbide and oxynitride-bonded SiC. On the basis of laboratory studies, refractories containing 23.4% C, 66.7% Si and 7.7% N are recommended for use in the shoulders of blast furnaces [1, 2]. The increased thermal conductivity [λ = 10.3 W/m·°K] provides an inertness to these refractories, in blast-furnace cooling conditions, to the destructive factors at the lower reaction temperatures of 1150°C and with a structure thickness of 530 mm.

The SiC refractories Annasikon 93 from the Annawerk (FRG) firm have been tested in the lower part of the shafts of five blast furnaces, and showed a slight wear compared with chamotte bricks [3].

In the lower part of the shaft of a blast furnace that has a diameter of 9 m, the wear of silicon-carbide refractories bonded with oxynitride is half that of phosphate-impregnated firebrick, and 1.5 times less than for SiC refractories containing graphite and clay bonded materials [4].

In the USSR we have also developed the production of SiC bricks with nitride bonding (GOST 10153-70) which are being successfully used in various furnaces [6]. They are made from SiC and crystalline silica. Firing is done in nitrogen at 1450°C. The open porosity of the articles is about 20%, the compressive strength more than 100 MPa. SiC refractories with an oxynitride bond have a higher thermal-shock resistance than nitride-bonded ones [7].

*Here and subsequently mass proportions are indicated.

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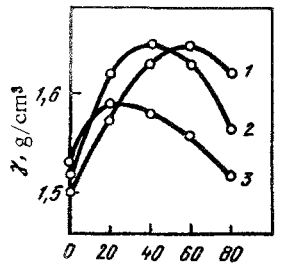

Fig. 1. Relationship between the packing density γ of bodies from silicon carbide fractions No. 160 (1) and 125 (2) and 100 (3) and the weight proportion of SiC No. 63 in them.

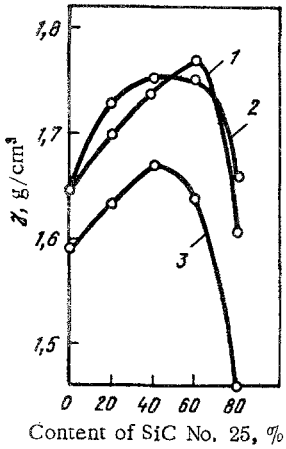

Fig. 2. Relationship between the packing density γ of silicon—carbide bodies consisting of 40% fractions No. 160 and 60% No. 63 (1), 60% No. 125 and 40% No. 63 (2), 80% No. 100 and 20% No. 63 (3) and the weight proportion of SiC No. 25 in them.

Silicon carbide refractories based on a combined nitride—oxynitride bond were previously fired in a carbon filling. The process is rather laborious and connected with heavy working conditions. In recent years it has become possible to produce SiC refractories with a bond of silicon oxynitride by firing the raw materials in nitrogen* [8, 9]. To synthesize silicon oxynitride use was made of crystalline silicon and quartz. Specimens were prepared from mixtures of Si and SiO_2 with ratios of from 25:75 to 65:35 (by weight).

At a firing temperature of 1450°C and a weight ratio of Si:SiO = 58.37:41.63, which corresponds to the molecular ratio of 3:1, silicon oxynitride is formed. The theoretical increase in weight in this case should equal about 38% [10]. To check the statement that silicon oxynitride is formed by means of the intermediate formation of silicon monoxide, specimens were prepared from a mixture of silicon monoxide and silicon in the weight ratio of SiO:Si = 1.57:1. Firing was done in nitrogen at 1450-1470°C. Only silicon oxynitride was obtained. The increase in weight was about 30%. The chemical composition of the silicon oxynitride after alkali treatment in % was: Si 53.7, N_2 27.04, O_2 16.6, RO + R_2O_3 1.1.

*I. Ya. Guzman, "Investigations into the field of reaction sintering of ceramics based on compounds of silicon in the system Si—C—O—N," Author's Abstract of Doctoral Dissertation, Moscow (1979).

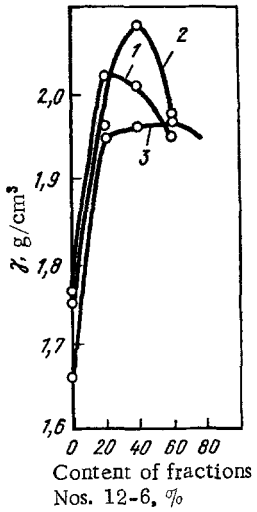

Fig. 3. Relationship between the packing density γ of bodies made of SiC consisting of 16% fractions No. 160, 24% No. 63 and 60% No. 35 (1); 36% No. 125, 24% No. 63 and 40% No. 25 (2); 48% No. 100, 12% No. 63 and 40% No. 25 (3), and the weight proportion in them of silicon carbide Nos. 12-6.

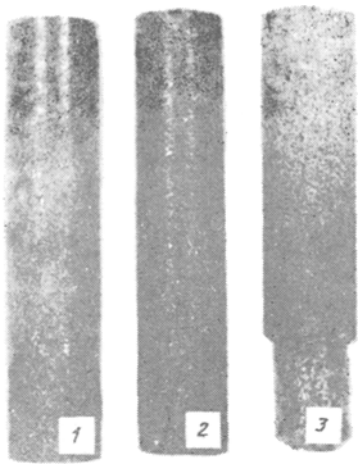

Fig. 4. Specimens after slag testing by rotating in slag: 1) silicon carbide refractory bonded with silicon oxynitride; 2) SiC refractory with a silicon nitride bond; 3) chamotte grade ShPD-41.

Also known is a method of obtaining silicon oxynitride from a mixture of silicon dioxide, silicon, and additions of iron, magnesium, copper, manganese, nickel, and their salts. Firing is done in nitrogen. The formation of silicon oxynitride occurs according to a staged scheme: development of fusible eutectics between metals and their salts, solution of silicon and silica, the formation of silicon monoxide ($1/2\ Si + 1/2\ SiO_2 \rightarrow SiO$), reduction of the silicon monoxide by the silicon ($SiO + Si \rightarrow Si_2O$) and the formation of silicon oxynitride ($Si_2O + N_2 \rightarrow Si_2ON_2$). Firing is done at 1420°C.* According to data in [1] silicon oxynitride is obtained by the thermal oxidation of silicon nitride at temperatures above 1300°C in an atmosphere containing oxygen.

This article gives the results of studies concluding in the development of a rational substance and grain-size compositions which ensure, in actual industrial conditions, the pro-

*Patent No. 53-25320 (Japan), 1978.

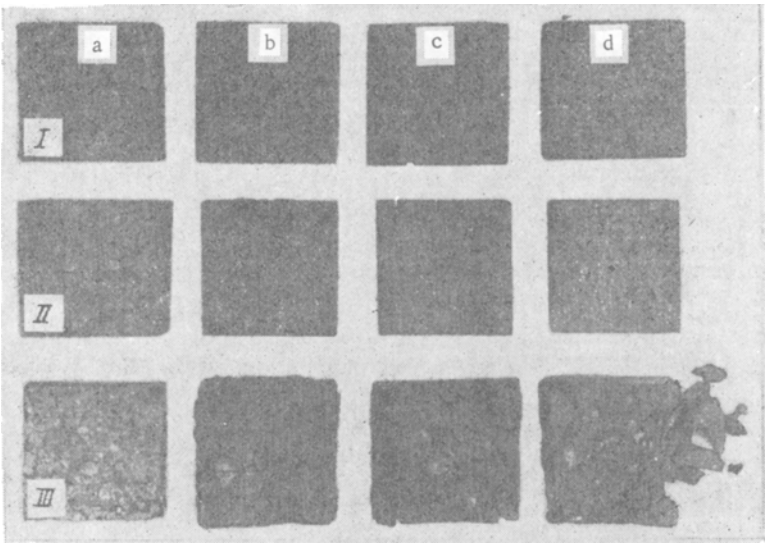

Fig. 5. Specimens after testing in a coke filling (a) and a mixture of coke and K_2CO_3 (b-d) in the ratio 80:20; I) SiC refractory with a silicon nitride bond; II) SiC refractory with a silicon oxynitride bond; III) chamotte refractory grade ShPD-41; a, b) at 1200°C; c) at 1300°C; d) at 1400°C.

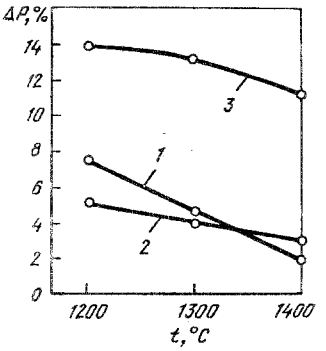

Fig. 6. Increase in weight ΔP due to the absorption of alkali by test specimens in relation to test temperature t: 1) SiC bonded with silicon nitride; 2) with a silicon oxynitride bond; 3) chamotte grade ShPD-41.

duction of articles measuring 345 × 150 × 75 mm from silicon carbide with an oxynitride bond and a homogeneous structure, and with prescribed porosity and strength values.

Previously, the possibility was established of producing SiC brick with an oxynitride bond on the basis of batch containing 70% SiC, 18% crystalline silicon, and 12% quartz sand [8]*. However, in the preparation of refractories for blast furnaces with thicknesses of less than 75 mm difficulties arose due to the formation of a zoned structure, caused by the unreacted silicon in the central part of the articles in the firing process. This impaired the quality of the articles. In the Ukrainian Institute laboratory work was done to determine the optimum technological parameters for the production of SiC bricks with an oxynitride bond.

The density of packing the SiC bodies to a large degree depends on their ratio of coarse-grained (Nos. 160, 125, and 100), average, and fine (Nos. 63, 25 and 12-6) fractions of silicon carbide.

*See reference to Guzman above.

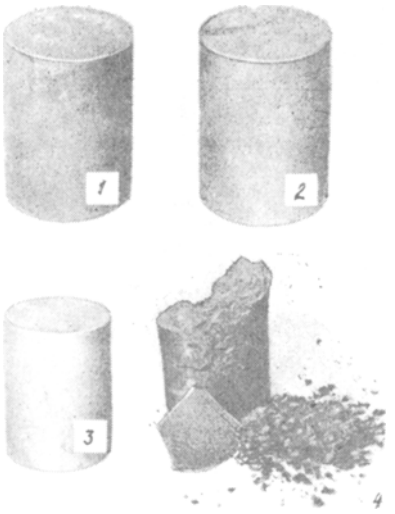

Fig. 7. Specimens of refractories following the action of sooty carbon: 1) SiC with nitride bond (TU 14-8-138-75); 2) SiC refractory with an oxynitride bond (trial batch using TU 14-8-343-80); 3) chamotte, dense, blast-furnace refractory ShPD-41 (GOST 1598-75); 4) silicon carbide refractory KA-3 with a silicate bond from the Semiluksk factory (GOST 10153-70).

Dense bodies are obtained by introducing 40-60% fine-grained SiC. The packing density of bodies is increased from 1.50-1.53 to 1.59-1.65 g/cm^3 with the use of relatively fine grained constituent in the form of the optimum amounts of SiC grains No. 63 (Fig. 1).

The packing density of bodies consisting of SiC powders of triple-fractional compositions is significantly higher. With the addition of the optimum amount of fine-grained SiC No. 25 to mixtures consisting of coarse grains of SiC (Nos. 160, 125, or 100) in combination with No. 63 SiC, the packing density increases from 1.59-1.65 to 1.68-1.78 g/cm^3 (Fig. 2). An even greater packing density reaching 2.08 g/cm^3 occurs with the use of four fractions of silicon carbide (Fig. 3).

For the preparation of SiC bonded with oxynitride, use was made of black silicon carbide of various fractions, crystalline silicon grade KrO, and Vodolazhsk quartz sand containing not less than 98% SiO_2. The crystalline silicon and the sand were milled in a vibromill to a specific surface of about 10 m^2/g.

An increase in the amount of finely milled constituent leads to overpressing cracks, and increases the resistance to nitrogen diffusion into the deep layers of the articles during firing. Laboratory studies established the optimum ratio for the various fractions of SiC and the finely milled mixture (Si + SiO_2).

Introducing special additives to the batch increases the rise in weight and the strength of the articles, which is due to the activation of the synthesis of the silicon oxynitride and the rapid formation of the silicon monoxide as a result of the reduction of SiO_2.

Laboratory investigations showed that to prepare silicon carbide articles with a silicon oxynitride bond it is necessary to use a body consisting of coarse-grained SiC (2-0.5 mm) and finely milled mixture of crystalline silicon, quartz sand, and additives.

Specimens were tested for alkali- and slag-resistance in a reducing atmosphere at 1400°C for 2 h with the crucible method and the rotational method in slag. For comparison we used chamotte specimens grades ShPD-41 and ShUD-37, silicon carbide articles with clay and nitride bonds. It was established that the silicon carbide refractories with the nitride and oxynitride bonds possess a high resistance to blast furnace slags. Experiments showed that the

dense chamotte refractories ShPD-41 at 1400°C in 1 h are washed out to the extent of 3-5 mm [0.4 g/(cm²·h)], while the silicon carbide refractories did not show any signs of damage (Fig. 4).

Alkalis (K_2CO_3) at 1200, 1300, and 1400°C in reducing conditions (coke filling) have a more active effect on the chamotte (Fig. 5). The dense chamotte refractories (porosity less than 12%) at 1200°C for 10 h are saturated with K_2O up to 15.28%, while the silicon carbide refractories bonded with nitride and having a porosity of 20% take up to 7.1% K_2O; and the oxynitride-bonded SiC brick with a porosity of 22% only up to 2.8%. At higher temperatures (1300 and 1400°C) saturation by alkalis is slower (Fig. 6). The increase in weight due to the alkali absorption and precipitation of sooty carbon, at elevated temperatures, is reduced.

Testing at 600°C for the action of sooty carbon in 500 h showed that SiC refractory bonded with oxynitride and nitride of silicon and chamotte ShPD-41 is not destroyed by carbon monoxide. Silicon carbide refractory bonded with clay was completely destroyed (Fig. 7).

It is found that SiC with oxynitride and nitride bonds is characterized by a high resistance to the action of various corrosive chemical agents, and can be recommended for use in the lining of the superstructures of blast furnaces.

Using the results of laboratory tests at the Semiluksk factory, an experimental batch of goods with a silicon oxynitride bond was produced.

Grinding of the mixture of crystalline silicon, Ovruchsk quartzite, and additives was done in a tube mill. The fineness of milling was typified by a residue of not more than 7% on a screen containing 0.06-mm apertures.

Silicon-carbide powders were moistened with a concentrate of sulfite-lye and mixed in the mixer. Then the combined grist of silicon, quartzite, and additives was placed in the mixer, and the components were blended to obtain a homogeneous mass. The articles were pressed (345 × 150 × 75 mm) on a friction press. The dried articles were fired in nitrogen at 1450°C.

The fired articles had a uniform structure. There were no volume changes in firing. The composition of the articles was 75.0% SiC and 5.3% N_2. The properties of the articles were: open porosity 19.0%, apparent density 2.48 g/cm³, gas permeability 0.01 μm², compressive strength 110 MPa, refractoriness under load of 0.2 MPa, above 1700°C, thermal expansion at 1100°C 0.21%, at 1300°C 0.56%, coefficient of thermal expansion $4.1 \cdot 10^{-6}$ deg C^{-1}, specific heat 1.17 kJ, thermal conductivity at 500°C 11.6 W/(m·K), at 1200°C 8.5 W/(m·K), and thermal-shock resistance (water — 1300°C) more than 25 heat cycles.*

The results obtained showed the advantages of using SiC refractories with bonds made of oxynitride and silicon nitride in industry, and using them in the linings of the shoulders, bottoms, and the lower parts of the shafts of large blast furnaces. Special technical specifications were worked out for these refractories.

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*After 25 heat cycles no signs of damage were noted.