GLAZE FOR CARBON-CONTAINING REFRACTORIES

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Regarding the combination of properties determining the resistance of refractories in different working conditions, carbon-containing articles are better than many of the refractory materials available [1, p. 418]. Together with conventional graphitic-chamotte refractories obtained by plastic molding greater use is now being made of refractories based on semidry bodies [2, 3].

Carbon refractories, regardless of production methods, have a serious drawback — high oxidation of the carbon constituents [4, p. 8] which makes their firing very complicated. Muffle firing in coke filling is very laborious, requires high temperatures in the kiln, and impairs the health conditions in the plant.

At present muffleless firing is gaining ground, using protective coatings [1, p. 429]. The coatings should be impermeable to oxygen in a wide temperature range, possess the necessary adhesiveness, good wetting capacity on the refractory, be resistant to thermal shock, and have an available application technology. Glazes meet these requirements. Existing glaze coatings [5] satisfactorily protect articles obtained by plastic shaping (graphite—chamotte) [4, p. 100; 6, p. 371]. But for dry pressed articles such glazes do not provide a continuous coating owing to the low wettability of the material. The difference in wettability on articles obtained by plastic and dry methods of production is explained by the different degree of envelopment of the waterproofed graphite particles by clay.

The processes of wetting the body with highly viscous melts are characterized, in particular, by the mechanical resistance to spreading, leading to wetting hysteresis. In this case the increase in the wetting capacity is determined not by the increase in the spreading, but by a reduction in the tendency of the molten coating to coagulation, since during firing the particles of glass tend to blend, and there is no spreading [7, p. 44]. To weaken the tendency of melts to coagulation it is usual to employ a reduced coating thickness, increase the viscosity of the melt, and reduce its surface tension. However, a reduction in the surface tension of the glaze helps to form one of the spatial defects of the coating — "boiling," and an excessive increase in the viscosity of the melt — the formation of "pinhole" type defects [8, p. 135]. The processes of forming glaze coatings on carbon-containing ceramics are even more complicated, and are caused by the presence of practically unwettable carbon and the high porosity of the refractory.

This article gives data on the development of a composition and technology for making a glaze for carbon refractories obtained by semidry shaping. The wetting capacity is normally improved by introducing V_2O_5, CrO_3, S^{2-}, P_2O_5, and other surface-active agents which have low and even negative partial surface tensions [9, p. 326]. Most interest here is attached to P_2O_5. Phosphates possess cementing properties [10, p. 15]. Alkaline phosphates having a low fusion temperature are fluxes, and are also widely used as electrolytes for deflocculating slips [6, p. 418].

TABLE 1. Characteristics of Raw Materials

Material	Content, *				
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3
Nizhnetagilsk blast furnace slag	29,3	16,8	33,4	11,4	0,4
Pobuzhsk thermic ore slag	47,9	7,2	23,2	9,1	11,6
Nizhneuvelsk fireclay	57,6	29,2	0,2	0,9	2,9
Vishnevogorsk pegmatite	68,5	20,5	0,8	0,3	0,5
Quartz sand	99,1	0,3	0,2	—	0,04
Bogdanovich chamotte from Nizhneuvel'sk clay	63,5	32,2	0,2	1,0	3,2

*The blast furnace slag contains, in addition, 7.5% TiO_2 and 0.8% S^2; the thermic ore slag, 2.8% Cr_2O_3, and the pegmatite 8.7% Na_2O.

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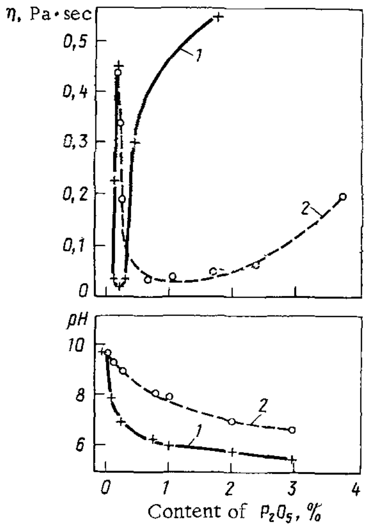

Fig. 1

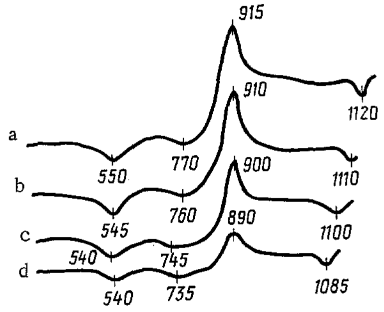

Fig. 2

Fig. 1. Change in viscosity η and pH of glaze suspensions as a function of the P_2O_5 concentration, added as orthophosphoric acid (1) and sodium polyphosphate (2).

Fig. 2. Differential curves DTA for glaze I without addition of sodium polyphosphate (a) and with additions of it in amounts (as P_2O_5) of 2 (b), 5 (c), and 10% (d).

In amounts of up to 20%* (on 100%) P_2O_5 was added to the glaze batch as orthophosphoric acid and sodium polyphosphate, containing up to 30% Na_2O and up to 60% P_2O_5 (GOST 20291-74). In selecting the original components for preparing glaze slips we considered the possibility of introducing them with surface-active agents V_2O_5, S^{2-}, etc. Metallurgical slags were used for this reason. The other raw materials consisted of pegmatite, quartz sand, chamotte, fireclay (Table 1), and water glass with a modulus of 2.8 and a density of 1.46 g/cm^3.

Six series of glaze batches (Nos. 1-6) were studied (Table 2). Using amounts of 10 kg per batch the original materials were milled together for 5-12 h in laboratory ballmills. The water content of the slip was 30-45%. Corundum-graphite articles obtained by semidry pressing were glazed by dipping in the slip and also by spraying. Orthophosphoric acid added in amounts of more than 0.01% caused the suspension to thicken. Alkaline phosphates added in amounts of 0.1-3.0% (calculated as P_2O_5), on the other hand, reduced the viscosity of the slip, and the glaze layer after drying was very strong and of uniform thickness without shrinkage cracks.

Specimens were fired in an industrial tunnel kiln at 1360-1390°C. Studies indicated that the glazes without slag and phosphates did not provide satisfactory protection against oxidation. The best results were obtained from compositions Nos. 5 and 6 and the addition of more than 1.5% P_2O_5. When smaller amounts of

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* Here and subsequently weight proportions are stated.

TABLE 2. Glaze Batch Compositions (%)

Component	Content of component* in series					
	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6
Quartz sand	45—95	—	15—55	15—55	—	—
Pegmatite	—	—	—	—	15—60	15—60
Chamotte	—	45—97	—	—	—	—
Clay	5—55	3—55	5—20	5—20	5—20	5—20
Blast-furnace slag	—	—	25—80	—	20—80	—
Thermic-ore slag	—	—	—	25—80	—	20—80

* Content of phosphate (as P_2O_5) in all batches was 0-20% (on 100%); water glass in amounts of 0-20% (on 100%) was added to series Nos. 1-4.

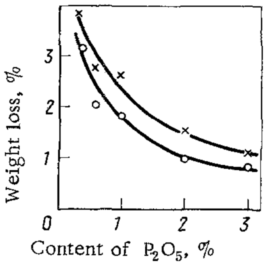

Fig. 3

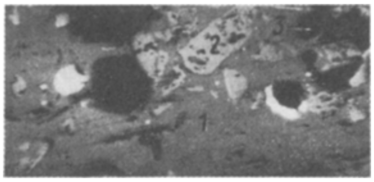

Fig. 4

Fig. 3. Effect of P_2O_5 on the burning-out of graphite during low-temperature firing (at 1200°C) of goods coated with glaze I (×) and II (○).

Fig. 4. Microstructure of specimen coated with glaze I: 1) glaze; 2) corundum of intermediate layer; 3) graphite; × 50; reflected light.

P_2O_5 were used the glaze had a clear tendency to run up into droplets. The optimum composition was (%): pegmatite 45-48, slag 38-42, clay 12-15, sodium polyphosphate (as P_2O_5) 2-3.5. Two glazes (I and II) can be proposed for industrial use: I, SiO_2 52.5, Al_2O_3 20.6, CaO 14.4, MgO 4.8, Na_2O 5.0, Fe_2O_3 0.7, P_2O_5 2.0; and II, SiO_2 58.2, Al_2O_3 16.2, CaO 9.7, MgO 3.9, Na_2O 4.8, Fe_2O_3 5.2, P_2O_5 2.0.

Figure 1 shows the pH and viscosity changes in the glaze slip (viscosity determined on the ÉVI-57P viscometer) as a function of the phosphate content. It should be mentioned that phosphoric anhydride prevents the oxidation of graphite [11], and sodium polyphosphate further reduces the temperature of the main physicochemical processes taking place in the glaze layer during firing (Fig. 2). Probably, these two factors are the cause of the reduction in the burning-out of the graphite in the low-temperature region (Fig. 3). Thus, the data obtained show that the optimum P_2O_5 concentration in the glaze lies within the range 2-3.5%.

The coating quality is markedly affected by technical factors: degree of milling the materials, temperature, and atmosphere in the kiln. The usual milling fineness for ceramic glazes is characterized by a concentration of fractions > 0.063 mm of 0.07-0.1% [8, p. 144]. This degree of milling for the glazes studied was not acceptable. Due to the high open porosity (more than 20%) of carbon-containing refractories the suspensions exhibit marked penetration; pinholes and other defects are formed in the coating. Furthermore, the finely milled glaze spreads at a lower temperature [6, p. 513] and during firing flows off the goods. It is established that the optimum fineness is characterized by a > 0.1 mm fraction of 1%. In addition the coarse-grained suspensions as a rule are unstable in sedimentation.

To eliminate segregation it is desirable to increase the concentration of sodium polyphosphate and increase the density of the slip to 1.68-1.73 g/cm^3. A favorable effect on the system's stability resulted from prolonged (20-30 h) mixing and heating the slip to 50-65°C, after which it was quite rapidly changed into the thixotropic condition and was characterized by complete sedimentation stability.

The spreading temperature for glazes I and II comes within the range 1340-1360°C, and can be corrected by altering the chemical composition. To prevent running of the glaze it is necessary to carefully observe the firing schedule, reduce the thickness of the coating, and use coarse-grained slips.

The firing atmosphere has a big influence on the quality. Glazed specimens of corundum-graphite refractory were fired in a furnace with silit heaters at 1380°C for 2 h in oxidizing (partial pressure of oxygen $\geq 10^{-2}$ MPa), reducing ($p < 10^{-11}$ MPa), and neutral ($p \simeq 10^{-4}$ MPa) atmospheres.

In reducing conditions the glaze curled up into droplets and did not protect the articles (crawling fault). The oxidizing atmosphere causes the bubbles to form in the glaze, and there is a certain deterioration in its protective properties. In a neutral atmosphere good coatings are formed without defects, and, apparently, it is more acceptable for firing glazed, carbon-containing refractories. The necessary condition for wetting the surface of the articles by the glaze is probably oxidation of the surface layer of graphite.

Figure 4 shows the microstructure of glaze coating on a corundum-graphite refractory. The thickness of the coat is less than 0.25 mm. The necessary strength of bonding with refractory is ensured by the development of an intermediate layer 0.1-0.2 mm thick, which is formed as a result of oxidation of graphite and interaction of glaze with the clay bond of the refractory.

Consequently, moderate oxidation of graphite at the surface of the article plays a positive role in forming a protective layer. The latter suggests that an individual gas phase should correspond to each phase of firing. For example, in firing corundum-graphite glazed articles it is necessary in the first stage (before the glaze melts) to maintain a moderate oxidizing atmosphere, and after melting — a neutral one.

It is of interest to assess the effect of iron oxides on the glaze quality. It is possible that the iron oxides play a double role here: firstly, they contribute to oxidation of the graphite from the surface layer of refractory, and secondly together with other variable valence oxides they may serve as sources of bubbles in the glaze layer with a sudden change in the composition of the gaseous medium. Glazes I and II have different concentrations of FeO + Fe_2O_3. The investigation showed that glaze II with the higher iron oxide content gives a better coating, and has better protective properties (Fig. 3) than the low-iron glaze I. Furthermore, it would be premature to ascribe definitely the observed improvement in the protective properties of the glaze to iron oxides as a result of the different chemical composition of the glazes. On the whole, the effect of variable valence oxides on the formation of protective coatings on carbon-containing ceramics is complex, and may constitute an object of independent investigation.

Industrial tests of glazes I and II showed that product loss during firing does not exceed 8-12%. The basic factors of the glazes are: P_2O_5 concentration 2%, density of slip 1.69 g/cm^3, water content 35%, thickness of protective layer not more than 0.4 mm, spread temperature 1360°C (glaze I) and 1350°C (glaze II), viscosity 0.8 Pa·sec (glaze I) and 1.2 Pa·sec (II).

CONCLUSIONS

It is possible to protect corundum refractories made by semidry molding during firing by using glazes based on metallurgical slags. Alkaline sodium polyphosphate can be used as a component improving the wetting capacity and other properties of the glaze and glaze suspension.

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