and zirconium inserts increased to a much lesser extent as the temperature was raised.

On the basis of the experimental and theoretical data we have plotted a nomogram for selecting the initial diameter of the stopper for drawing slabs of various sections in accordance with the level of the metal in the intermediate ladle and linear velocity of drawing (Figure 7). In order to make allowance for a certain narrowing of the orifice (particularly at the commencement of the pouring), the left-hand side of the nomogram shows two straight lines which make it possible to determine the working diameter of the nozzle, which has to be greater than the initial theoretical diameter.

The working surface of the tested nozzles and inserts after service was covered with a crust; the chemical composition of the crust is shown in Table 2. The crusts are basically made of vitreous metal, corundum, spinel and mullite (Figures 8 and 9).

These formations are basically interaction products of the oxidizers of the steel and the refractory, helping the channel to decrease in size during the pouring.

No corundum or mullite was observed on the working surface of the zirconium inserts. The inserts exhibited least closure during service.

CONCLUSIONS

The lining of intermediate ladles should be heated up to 1300 or 1400° in order to prevent the steel cooling excessively and in order to reduce the thermal shock experienced by refractories when the metal is being tapped.

The best results in continuous pouring of boiling steel are shown by chamotte nozzles with high-alumina inserts, and these are recommended for use.

In the continuous pouring of killed steel, the least filling in is observed in chamotte nozzles with zirconium inserts and with a clay-graphite layer; the clay-graphite layer, nevertheless, wears out more easily and this gives rise to an increase in the steel pouring rate.

The main reason for the closure of the stoppers is the formation on the working surface of a vitreous crust containing mullite, corundum, spinel formed by the aluminum added to deoxidize the steel.

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PHASE VARIATION WITH FORMATION AND DESTRUCTION OF OPEN HEARTH WORKING LAYER DURING SINGLE-LAYER REPAIRS

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During the last few years a progressive method of repairing hearths with one or two layers of metallurgical powder by briefly heating them and then slagging with scale has become very popular.

The use of this method has radically changed the nature of mineral formation, compared with multi-layer repairs with metallurgical powder and open-hearth slag.

The processes of mineral formation during multilayer repairs to hearths has been studied in detail [1, 2]; the processes occurring when single-layer repairs are made have not been adequately studied [3].

There are two methods of single-layer repairs: one using a magnesian-dolomite mixture [4], and the other using magnesite metallurgical powder by itself [5, 6].

Our study of the processes of the formation of hearths with the use of scale was carried out in large-capacity open-hearth furnaces operating by the scrap ore process and using liquid pig iron.

Samples of the hearths were taken just before repairs, after the powder loaded in the furnace had been preheated, after slagging of the hearth with scale, and after 1, 2, 3, 4, 5, 10, 15 and 20 melts.

Preventive maintanance using 1 or 2 layers and scale was conducted by the conventional method [7].

The melts during the period between repairs were numbered starting at the first melt after the latest studied repair.

The samples taken were chemically analyzed and studied mineralogically.

The variations in the chemical composition of the hearth working layer are shown in Figure 1 (for hearths repaired without dolomite see an earlier publication).

The mineralogical composition and microstructure of the hearth are considerably modified during the repairs.
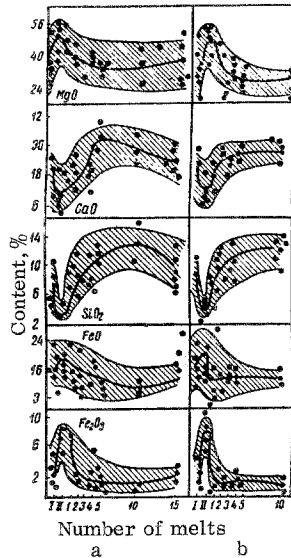

Fig. 1. Composition of oxides in hearths repaired with mixture of 75% of MPK powder and 25% dried dolomite:

a – uncovered hearth; b – hearth covered with metal; I – composition just before repairs; II – composition of repaired hearth; subsequent samples taken after charge melted (under metal) and after tapping of melt (uncovered hearth).

When metallurgical powder is introduced into the furnace, there is an increased amount of cracking in the larger fragments (grains) of the powder, evidently on account of thermal shock (Figure 2a). The cracks sometimes become filled with slag left on the hearth or dripping from the walls (Figure 2b). There is hardly any change in the periclase crystals in aggregates, whether impregnated or not impregnated with slag.

After the metallurgical powder has been slagged with rolled scale, the gaps between grains fill up with liquid oxides. Fine fragments of powder and separate periclase crystals dissolve in the ferruginous melt, raising its melting point. There is penetration of the FeO into the peripheral areas of the larger aggregates of periclase crystals at the same time, accompanied by formation of a solid solution of bivalent iron in the crystal lattice of the periclase; this intensifies the growth of its crystals (Figure 2c).

The dissolution of fine periclase grains in the ferruginous melt and the saturation of the peripheral areas of larger periclase aggregates with iron oxide blends the composition at the point of contact between grains and binder, causing disappearance of clear-cut boundaries between the ferruginous binder and magnesian filler.

The densification of the working layer due to intensive recrystallization of the periclase crystals and to the minimum content of non-refractory silicate binder between them helps to create a hearth, stable during operation, with a minimum amount of time spent on the repairs.
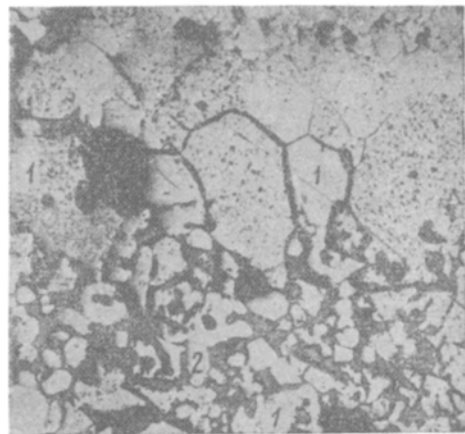
As distinct from this, the formation of a working layer of
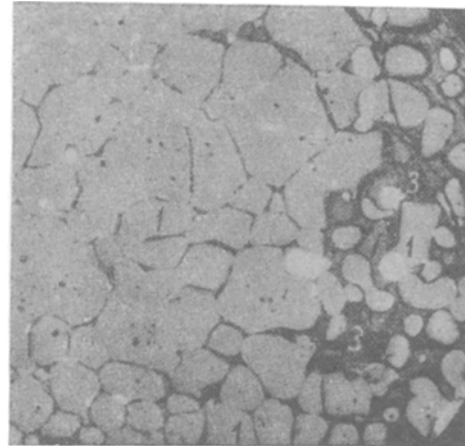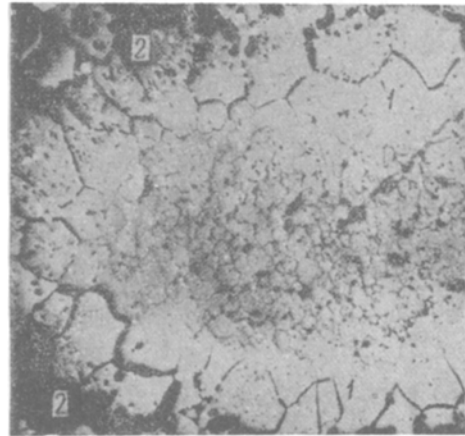
Fig. 2. Microstructure of working layer of hearth at different times during repairs:

1-periclase; 2-magnesio-wustite; 3-calcium silicates; 4-pores and cracks; a-periclase grains (pseudomorph after magnesite) when metallurgical power has been charged in furnace during repairs; b-periclase aggregates after heat-up of layer of powder; c-working layer of repaired hearth after slagging with scale. × 18.5. Reflected light.

hearth during multilayer repairs with metallurgical powder and slag is not accompanied by recrystallization of the periclase, since the slag components do not promote the growth of the periclase crystals when heated [9].

The densification and formation of a fairly wear-resistant working layer during multilayer repairs to hearths with slag were ensured by uniform distribution of the slagging material between the powder grains and between the periclase crystals in them. To make the distribution of the slag uniform, the metallurgical powder needed to be heated for some time (more than 5 hours) and was applied to the hearth in thin layers of 10-20 mm.

Distribution of the non-refractory binder between the periclase crystals aided in their rapid elution and dissolving in the melt reagents; hence multilayer hearths made of metallurgical powder and slag proved less wear-resistant than single layer repairs with scale.

During operation the hearth is in contact with the ore, then with the liquid steel and, finally, with the melted slag.

The sequence used at most metal works for loading non-metallic charge components precludes the possibility of contact between the hearth and the line. The latter may only find its way into the hearth if the steel-smelting techniques are violated.

The sequence of contact between reagents is maintained throughtout the period between repairs, thus furthering the corresponding variation in chemical and mineralogical composition of the hearth.

During the first melt the hearths repaired with scale show a reduction in the iron oxide content on account of dilution of the original components of the working-layer binder with melt reagents, and there is transition of some of the iron oxides into the liquid steel [8, 10].

TABLE 1

VARIATION IN SiO_2, IRON OXIDE, CaO AND CONTENT, WEIGHT %, IN HEARTH DURING FIRST AND SECOND MELTS*

Period of melt	Distance from working surface, mm	First melt				Second melt			
		SiO_2	Fe_2O_3**	CaO	MgO	SiO_2	Fe_2O_3**	CaO	MgO
After scale slagging	0—15	6,2	36,3	8,1	44,8	—	—	—	—
	7	5,4	22,4	5,6	64,0	7,1	17,8	23,1	39,0
Fusion	15	4,6	13,6	9,4	62,7	—	—	—	—
	7	8,9	24,7	19,7	39,7	6,0	33,7	16,7	37,5
Tapping steel	15	9,7	20,0	20,9	39,1	5,7	36,3	11,5	39,0

*Repairs carried out with MPK powder
**All iron in terms of Fe_2O_3.

TABLE 2

VARIATION IN ACTIVITY OF HEARTH, PULSE/MIN

Sample of hearth		Activity of sample at distance from working surface, mm					Activity	
Melt	No. of charging window*	7	15	23	30	37	Slag	Steel
End of fusion	1	37	10	10	7	3	} 12	115
	5	1	0	1	0	0		
Tapping of melt	1	16	18	16	—	—	} 8	105
	5	2	5	1	3	2		

*Ore containing radioactive Fe^{59} only loaded through first window.

This transition is only possible when there is more than 35-45% iron oxide in the hearth (Table 1).

Determination of the activity of samples from the hearth metal and slag taken while the furnace is operating enables us to determine the transfer of radioactive iron in the acid state from the ore to the hearth; no transition of iron to the hearth from the liquid bath was observed (Table 2).

Since the working layer of the hearth, both on a macro- and micro-scale, is not a homogeneous material, the chemical composition of an average sample is not an indication of the phase changes proceeding when the hearth reacts with the ore, steel and slag. For the purpose of elucidating these changes, the samples taken were viewed in reflected light under the microscope.

When in contact with the ore during fusion, the hearth first reacts with the melt appearing as the ore is heated up.

The probability of fayalite appearing during the process and then reacting with the hearth is confirmed by the varia-tion in mineralogical composition of its binder. Enrichment of the hearth with silica from the silicate ore component transfers the composition of the hearth binder to the region of primary merwinite crystallization (Figure 3a).

During subsequent contact between the repaired layer and the liquid steel there is a shift in the iron surplus to the bath, and redistribution of it within the larger magnesite grains. The difference between the FeO concentration in the peripheral and central areas of periclase crystal aggregates either disappears or is reduced.

The silicate content in the binder is slightly increased.

When the working surface of the hearth comes into contact with slag during tapping of the melt, there is a change in the composition of the binder between the magnesite grains. The boundaries of the larger periclase grains acquire a sharp outline and the magnesian ferrugineous compounds and the merwinite in the binder almost completely disappear. They are replaced by olivine glass and bicalcium silicate crystals. The growth of the peripheral pericalse crystals in the larger
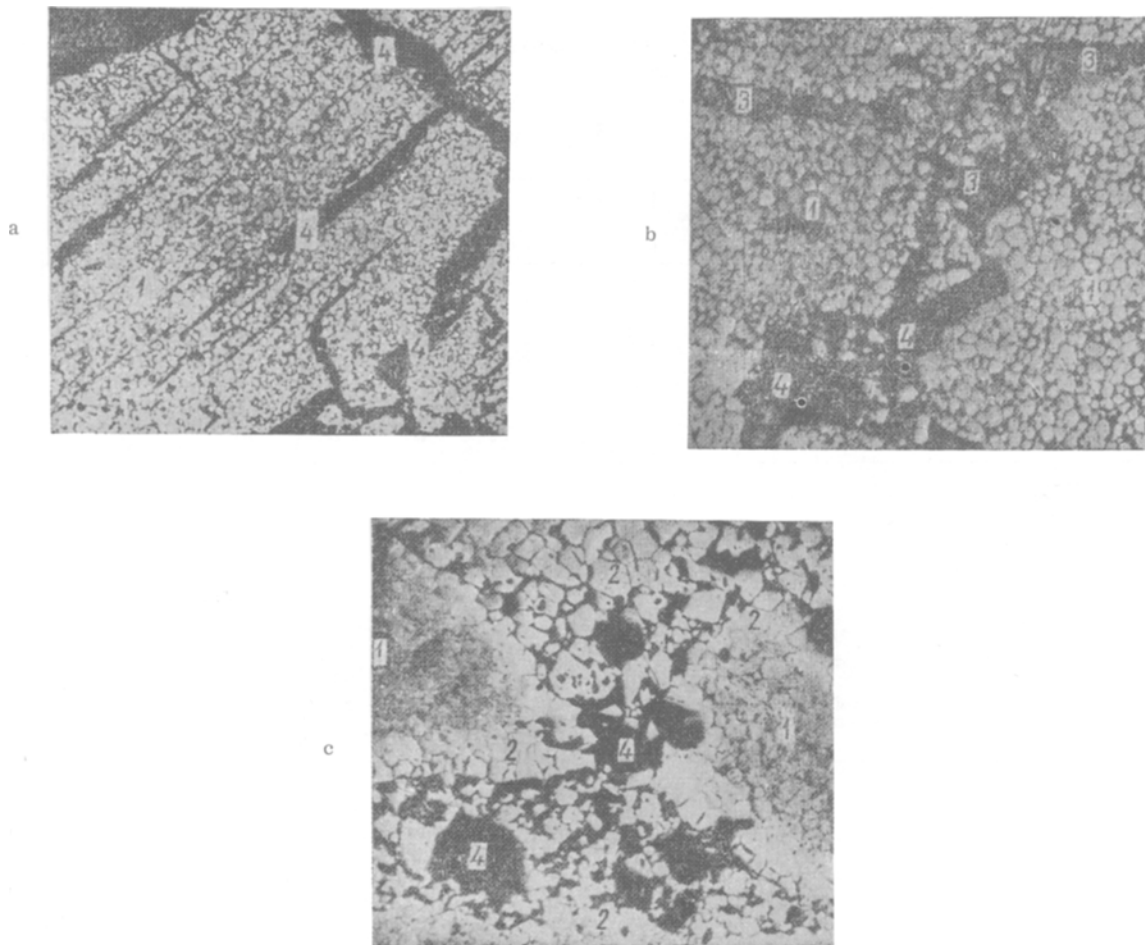

Fig. 3. Microstructure of working layer of hearth during
operation; reflected light:

1-magnesio-wustite; 2-calcium silicate; 3-merwinite;

a-at end of first melt, x 86; b-after tapping first melt, x 18.5;
c-after tapping third melt, x 18.5.

periclase aggregates continues, and radial cracks appear, separating the larger crystals (Figure 3b). The cracks then fill up with binder melt, their dimensions increase and the larger periclase crystals separate from the aggregates. As they enter the binder, the periclase crystals dissolve in it (Figure 3c).

When they come into contact with the slag from the first melt, the merwinite crystals only disappear in the contact layer (a few mm thick). During the second melt, the bicalcium silicate in the binder disappears and the merwinite reappears.

The relatively slight penetration of calcium silicates into the hearth after the first melt is due to the absence of bumps or cavities in the hearth, which means that the slag can be removed completely and speedily from the furnace. From then on the unevenness of the hearth makes it easier for the slag to accumulate on it and to penetrate to a great depth, on account of which bicalcium silicate predominates in the binder composition. The merwinite in the binder disappears completely after the fifth or sixth melt, irrespective of the time at which the sample is taken.

Merwinite crystals can be observed most clearly in hearth samples at the end of the second or third melt (Figure 4).
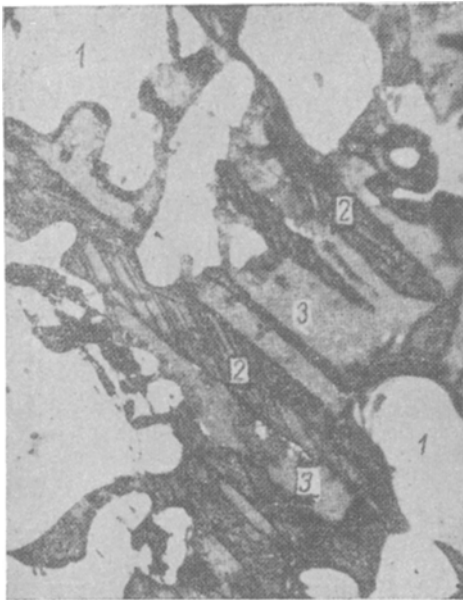

Fig. 4. Merwinite crystals in hearth binder after fusion:

1-periclase; 2-merwinite; 3-glass. x 200. Reflected light.

The study of a large number of samples under the microscope suggests that hearths repaired with metallurgical powder and scale consist of large magnesite powder grains, saturated to a greater or lesser degree with iron oxide, and of lime-silicate binder with a complex composition changing according to operational conditions.

The magnestie grains become enveloped in binder, the

composition and amount of which also conditions the rate of wear of the hearth.

Investigation of samples taken from the hearth at various periods during repairs and smelting suggests that the binder composition is limited to the region of the minerals $2CaO \cdot SiO_2 - 3CaO \cdot MgO \cdot MgO \cdot 2SiO_2 - CaO \cdot MgO \cdot SiO_2 - CaO \cdot FeO \cdot SiO_2$.

Monticellite and ferrimonticellite are rarely encountered on account of the formation of olivine glass from these two minerals. The solid phase under operational conditions is represented by magnesio-wustite.

If we disregard a certain amount of Al_2O_3, the region where there are binder and refractory hearth components may be located on the equilibrium diagram $SiO_2 - CaO - MgO - FeO$ [8]. Here the composition of the refractory components in the magnesio-wustite lies on the straight line MgO-FeO.

The region of the magnesio-wustite is extensive. In a $CaO - SiO - MgO - FeO$ section it stretches almost as far as the straight line $CaO \cdot MgO \cdot SiO_2 - CaO \cdot FeO \cdot SiO_2$, and borders close to this line on the region of olivines formed through mutual dissolution of the magnesian and ferruginous orthosilicates as well as ferromonticellite and monticellite.

The interface between the magnesio-wustite and the olivines stretches as far as the intersection with the $MgO - SiO_2 - FeO$ plane, somewhat below the straight line $2FeO \cdot SiO_2 - 2MgO \cdot SiO_2$.

The region of the silicate binders of the hearth is located in the plane $2CaO \cdot SiO_2 - CaO \cdot MgO \cdot SiO_2 - CaO \cdot FeO \cdot SiO_2$ which intersects with the plane already considered $CaO \cdot SiO_2 - MgO - FeO$, or lies between them.

At the present time it is only the triangle $CaO \cdot SiO_2 - CaO \cdot MgO \cdot SiO_2 - CaO \cdot FeO \cdot SiO_2$ which has been studied, hence the temperature at which the liquid phase appears in the bond can only be determined approximately from the diagram $CaO \cdot SiO_2 - 2CaO \cdot SiO_2 - CaO \cdot MgO \cdot SiO_2 - CaO \cdot FeO \cdot SiO_2$. Nevertheless analysis of this diagram may help to assess the wear resistance of a hearth containing a particular binder.

Figure 5 is a schematic representation of the region of primary crystallization of the minerals or existence of solid solutions of the tetrahedron under consideration.

Some simplifications we have made in the representation of the boundary lines and surface do not affect the size of the areas they enclose. In the drawing the shaded area shows possible compositions for the hearth binder.

Judging by the temperatures of certain points on the diagram, the refractoriness of the binder drops when the SiO_2 content, and particularly FeO content, are increased; these oxides are therefore considered agressive reagents.

The saturation of the hearth with silica is considered most desirable, since by entering the hearth it is transferred completely to the binder, shifting the composition of the latter from the region of primary crystallization of high-refractory bicalcium silicate to the region of relatively light-melting olivines. According to petrographic investigation, the iron oxides present in the hearth are mainly compounded with MgO, forming magnesio-wustite with a melting point of about 2000°.

Study shows that the basic reagents affecting the composition of the binder, and therefore the operational characteristics of the hearth are ore and slag.

The composition of the binder and the reduction in its refractoriness during the melt are due to the transition of silica
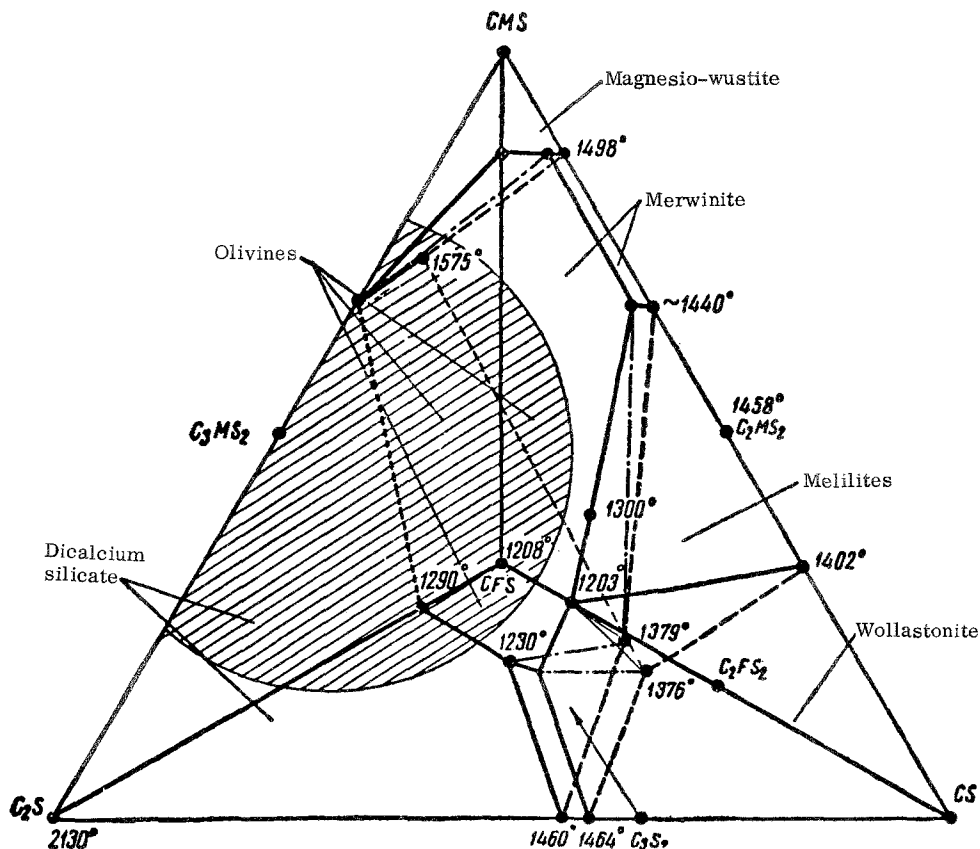
Fig. 5. Equilibrium phase diagram for system $2CaO \cdot SiO_2$ - $CaO \cdot MgO \cdot SiO_2$ - $CaO \cdot FeO \cdot SiO_2$ - $CaO \cdot SiO_2$.

—— lines on planes C_2S - CMS-CFS, C_2S-CS and CMS-CFS-CS; ---- lines on plane C_2S-CMS-CS; ······ assumed lines; —·—·— lines in tetrahedron.

and iron oxides from the ore to the hearth. The erosion of the upper working surface of the hearth with an increase in the amount and variation in the chemical composition of the binder during the final firing is due to the high temperature and mechanical effect of the bath on the hearth. During this period manganese oxides move from the bath to the hearth and iron oxide surpluses move from the hearth to the bath.

The amount of binder is increased when the steel is tapped, owing to saturation of the hearth with slag. Erosion of the upper working layer of the hearth with an increased amount and modified chemical composition of the bond during the final firing is due to the high temperature and mechanical effect of the bath on the hearth. During this period manganese oxides are transferred from the bath to the hearth and iron oxide surpluses from the hearth to the bath.

The amount of binder is increased when steel is being tapped owing to the saturation of the hearth with slag.

The relatively permanent chemical composition of the working layer during the period between repairs is due to the content in it of 30-35% MgO. Further saturation of the hearth with silicates increases the amount of binder beyond the norm and reduces the MgO content. The area of the working layer with an increased silicate content can easily be washed off with liquid steel. There is removal of the re-action layer during every melt.

The uneven surface formed on the hearth helps the slag

to accumulate, promotes nonuniform saturation of the working layer and causes a reduction in its service life.

An increase in the service life of the hearth can be brought about if the recrystallization of the periclase component during repairs is as complete as possible; if the reduction in the silicate content in initial materials is maximum; if the time over which the hearth is in contact with the ore and slag is reduced; and if no overheating of the liquid steel is permitted. Immediate repairs when unevenness occurs on the hearth and removal of the slag from it also helps to increase the stabil-ity of the hearth.

Volumetric changes in the hearth can only be due to var-iable temperature.

Volumetric changes associated with the oxidizing-reducing processes, no matter whether the furnace is charged or not, should not be expected on account of the presence of a con-stantly reducing medium at the contact point between the hearth and the flames in the working layer of the open-hearth.

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RESEARCH WORK

TECHNOLOGICAL FEATURES OF CASTING ZIRCONIA PARTS

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The technique of casting zirconia parts from aqueous suspensions of stabilized zirconium dioxide is of definite practical value, despite its complexity and laboriousness.

The parts are cast from slurries with a relatively low moisture content and the green ware is fairly dense and strong, which keeps the shrinkage down during firing and reduces the possibility of flaws occurring during this technological process [1-3].

The method makes it possible to use parts made from "damp" mixtures which had been spoiled by firing. The method is also useful for the manufacture of zirconia parts with improved thermal stability by synthesizing them from cubic ZrO_2 with the addition of monoclinic ZrO_2 [4-6].

As a result of a number of investigations [1-3, 7-9], a technological procedure has been worked out for water casting parts from stabilized ZrO_2, and the possibility has been shown in principle of casting parts both in acid and alkaline mediums.

The following methods have been put forward for finely pulverizing the material: a) rubber lined mills with zirconia balls producing "alkaline" slips; b) steel mills with subsequent treatment of the material with hydrochloric acid to remove the iron, producing "acid" slips.

The technological advisability of these methods of preparing the material, however, the acid treatment and casting of the parts in different media have not been described adequately in technical literature.

This article is devoted to the study of these processes.

For the investigation we used zirconium dioxide stabilized with 6% CaO. The industrial zirconium dioxide contained 97.55% ZrO_2 and 1.15% TiO_2. The initial materials were industrial ZrO_2 and $CaCO_3$ (type 'ch') and were pulverized in ball mills by the wet method. The zirconium dioxide spent 40 hours in the metal mill, after which it was washed with HCl and decanted with water unitl the pH value was 3; the $CaCO_3$ was ground in a rubber-lined corundum-ball mill for 15 hours. The amount of corundum impurity was not more than 0.2% of the CaCO weight.

The materials were mixed by the slip method and then dehydrated; the mixutre was dried, pulverized and pressed at 500 kg/cm² into cylindrical compacts 50 mm in diameter and length. The compacts were fired at 1750° for 2 hours. the fired compacts were then ground in jaw and roller crushers, the powder was passed through a 0.5 mm screen and then underwent magnetic separation. Microscopic and x-ray analyses showed virtually complete stabilization of the zirconium dioxide in the fired products.

The slip for casting the parts was made with powder by two methods:

a) by the wet method of grinding for 80 hours in a rubber-lined mill with zirconia cylinders or in certain cases with corundum balls. The weight ratio of the balls, material and water was 2.5 : 1 : 1. The zirconia were made as rolled stabilized ZrO_2 cylinders 15-20 mm in diameter and height; the bulk density of the cylinders was 5.1-5.3 g/cm³ and their porosity 1-2%.

The grinding impurity resulting from abrasion of the zirconia cylinders amounted to 40% of the weight of the zirconium dioxide charged. A grinding time of 80 hours was selected on the basis of [1] which states that 52 hours grinding produces adequate dispersion of the material.

b) by the wet method of grinding in a steel mill for 45, 60, 80, 100 and 120 hours with similar load ratios and subsequent treatment with hyrdochloric acid and decantation with water to a pH value of 1.5-1.7 (bulk); the effect of the difference in the pulverization time was studied since there is no relevant data on steel-mill grinding.

Thus, for our work we used two types of initial slip: alkaline slip with a pH value of 10.5 and acidic slip with a pH value of 1.5-1.7.

Study of the castability of alkaline slip. Sedimentation analysis of diluted slip suspensions shows that in the alkaline medium the ZrO_2 particles are present in a more aggregated state than in an acid medium at a pH value of 2.0-2.5 (Fig. 1).

The number of ZrO_2 particles less than 5 microns, even in the acid medium, did not exceed 36%, whereas the