

GRANULAR-STRUCTURE CHROMIUM-BEARING REFRACTORIES: PROPERTIES AND USES

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Results are presented on the corrosion resistance of chromium-bearing refractories of granular structure acted on by corrosive molten slags, metals, and glasses. It is possible to recommend these refractories to customers for particular conditions of use. Chromium-bearing refractories increase the working lives of furnaces considerably.

Innovative technologies are being widely introduced in ferrous and nonferrous metallurgy, the chemical industry, the petroleum industry, the building industry, and other such, which is related to a considerable extent to intensify high-temperature processes in furnaces. This greatly increases the importance of refractory materials that must provide prolonged operation [1].

About two-thirds of refractory materials are damaged by chemical interaction with corrosive media, so particular attention attaches to research to improve existing refractory materials and produce new ones for use at high temperatures subject to the action of corrosive liquids: slags, fluxes, glasses, glazes, and enamels [2].

The Bakor Company has for more than 15 years developed and produced refractory materials and components providing prolonged service in important lining elements [3]. The materials most resistant to various corrosive media are highly refractory ceramic ones containing chromium oxide [4, 5]. Research at the company has provided a technology for making various chromium-bearing refractory materials of granular structure resistant to corrosive melts and of thermal resistance elevated by comparison with dense materials [6]. Figure 1 shows the scheme for producing them. Table 1 gives the physicochemical properties of these chromium-bearing refractories.

The research included the reactions of corrosive melts of various types with the chromium-bearing refractories of granular structure developed by the company. The crucible method [7] was applied to the corrosion resistance. This method is a static one for testing materials for corrosion resistance in corrosive liquids, which quite fully reproduces

the corrosion conditions for refractory materials in furnaces. The crucible method also gives a clear idea of the corrosion resistance at the level of the liquid under conditions of three-phase separation.

The test specimens were made as cylinders (diameter and height 60 mm) or as cubes of edge 60 mm with recesses of diameter 22 mm and depth 35 – 40 mm. The crucibles contain materials for making liquids. The heat treatment was in a muffle furnace with chromite-lanthanum heaters at temperatures corresponding to the actual working conditions. After test, the specimens were sectioned parallel to the axis of the hole and photographed. To examine the damage mechanisms and phase transformations we performed micro-

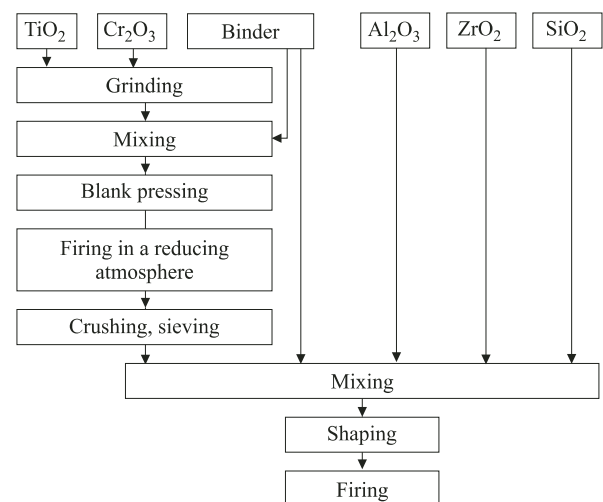


Fig. 1. Scheme for making granular-structure chromium-bearing refractories.

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TABLE 1. Physicochemical Properties of Chromium-Bearing Refractories Developed by the Bakor Company

Parameters	KhATs-T	KhKT-10,30	KhKT-45	KhKT-60	KhS-MVU
Composition, wt. %:					
Al ₂ O ₃ , not less than	32.0	68.0	50.0	33.0	–
ZrO ₂ , not less than	18.0	–	–	–	–
SiO ₂ , not more than	14.0	–	–	–	–
Cr ₂ O ₃ , not less than	28.0	10 – 30	45.0	60.0	92.5
TiO ₂ , not more than	–	–	2.0	3.0	4.0
Apparent density, g/cm ³ , not less than	3.1	2.8	3.4	3.6	4.2
Open porosity, %, not more than	17.0	19.0	18.0	18.0	18.0
Compressive strength, MPa, not less than	75.0	50.0	75.0	75.0	100
Temperature for start of deformation under load, °C, not less than	1700	1650	1750	1750	1720
Thermal resistance (1300°C – water) thermal cycles, not less than	8	6	5	3	1

scopic and petrographic tests in immersion specimens. The laboratory tests on the corrosion of these chromium-bearing refractories are given below for various corrosive liquids.

Effects of molten glass E (*Stekloplastik Company, Stupino*) on the corrosion resistance of chromium-bearing refractories. The chemical composition of glass E in mass % is SiO₂ 54, Al₂O₃ 15, MgO 5, CaO 17, B₂O₃ 9; test conditions: heating rate 150 – 200°C/h to 1500°C, hold 8 h. The following are the petrographic results after test in molten glass E:

- KhKT-10** After the glass had melted, it impregnated the refractory on the pore structure. The reaction involved dissolution of the binder components. The glass (at the surface) was amorphous with zoning and crystallization nuclei for that glass. With the lapse of time, the glass crystallized completely. The liquid impregnated the refractory completely, and when the concentrations of the components of the binder dissolved in the liquid attained a certain level, there was crystallization in the pores. The grains of electromelted corundum remained unaltered.
- KhKT-30** There was no impregnation. At the boundary between the glass and the refractory one could not say whether there was microcracking with any certainty.
- KhKT-45** The material impregnates the refractory on the pore structure, but the impregnation zone is narrower by a factor 2 than in KhKT-60 refractory; there were microcracks.
- KhKT-60** The liquid impregnates the refractory. There is no interaction between the liquid and the refractory material. As there are differences in thermal-expansion coefficient between the zones in the refractory impregnated and not impregnated by the liquid, it is possible for the refractory to fail on cooling. At the boundaries between corundum grains and the liquid glass, there were microcracks due to the difference in thermal-expansion coefficient of α -Al₂O₃ and the glass.
- KhS-MVU** In the contact zone between the glass and the material there were microcracks 6 – 7 μ m long distributed parallel to the contact surface. There was no impregnation on the pore structure, and no reaction between the liquid and the refractory material. The solidified liquid was a glass without crystallization nuclei.

Figure 2 shows the specimens after test.

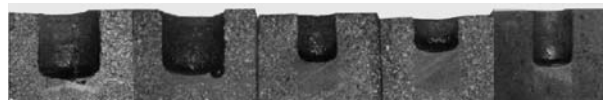


Fig. 2. Chromium-bearing refractory specimens after test in molten glass E: from left to right: KhKT-10, KhKT-60, KhKT-45, KhKT-30, KhS-MVU.

Materials KhKT-30 and KhS-MVU are thus stable in molten glass E.

Effects of molten glass S (*IRSA Company, Serpukhov*) on the corrosion resistance of chromium-bearing refractories. Chemical composition of glass S, wt. %: SiO₂ 62.8, Al₂O₃ 2.0, MgO 3.6, CaO 7.8, B₂O₃ 5.0, R₂O 18.8. Test conditions: heating at a rate of 150 – 200°C/h to 1400°C, hold 8 h. Petrographic data on chromium-bearing refractories after test in molten glass S are as follows:

- KhKT-10** The refractory material is impregnated by the molten glass by corrosion of the binder. It dissolves completely, while the electromelted corundum does not interact with the liquid. The TiO₂ recrystallizes through the liquid state.
- KhS-MVU** The glass components crystallize at the walls of the pores, which they enter through the vapor state. A large amount of the chromium is transferred to the glass through that state, but it does not cause the glass to crystallize, although it should alter the technological characteristics of the liquid. No reactions between the refractory and liquid are observed. The surface material in the refractory is very readily wetted by the liquid, but this does not lead to cracks in the refractory. There is no impregnation through the pore structure.

The specimens after test are shown in Fig. 3.

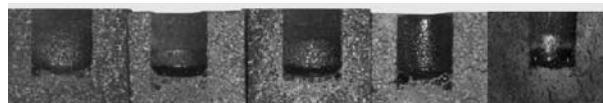


Fig. 3. Chromium-bearing refractory specimens after test in molten glass S. From left to right: KhKT-10, KhKT-30, KhKT-45, KhKT-60, KhS-MVU.

Then the KhS-MVU material is stable in molten glass S.

Effects of mineral fiber liquid (VKSM Company, Voronezh) on the corrosion resistance of chromium-bearing refractories. The mixture for making the mineral fiber had the following wt.% composition: SiO₂ 49.06, TiO₂ 1.36, Al₂O₃ 15.70, Fe₂O₃ 5.38, FeO 6.37, MnO 0.31, K₂O 1.52, P₂O₅ 0.45, H₂O 1.62. Test conditions: heating at 150–200°C/h to 1480°C, hold 8 h. Petrographic analysis after testing in the liquid mineral fiber gave the following:

- KhKT-60 The liquid impregnates the refractory completely. There is no interaction between the liquid and the refractory. When the item works with temperature differences, there is a high probability of cracking and failure arising from the differences in thermal expansion coefficient between zones of the refractory impregnated and not impregnated by the silicate liquid.
- KhKT-30 The liquid does not wet the refractory material, so pore-space (structure) impregnation does not occur. Some of the Cr₂O₃ from the refractory passes into the liquid.

Figure 4 shows the specimens after test.

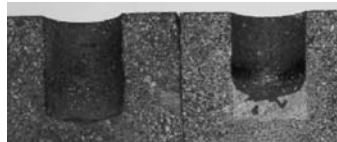


Fig. 4. Chromium-bearing refractory specimens after test in a mineral fiber liquid. From left to right: KhKT-60, KhKT-30.

The KhKT-30 material is stable in molten mineral fiber.

Effects of a basalt fiber liquid (Thermal Insulation Plant Ltd, Dmitrov) on the corrosion resistance of chromium-bearing refractories. The charge for making the basalt fiber had the following wt.% composition: SiO₂ 46.2–49.7, Al₂O₃ 13.9–16.9, TiO₂ 1.3–3.1, MgO 7.9–9.7, CaO 6.6–11.9, Fe₂O₃ 1.0–5.6, R₂O 2.6–8.0. Test conditions: heating at 150–200°C/h to 1400°C, hold 8 h. Petrographic examination after test in the basalt fiber liquid gave results as below:

- KhKT-10 When the basalt melts, the liquid interacts with the binding agent and filler in a working zone of width 2–3 mm. When the binder interacts with the liquid, mullite and calcium aluminates crystallize; the chromium oxide enters into solid solutions with corundum and titanium; the valencies of the chromium vary. The grains of electromelted corundum are corroded and a mullite crust is formed; the working impregnation zone does not proceed further.
- KhKT-30 When the basalt melts, the liquid does not interact with the refractory (neither with a filler nor with the bonding agent). In pores at the surface of the crucible wall, mullite crystallizes from the liquid with a crystal size of 8–16 μm (positive effect of chromium), and there is also crystallization of calcium aluminates, and solid solutions of Fe₂O₃ and FeO. As a result, the pores at the contact surface with the liquid are closed and no further impregnation occurs.

KhKT-45 After the basalt melts, the liquid does not interact with the refractory (neither the filler nor the binder). In the pores at the surface of the crucible, mullite crystallizes from the liquid with a crystal size less than 8 μm (positive effect of chromium), together with calcium aluminates and solid solutions of wüstite in fayalite (dendritic structures). The chromium partially passes into the liquid. Part of the liquid does not crystallize, while microcracks occur because of the differences in thermal expansion coefficient.

KhKT-60 After the basalt melts, the liquid impregnates the refractory through the pore structure and interacts with the grains of electromelted corundum, with the formation of mullite, solid solutions of chromium in mullite, and so on. The sizes of the mullite crystals vary (from 2–3 μm in the presence of chromium, which retards the growth of the mullite crystals). The extensive diffusion of chromium into the liquid alters its physico-chemical characteristics.

KhS-MVU It is not found that the material interacts with the basalt liquid. In the pores at the surface there is liquid in an amorphous state containing a small number of crystallization nuclei; the liquid is enriched in chromium oxide.

Figure 5 shows the specimens after test.



Fig. 5. Chromium-bearing refractory specimens after test in basalt fiber liquid. From left to right: KhKT-10, KhKT-30, KhKT-45, KhKT-60, KhS-MVU.

Material KhKT-30 is thus stable in a basalt fiber liquid.

Effects of a liquid from a charge for making steel (Oskol'sk Electrometallurgical Corporation) on the corrosion resistance of chromium-bearing refractories. The charge contained up to 20% of the following impurities: 2CaO, SiO₂ (larnite), CaO·MnO·FeO·SiO₂, MgO·Fe₂O₃ (magnesiowüstite), FeO (wüstite), and so on. Test conditions: heating at a rate of 150–200°C/h to 1600°C, hold 32 h. Petrography after test gave the following results:

- KhKT-10 The liquid does not wet the surface but forms drops on the surfaces of the grains of chrome spinel and corundum. Impregnation and interaction do not occur. There is some reduction in the open porosity, which is evidently due to partial sintering.
- KhKT-30 The liquid does not wet the surface but forms drops on the grains of chrome spinel and corundum. Impregnation and interaction do not occur. The diffusion of chromium into the corundum leads to partial sintering.
- KhKT-45 The pore structure is impregnated by the liquid composed of metal and impurities, after which the liquid begins to interact with the chrome spinel with the formation of silicate liquids of more complicated phase composition (monticellite CaCr₂O₃·SiO₄). The resulting liquid does not crystallize but remains in the amorphous state and is distributed in the matrix of the

refractory in the form of thin layers at the boundaries of the chrome spinel grains. There is an interaction between the chrome spinel phase and the metal involving the formation of Cr_2O_3 -metal solid solutions, with the reduction of the chromium to the metal. This increases the diffusion of Cr_2O_3 in the corundum. The structure of the refractory becomes more open with the formation of branching microcracks, which arise from the difference in thermal-expansion coefficient between the matrix and the Cr_2O_3 -metal solid solution.

KhKT-60 The refractory material is impregnated on the pore structure by the liquid, after which there begins vigorous interaction between the liquid and the chrome spinel: the chrome spinel dissolves in the liquid with the crystallization of phases with more complicated compositions. The corundum is inert in relation to the liquid and is not wetted by it. There are branching microcracks in the body of the refractory (structural opening up), which evidently is due to the differences in thermal-expansion coefficient for the chrome spinel phases formed by the interaction.

Figure 6 shows the specimens after test.

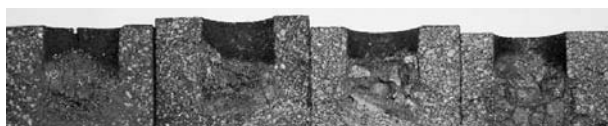


Fig. 6. Chromium-bearing refractory specimens after test in a liquid produced from a charge for making steel. From left to right: KhKT-60, KhKT-45, KhKT-30, KhKT-10.

The KhKT-10 and KhKT-30 materials are not wetted by the liquid in this case and do not interact with it.

Effects of liquid slags used in melting steel (Sib-elektrostal' Company) on the corrosion resistance of chro-

mium-bearing refractories. Table 2 and Fig. 7 show the results from petrographic analysis of these refractories after testing in a liquid composed of the slag from electrosteel melting. Test conditions: heating at a rate of 150–200°C/h to 1630°C, hold 8 h.



Fig. 7. Specimens of KhKT-10 refractory after testing in slags Nos. 1–4 from electrosteel melting (from left to right).

Material KhKT-10 is stable on exposure to the liquid of slag No. 1.

Effects of liquids from experimental slags (MISiS) on the corrosion resistance of chromium-bearing refractories. Table 3 gives the chemical compositions of the slags. Test conditions: heating at a rate of 150–200°C/h to 1560°C, hold 24 h. The following are the results from petrography after test in the experimental slags:

Slag No. 1

KhKT-30 The liquid impregnates the material to a depth of up to 1 mm. The surfaces of the corundum grains in the impregnation zone form solid solutions of chromium oxide with aluminum oxide. The slag in the pores crystallizes. The liquid does not interact with the material. At the material-liquid boundary there is a clearly defined zone of width up to 400 μm characterized by numerous bubbles of gas with sizes from 20 to 70 μm; the slag crystallizes completely.

KhKT-45 Liquid completely impregnates the material. The slag crystallizes in the pore structure with the formation of small crystals, with part of the liquid remaining in the

TABLE 2. Petrographic Analysis Results for KhKT-10 Chromium-Bearing Refractories After Testing in Liquid Slags

Slag composition, %	Main crystalline phases	Analysis results
CaO 35.3, FeO 1.1, MgO 10.0 (slag ¹ 1)	Larnite (calcium flux, dicalcium silicate); short prismatic crystals of monticellite (CaMgFe) SiO_4 ; grains of MgO (from additive for purifying metal) ranging from transparent to brown (magnesite spinel); free iron not observed	Interactions between slag and refractories not observed. Impregnation occurs in the pore structure of the refractory binder, matrix grains not affected. The surfaces of the spinel binder grains are not wetted by the liquid. If subsequently the chrome passes into the liquid, wetting and refractory cracking occur
CaO 29.7, FeO 0.6, MgO 10.0 (slag ¹ 2)	Monticellite (CaMgFe) SiO_4 ; merwinite; tricalcium silicate (small amounts); a little free CaO; free iron oxide present	The liquid impregnates the refractory completely and forms layers around the grains of binder and electrocorundum of thickness 2–4 μm. Dissolution in the vitreous phase occurs for some grains of electrocorundum
CaO 44.5, FeO 7.7, MgO < 10.0 (slag ¹ 3)	Monoclinic prismatic crystals of larnite; small amounts of monticellite (CaMgFe) SiO_4 in the form of orthorhombic crystals; a complicated phase produced when there is a high CaO content; magnesiowüstite (Mg, Fe)O; chromium-bearing spinel phases; complicated aluminoferrites	The slag liquid impregnates the refractory and reacts vigorously with the Al_2O_3 and to a smaller extent with the spinel grains. A large amount of liquid phase is not formed when the material interacts with the liquid, because refractory phases arise: calcium aluminoferrites and solid solutions. On subsequent addition of the slag liquid, there is further impregnation and interaction
CaO 45.9, FeO 1.4, MgO < 10.0 (slag ¹ 4)	Small crystals of dicalcium silicate, at the boundaries of which there are distributed monticellite, merwinite, aluminomagnesium spinels; ferrites; large lumps of sintered MgO	Vigorous interaction at the surface because of the high content of CaO in the liquid, with the deposition of crystalline phases. Traces of active gas release are associated with carbonization of the calcium; there are changes in chromium valency.

TABLE 3. Slag Characteristics

Slag	Content, wt. %							$\frac{\text{CaO} + \text{MgO}}{\text{Al}_2\text{O}_3 + \text{SiO}_2}$	$\frac{\text{CaO}}{\text{SiO}_2}$
	Fe _{tot}	SiO ₂	CaO	Al ₂ O ₃	MgO	MnO	balance		
¹ 1	17.6	34.5	23.5	13.3	2.4	—	8.7	0.54	0.68
¹ 4	3.4	38.4	33.4	14.6	5.2	2.1	2.9	0.73	—
B	40.0	30.0–35.0	—	—	—	—	25.0–30.0	—	0.87

	amorphous state. It is not found that the material interacts with the slag liquid or that chromium diffuses into the liquid. If for some reason the liquid begins to crystallize in the pore structure, the material may break up.
KhKT-60	The refractory cannot operate in contact with the slag. The liquid impregnates the material to a depth of 2–3 cm. One can distinguish three zones from the slag crystallization and interaction with the refractory: 1) impregnation boundary. The slag occupies the entire pore space and crystallizes with the formation of large acicular prismatic crystals, at the boundaries of which there are large branching microcracks (the crystals force the refractory grains apart). It is assumed that this is due to the interaction of the liquid with the material; 2) the slag liquid is present in the pore structure in the amorphous state; 3) bottom of crucible. The slag crystallizes with the formation of large acicular prismatic crystals.
KhS-MVU	Impregnation on the pore structure. The slag crystallizes completely with the formation of isometric orthorhombic crystals. Microcracks are not observed.
KhKT-30	The material is not impregnated on the pore structure. The refractive index of the amorphous part of the solidified slag is unaltered, and new crystalline phases are not formed. It is not found that chromium diffuses into the slag liquid. The boundaries of the binder particles at the contact with the slag liquid are modified with melting (adhesion-chemical interaction). Probably, during the tests there has been crystallization in the slag liquid, and pads of crystals are formed at the crucible surface. The crystallization increases the viscosity of the slag liquid to such an extent that impregnation cannot occur.
	<i>Slag No. 4</i>
KhKT-45	The liquid completely impregnates the material and is present in the pore structure in the amorphous state. The refractive index of the amorphous phase is the same as that of the initial slag. We do not find interaction of the material with the slag liquid or diffusion of chromium into the liquid. If for some reason the liquid crystallizes in the pore structure, the material may break up.
KhKT-60	Ditto.
KhS-MVU	The liquid completely impregnates the material and is present mainly in the amorphous state in the pore structure. The refractive index of the amorphous phase is the same as that for the initial slag. However, there are parts of the liquid in which crystallization begins evidently on account of inhomogeneity in the slag. We do not find interaction between the material and the liquid or the diffusion of chromium into the liquid.

KhKT-30 Impregnation does not occur and interaction is not found. The solidified liquid in the crucible crystallizes to 95%.

Slag B

KhKT-45 Impregnation does not occur and interaction is not found. The content of crystalline phase in the solidified liquid is 40%.

KhKT-60 Impregnation does not occur, and interaction is not found. The refractory is well wetted by the liquid, which after cooling is in the amorphous state.

KhS-MVU Ditto.

Figure 8 shows the specimens after test.

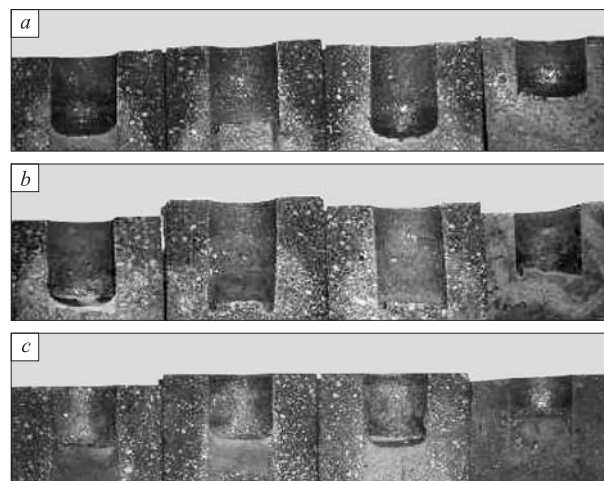


Fig. 8. Chromium-bearing refractory specimens after test in a liquid composed of experimental slags No. 1 (a), No. 4 (b), and B (c). From left to right: KhKT-30, KhKT-45, KhKT-60, KhS-MVU.

Material KhKT-30 is resistant to the liquids from the experimental slags; and all the tested materials are resistant to the liquid from slag B.

These tests lead to recommendations on using these materials for particular conditions:

KhKT refractories:

- at the Ul'yanovsk thermal insulation component plant, the regenerative basin furnace was lined with chromium-corundum refractory. The liquid for making ultrabasic mineral fiber is particularly corrosive. The furnace has been operated since August 2002 up to the present. Before this, electromelted bacor was used, which failed every 1.5–2 months. Similar problems were resolved at the firms of Tizol (Nizhnyaya Tura) and Tisma (Tyumen');

- tests have been done under the conditions of the corrosion occurring in frit-melting ovens at the Velor factory. The drainage channels are subject to the most wear in these ovens. The problem was that a channel made from fused Bk-37 failed after 1.5 months. One made of chromium-corundum refractory prepared by the Bakor Center Company withstood use for a year.

High-chromium refractories:

- at the Stupa glass-plastic plant, high-chromium refractories were used in the flow section, arch, and floor lining and walls in the working zone of a bath oven of regenerative type for producing ShSB-7.5 glass spheres. After three years of use, the furnace was taken down. The high-chromium refractories showed hardly any signs of wear and were retained for a second run;

- at the Novgorod glass fiber plant, tests were made on slotted stones made of high-chromium refractories. Tests over one and a half years confirmed their good working characteristics;

- at the Ufa plant for producing glass fiber (Steklonit Ltd), the linings of the oven and collectors were made with high-chromium refractories. After three years of use, there was only slight wear in the lining.

KhATs grade refractories: these have been tested under industrial conditions. The results are as follows:

- at the Dmitrov plant for thermal insulating components, the lining of a small furnace for producing basalt fiber operated continuously at 1550°C, and it was entirely made of KhATs refractory (Cr₂O₃ 31.5%, Al₂O₃ 33.5%, ZrO₂ 18.0%; it replaced high-alumina refractory and increased the working run for the furnace from 2 months to 1.5 years. There was also a considerable improvement in the quality of the basalt filaments, and a marked reduction in the labor required to service the furnaces. The plant has gone over completely to lining with chromium-bearing refractories;

- at the Izorok Tambov thermal insulation material plant, the lining of the bath oven of area 63 m² was made of electromelted bacor and mullite. After three months of use, there was failure in part of the upper structure composed of mullite. During the year of operation, there was repeated replacement of parts of the lining in the basin in contact with the mineral liquid. At the end of the present run, the state of the lining was analyzed, which showed slight corrosion of the refractories of the composition chromium-corundum (Cr₂O₃ 30.1%, Al₂O₃ 68.2%) and chromium-aluminum zirconium (Cr₂O₃ 31.5%, Al₂O₃ 33.6%, ZrO₂ 18.1%, SiO₂ 12.9%), which constituted 5 – 7%.

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