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RAW MATERIALS

FEATURES OF CHROMITE ORES FROM DIFFERENT DEPOSITS AND THEIR EFFECT ON THE MICROSTRUCTURE AND PROPERTIES OF PERICLASE-CHROMITE REFRACTORIES

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With the aim of selecting possibilities for use in industry of chromite ores from different deposits in order to produce periclase-chromite refractories these ores are studied by optical and electron microscopy, and also chemical and differential thermal analysis: Indian, Iranian, South African and Turkish. High temperature changes that occur within them are described. Microstructural features for periclase-chromite refractories based on these chromite ores and the interconnection of indices are revealed that make it possible to recommend an ore for a specific application.

INTRODUCTION

As is well known, chromite ore is a promising high-temperature material for preparing refractory materials. Dense, loose and powder ores are valuable as raw material for the production of periclase refractories since during production of some refractories a coarse-grained fraction (for example 3 – 0.5 mm) is used, and in the production of others a finely-ground fraction (for example ≤ 0.06 mm) is used.

Use of chromite ores from different deposits for producing periclase-chromite (PC) refractories containing from 5 to 35% Cr_2O_3 [1] is only suitable from an economic pint of view (suitable material cheaper than technogenic, undesirable to use more expensive raw material for mass production or to use cheaper material losing quality), but also from the point of view of forming some refractory structures. Microstructural features of chromite ore, chemical composition, the content of impurity components and their nature determine possible application in industry for any ore. In refractory production it is most desirable to use chromite ores containing not less than 35% Cr_2O_3, not more than 6% SiO_2, and not more than 1.5% CaO [2]. The amount of basic impurity, i.e. serpentine, may be at the level of not more than 15%, a greater amount of it reduces refractoriness and deformation temperature under load. The content of iron oxides in ores should also not be more than 16%. In PC-objects for more critical purposes it is recommended to use ores of increased quality, and in fact with a high Cr_2O_3 content (not less than 45%) and lower SiO_2 content (not more than 4 – 6%). For example, in order to produce vacuum degassed steel chromite ores should be used with the minimum silicon and calcium impurity content (less than 1%).

STUDY OBJECTS

In view of the importance of providing the refractory industry with chromite ores a study was made in this work of four types of chromite ores from different deposits: Indian, Iranian, South African and Turkish. Raw chromite ores of different fractions were studied: Indian fraction 2 – 0 mm; Iranian fraction 300 – 0; 2 – 0 and 0.5 – 0; South African chromite concentrate DR-89, 2 – 0.5 mm, CM AFS, 0.5 – 0 mm; Turkish 3 – 0.5 mm. These chromite ores were also studied after high-temperature firing. Then in order to estimate the effect of these chromite ores on the structure and properties of objects test periclase-chromite refractories based on them were studied.

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METHODS AND STUDY RESULTS

Raw and fired chromite ores, and also PC-objects based on them were studied in a Axioplan microscope from Carl Zeiss and a scanning electron microscope (SEM) XL-30 from Philips using a secondary-reflection detector for electrons (BSE). In order to confirm certain phases the original chromite ores were studied in addition, i.e. X-ray phase analysis was performed in a XTRA diffractometer from the firm ARL. Thermal studies in a STA 409PG instrument from Netzsch were performed in order to predict the behavior of original chromite ores under the action of high temperature.

Optical and Electron Microscopy of Raw Chromite Ores

Indian chromite ore fraction 2 – 0 mm is represented by grains of three forms of chromium spinellide of dark-gray to black color with a metallic luster (Fig. 1*a*). The first form is grains with a massive monolithic microstructure (60 – 65% grains of the total mass) of irregular angular or angular-oval shape. The second form is monolithic grains of oval shape with toothed edges (~30%). The third form is grains with a cracked microstructure within which over the periphery and cracks there are developed veins of aluminum hydroxide $Al_2O_3 \cdot 3H_2O$ (gibbsite) and haematite Fe_2O_3 (~5 – 10%; Fig. 1*b*). The phases detected, i.e. haematite Fe_2O_3 and gibbsite $Al_2O_3 \cdot 3H_2O$ are confirmed by x-ray phase analysis. The average content of the basic components in grains of chromium spinellide according to microprobe analysis data (SEM) are, wt.%: MgO 12 – 14, Al_2O_3 8 – 11, Cr_2O_3 63 – 66, Fe_2O_3 11 – 12 (FeO – 0 %). The content of Cr_2O_3 in chromite grains, different with respect to microstructural indications, is almost the same. A group of very rich chromite ores [3] relates to the content of Cr_2O_3 component. In ore, apart from gibbsite and haematite, impurities are detected of silica and a rare allophane $m\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot p\text{H}_2\text{O}$; their overall content is 4 – 5%.

Iranian chromite ore is related to dense ore with a massive texture and a medium to fine-grained structure (Fig. 2). Grains of chromium spinellide are of irregular angular-oval shape with a cracked microstructure. In chromium oxide content (60 – 64%) Iranium chromite ore relates to very rich chromite ores. The average content of basic components in chromium spinellide grains is, wt.%: MgO 10 – 13, Al_2O_3 7 – 10, Cr_2O_3 60 – 64, $(Fe_2O_3 + FeO)_{tot}$ 15 – 17 (SEM). In the ore there is a considerable amount of serpentine impurity in the form of veins. In fractions 300 – 0 mm there are veins with a width up to 800 μm, and rarely up to 2400 μm (15 – 20%); in fractions 2 – 0 mm veins have a width to 100 μm and they predominate up to 50 μm (5 – 8%) and in fractions 0.5 – 0 up to 20 μm they predominate up to 10 μm (5 – 8%). Extremely rarely in chromite grains inclusions of minerals of the silicate class (chlorite, diopside) are encountered.

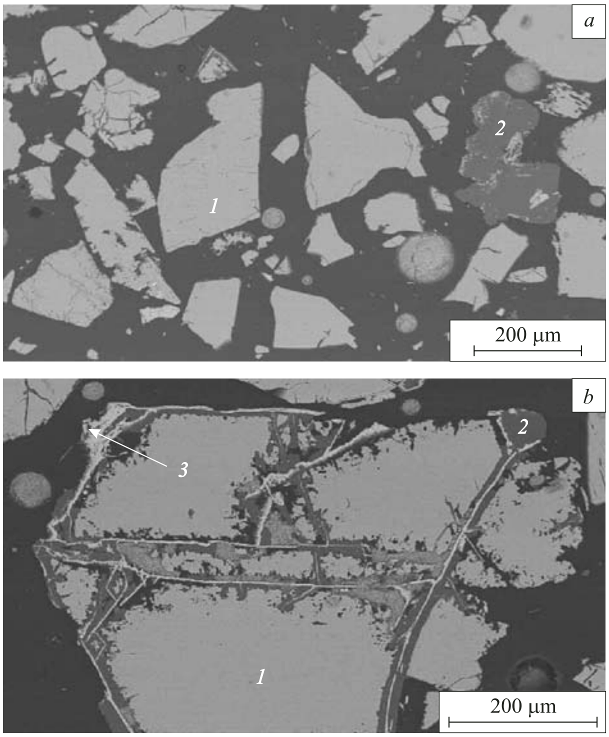

Fig. 1. Microstructure of grains of Indian chromite ore: *a*) grain of chromite fraction 2 – 0 mm (×107); *b*) grain of chromite with veins of gibbsite and haematite (×145); *1*) chromium spinellide; *2*) gibbsite; *3*) haematite (BSE. SEM).

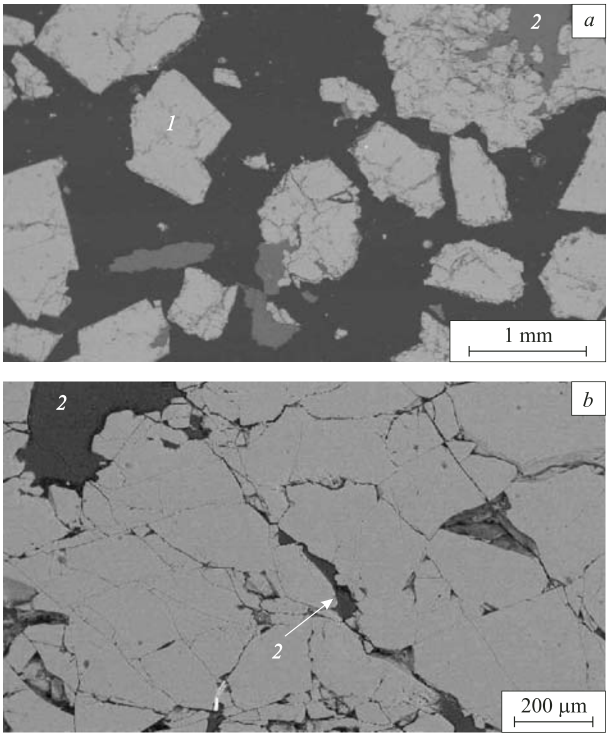

Fig. 2. Microstructure of Iranian Chromite ore fraction 2 – 0 (*a*) and 300 – 0 mm (*b*); *1*) chromium spinellide; *2*) serpentine (BSE. SEM); *a*) ×23; *b*) ×78.

South African chromite ore was studied in two grades: chromium concentrate AFS-50 of fraction 0.5 – 0 mm and DR-89 of fraction 2 – 0.5 mm.

Chromium concentrate CM AFS-50 of fraction 0.5 – 0 mm is grains of irregular oval shape, rarely angular-oval shape, with a massive monolithic microstructure (Fig. 3*a*) without any inclusions. In chromium oxide content chromium concentrate of the SAR CM AFS-50 relates to a group of rich chromite ores. The average content of oxides in grains of chromium spinellide is, wt.%: MgO 7 – 10, Al_2O_3 13 – 15, Cr_2O_3 46 – 49, $(Fe_2O_3 + FeO)_{tot}$ 25 – 30 (SEM). As impurities in the ore in the form of individual grains there are olivine (Mg, Fe)O·SiO_2, silica SiO_2, and rarely bytownite CaO·Al_2O_3·3SiO_2. Also rarely encountered are grains with inclusions of silicates (bytownite, chlorite). The overall content of impurities is 2 – 4%.

Chromium concentrate DR-89 fraction 2 – 0.5 mm is grains of angular-oval shape, mainly with a massive monolithic microstructure without inclusions, apart from rare grains with film inclusions of silicates (Fig. 3*b*). The average oxide content in chromium spinellide grains, wt.%: MgO 9 – 11, Al_2O_3 13 – 14, Cr_2O_3 46 – 48, $(Fe_2O_3 + FeO)_{tot}$ 27 – 30 (SEM), which is also confirmed by chemical analysis data. Grains have been detected with a high Fe_2O_3 content (up to 37%) whose overall fraction is small and it is about 1%. Materials detected are silicates (minerals associated with chromite ore): orthoclase K_2O·Al_2O_3·6SiO_2, sodium-containing bytownite CaO·Al_2O_3·3SiO_2 (Na_2O up to 5%), diopside CaO·MgO·2SiO_2, both in the form of inclusions in chromium spinellide, and in the form of individual independent grains. The overall content of silicate impurities is not more than 2 – 3%.

Turkish chromite ore fraction 3 – 0.5 mm is grains of chromite with a cracked microstructure, and irregular angular-oval shape. Grains of chromium spinellide are separated into two forms: monolithic with a massive texture, almost not containing associated rocks (88 – 92%) or containing a small amount of them, and grains with a brecciated structure containing 50% associated rock (8 – 12%) in the form of serpentine (Fig. 4). The average oxide content in chromium spinellide grains is, wt.%: MgO 14 – 15, Al_2O_3 8 – 9, Cr_2O_3 61 – 62, $(Fe_2O_3 + FeO)_{tot}$ 14 – 15% (SEM). Serpentinite is contained in an amount of 12 – 13%, and with an increased Al_2O_3 content (alumino-serpentine) that reaches 12%.

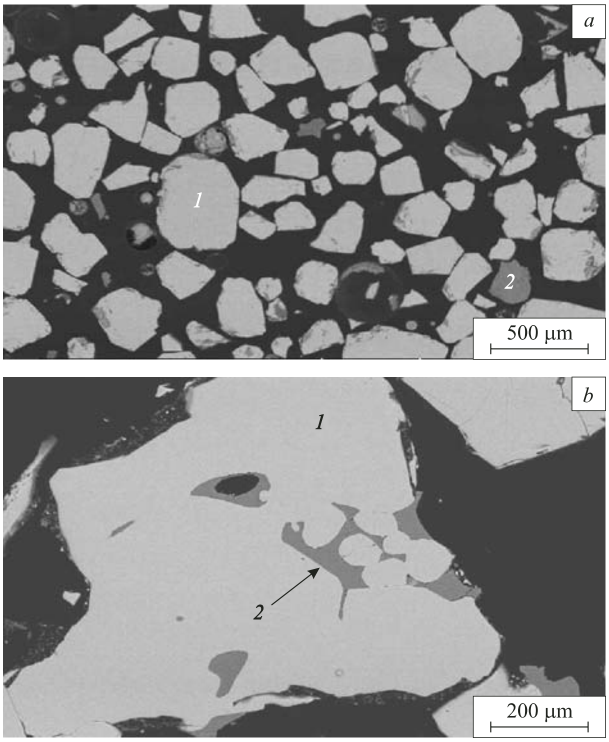

Fig. 3. Microstructure of South African chromite ore: *a*) CM AFS-50, fraction 0.5 – 0 mm; *b*) DR-89 fraction 2 – 0.5 mm with silicate inclusions; *1*) chromium spinellide, *2*) silicates (BSE. SEM); a) ×40; b) ×100.

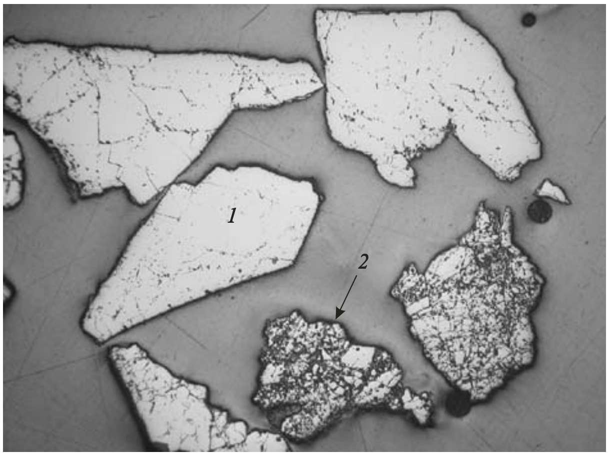

Fig. 4. Microstructure of Turkish chromite ore fraction 3.0 – 0.5 mm: *1*) chromium spinellide; *2*) serpentine. ×50.

TABLE 1. Chemical Composition of Chromite Ores from Different Deposits, wt.%

Chromite ore	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	Cr_2O_3	FeO	Δm_{fir}
Indian	13.0	11.54	0.37	0.10	14.5	60.0	0	–1.02
Iranian	16.2	9.87	2.48	0.10	4.5	57.2	9.46	+0.48
South African:								
CM AFS-50	12.8	10.57	0.72	0.10	9.99	47.6	18.1	+2.07
DR-89	10.3	13.70	0.40	0.10	28.46	47.4	Not det.	+1.72

TABLE 2. Mineral Composition of Different Chromite Ores, wt.%

Chrmite ore	Fraction, mm	Mineral						
		chromium spinellide	olivine	serpentine	alumino-serpentine	gibbsite	silicates	
							name	content
Indian*[1]	2 – 0,5	93 – 95	–	–	–	3 – 4	Silica	~1
Iranian	300 – 0	77 – 82	–	15 – 20	–	~1	Chlorite	~1
							Diopside	~1
	0,5 – 0	92 – 94	–	5 – 7	–	–	Chlorite	< 1
							Diopside	< 1
South African:								
CM AFS-50	0,5 – 0	96 – 98	1 – 3	–	–	–	Silica	<< 1
							Chlorite	< 1
							Bytownite	< 1
DR-89	2 – 0,5	97 – 98	–	–	–	–	Diopside	< 1
							Bytownite	~1
							Orthoclase	< 1
Turkish	3 – 0,5	82 – 85	< 1	–	12 – 13	–	–	–

*[1] Contains 1 – 2% haematite Fe_2O_3.

TABLE 3. Average Oxide Content in the Original (Numerator) and Fired (Denominator) Grains of Chromium Spinellide of Different Chromite Ores According to Microprobe Analysis Data (SEM), wt.%

Chromite ore	MgO	Al_2O_3	Cr_2O_3	Fe_2O_3 + FeO
Indian	12 – 14/14 – 16	8 – 11/10 – 12	63 – 66/64 – 66	11 – 12/9 – 11
Iranian	12 – 13/13 – 15	9 – 10/8 – 9	62 – 63/65 – 66	14 – 16/12 – 13
South African:				
CM AFS-50	7 – 9/18 – 19	13 – 15/16 – 17	47 – 49/54 – 55	28 – 30/11 – 12
DR-89	7 – 10/–	13 – 15/–	46 – 49/–	25 – 30/–
Turkish	14 – 15/18 – 20	8 – 9/7 – 10	61 – 62/65 – 67	14 – 15/7 – 9

Results of chemical analysis of chromium spinellide of the test chromite ores are presented in Table 1, the mineral phase composition is given in Table 2, and the results of microprobe analysis are given in Table 3.

Thermal Analysis

Experiments were performed in an oxidizing-air atmosphere up to 1400°C with a heating rate of 10 K/min.

On heating *Indian chromite ore* the following processes occur successively. At 35 – 130°C there is a reduction in weight on the TG-curve connected with release of adsorbed water. At 130 – 400°C there is an endothermic effect with a maximum at 276.6°C accompanying weight loss on the TG-curve that is caused by release of the basic mass of constitutional water from gibbsite and partial formation of an intermediate boehmite product $Al_2O_3 \cdot H_2O$ [4]. At 400 – 970°C there is a reduction in weight on the TG-curve with absence of thermal effects. At these temperatures there is total dehydration and decomposition of the boehmite formed with formation of Al_2O_3. At 1095 – 1400°C there is a weight reduction without appearance of energy effects that is explained by partial reduction of haematite with formation of magnetite. The overall weight loss in the range 35 – 1400°C was 2.07%.

On heating *Iranian chromite ore* the following processes occur successively. At temperatures up to 360°C there is first release of adsorbed and them structural water contained in serpentine. At 360 – 480°C oxidation of iron oxide (II) to iron oxide (III) commences by the reaction $4FeO + O_2 \rightarrow 2Fe_2O_3$ and its partial separation in the form of Fe_2O_3 at the surface of chromite grains. On the DSC-curve there is an exothermic effect with a maximum at 445.4°C with a weight increase on the TG-curve. At 480 – 720°C there is breakdown of the serpentine structure with simultaneous removal residual OH groups with formation of new mineral phases, i.e. forsterite and enstatite [4]. On the DSC-curve there is an endothermic effect with a maximum at 631.1°C. at 720 – 1115°C in chromite there is further oxidation of the remaining FeO accompanied by an exothermic effect with a maximum at 836.4°C, and also crystallization of forsterite and enstatite. On the TG-curve there is a weight increase by 0.19%. At 1115 – 1400°C there is a partial change of haematite with formation of magnetite with a weight reduction by 0.33%. The overall weight loss in the range 35 – 1400°C was 0.89%.

On heating *South African chromite concentrate grade CM AFS-50* the following processes occur successively. At 35 – 350°C there is release of adsorbed and structural water from chlorite, a weight reduction on the TG-curve by 13% without appearance of endothermic effects. At 350 – 475°C there is oxidation of FeO, contained in chromite in a considerable amount with formation of Fe_2O_3, and on the DSC-curve there is an exothermic effect with a maximum at 409.7°C. This process occurs with formation of surface films of haematite around chromium spinellide particles. The weight increase on the TG-curve here is 0.35%. At 475 – 1200°C FeO remaining in the chromite is oxidized with gradual diffusion of oxygen through the protective oxide film with a weight increase on the TG-curve. At 1200 – 1400°C of the TG-curve there is a weight reduction by 0.53% connected with partial change of haematite with formation of magnetite. The overall weight loss in the range 35 – 1400°C was 1.01%.

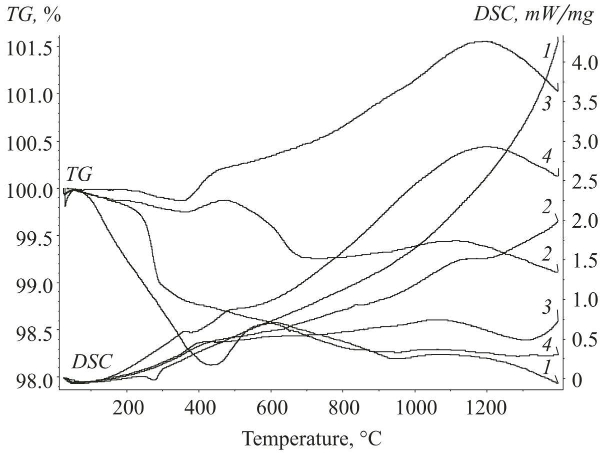

Fig. 5. Thermograms of chromite ores: *1*) Indian; *2*) Iranian; *3*) South African (concentrate CM AFS-50); *4*) Turkish.

On heating *Turkish chromite ore* the following processes occur successively. At 35 – 435°C there is release of adsorbed and then structural water contained in the aluminoserpentine with a weight loss of 1.87%. at 435 – 600°C FeO oxidizes with formation of Fe_2O_3. On the DSC-curve there is an

TABLE 4. Weight Change and Energy Effects During Thermal Analysis of Different Chromite Ores

Chromite ore	Progress of process	Temperature range, °C	Weight change, %	Energy effect	Maximum effect temperature, °C
Indian	Release of adsorbed water	35 – 130	–0.10	–	–
	Release of the main mass of constitutional water from gibbsite and partial formation of intermediate boehmite product $Al_2O_3 \cdot H_2O$	130 – 400	–1.14	Endo	276.6
	Total dehydration and decomposition of boehmite with formation of Al_2O_3 that is subsequently transferred into the spinellide composition	400 – 970	–0.57	–	–
	Partial reduction of haematite with formation of magnetite $FeO \cdot Fe_2O_3$	1095 – 1400	–0.31	–	–
	Total weight loss	35 – 1400	–2.12	–	–
Iranian	Release of adsorbed and then structural water contained in serpentine	≤ 360	–0.25	–	–
	Partial oxidation of FeO found at the surface of chromite grains with formation of haematite Fe_2O_3	360 – 480	+0.12	Exo	445.4
	Breakdown of serpentine structure with simultaneous removal of residual OH groups and formation and new mineral phases, i.e. forsterite and enstatite	480 – 720	–0.62	Endo	631.1
	Further oxidation of FeO in chromite and also crystallization of newly formed mineral phases, i.e. forsterite and enstatite	720 – 1115	+0.19	Exo	836.4
	Partial reduction of haematite with formation of magnetite	1115 – 1400	–0.33	–	–
	Overall weight loss	35 – 1400	–0.89	–	–
South African (concentrate CM AFS-50)	Release of adsorbed and structural water with dehydration of minerals of the weathered skin	35 – 350	–0.13	–	–
	Partial oxidation of FeO in chromite with formation of haematite	350 – 475	+0.35	Exo	409.7
	Oxidation of some part of the remaining FeO in chromite with gradual diffusion of oxygen through the protective oxide film	475 – 1200	+1.34	–	–
	Partial reduction of haematite with formation of magnetite	1200 – 1400	–0.53	–	–
	Overall weight increase	35 – 1400	+1.03	–	–
Turkish	Release of adsorbed and then structural water contained in serpentine	35 – 435	–1.87	–	–
	Oxidation of FeO in chromite with formation of haematite	435 – 600	+0.44	Exo	485.0
	Breakdown of serpentine structure with simultaneous removal of residual OH groups and formation of new mineral phases, i.e. forsterite and enstatite	600 – 942	–0.30	–	–
	Partial reduction of haematite with formation of magnetite	1295 – 1440	–0.05	–	–
	Overall weight loss	35 – 1400	–1.78	–	–

exothermic effect with a maximum at 485°C with a weight increase on the TG-curve by 0.44%. At 600 – 942°C the structure of the aluminoserpentine breaks down with simultaneous release of residual OH groups (weight loss 0.3%) with formation of new mineral phases, forsterite and enstatite as in Iranian chromite ore. At 1295 – 1440°C there is partial reduction of haematite with formation of magnetite with a weight reduction of 0.05%. The overall weight loss in the range 35 – 1400°C was 1.74%.

Results of thermal analysis are presented in graphical form in Fig. 5 and they are also provided in Table 4.

Mineral Formation in Chromite Ores During Firing

In studying chromite ores after firing it has been revealed that in all ores there is a change in the mineral-phase composition with formation of new spinellide and silicate phases (Table 5) that were previously predicted during thermal analysis in a STA 409 PG instrument.

Indian chromite ore only contains Fe_2O_3 and it is “naturally oxidized”, and therefore with firing temperatures up to 1600°C it is not subject to oxidation and at above 1600°C within chromite grains there is decomposition of chromite into solid solutions [5] of oxides of trivalent iron and chromium $Fe_2O_3 \cdot Cr_2O_3$ and spinellide containing bivalent iron, $FeO \cdot Cr_2O_3$. An example of the composition of the first solid solution is, wt.%: Al_2O_3 8 – 9, Cr_2O_3 50 – 51, Fe_2O_3 40 – 41, it is found in the form of acicular crystals. An example of a composition of the second solid solution is, wt.%: Al_2O_3 10 – 11, Cr_2O_3 80 – 81, FeO 7 – 8, it is found in the form of developed crystals of irregular shape. Crystallization of the two different solid solutions is a feature of Indian chromite ore. A compound of spinellide $Fe(Cr)_2O_4$ with a high Cr_2O_3 content (up to 20%) in an x-ray pattern is presented in the form of individual peaks. In the unchanged part of a chromite grain there is a small reduction in iron oxide content as a result of crystallization of solid solutions of secondary spinellides (in the original 11 – 12% Fe_2O_3 and 9 – 11% in the fired material). In silicate phase enstatite $Mg_2[Si_2O_6]$ (not more than 1%) is formed in an insignificant amount. Decomposing under the action of high temperatures gibbsite and haematite contained in the ore as a result of high temperature diffusion are transferred into the composition of chromium spinellides.

In Iranian chromite ore during firing from serpentine $3MgO \cdot 2SiO_2 \cdot 2H_2O$ there is formation of àkermanite $2CaO \cdot MgO \cdot SiO_2$ and olivine (Mg, Fe)$\cdot SiO_2$ (iron forsterite). In grains of chromite there is formation of angular crystals of a solid solution of trivalent iron oxides (approximate composition, wt.%: Al_2O_3 5 – 6, Cr_2O_3 59 – 60, (Fe_2O_3 + FeO) 33 – 34) as a result of partial oxidation of FeO in chromium spinellide with release of trivalent chromium and iron oxides that simultaneously form a series of solid solutions:

$$4CrO \cdot Cr_2O_3 + O_2 \rightarrow 2Fe_2O_3 + 4Cr_2O_3 \rightarrow 4Fe_2O_3 \cdot Cr_2O_3.$$

The overall content of iron oxides in unchanged chromite grains decreases, but the proportion of MgO increases: in the original ore 14 – 16% (Fe_2O_3 + FeO), in the fired ore it is 12 – 13%; in the original ore there 11 – 13% MgO, and in the fired ore it is 15 – 17%.

In *South African chromite ore* (*concentrate CM AFS-50*) during firing from olivine there is formation of monticellite and forsterite. Similar to Iranian ore, in chromite grains there are crystals of trivalent oxide solid solution. The overall content of iron oxides in chromite grains decreases by a factor of 2.5, and the proportion of MgO increases by a factor of two: in the original grains there 28 – 30% (Fe_2O_3 + FeO), and in fired grains there is 11 – 12%; in the original grains there is 7 – 9% MgO and in fired grains there is 18 – 19%.

In *Turkish chromite ore* after firing there is a reduction in grain cracking, and the mineral-phase composition changes: new silicates from aluminoserpentine, i.e. cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ and olivine (Mg, Fe)$O \cdot SiO_2$. Similar to the Iranian and South African ores in chromite grains there is crystallization of a solid solution of trivalent oxides with an approximate content of, wt.%: Al_2O_3 15 – 16, Cr_2O_3 51 – 52, Fe_2O_3 33 – 34. The overall content of iron oxides in chromite grains decreases: in the original grains it is 14 – 15%, in fired grains it is 7 – 9%, the weight fraction of MgO increases: in original grains it is 14 – 15%, and in fired grains it is 18 – 20%.

The chemical composition of grains of chromium spinellide before and after firing of different chromite ores according to microprobe analysis data is given in Table 3.

Discussion of the Results of Physicochemical Features of the Test Chromite Ores

Features of chromite ores are important in selecting ores for production of PC-objects since they have a marked effect the formation of their microstructure. The properties of chromite ores were analyzed as starting material as a result

TABLE 5. Mineral Composition of Different Chromite Ores After Firing, wt.%

Chromite ore	Chromium spinellide	Solid solution		Silicates	
		$Fe_2O_3 + Cr_2O_3$	$Cr_2O_3 + FeO + Fe_2O_3$	name	content
Indian	68 – 71	4 – 6	22 – 26	Enstatite	~1
Iranian	88 – 89	4 – 6	–	Olivine, àkermanite	5 – 8
South African (concentrate CM AFS-50)	94 – 95	3 – 4	–	Forsterite, monticellite	1 – 3
Turkish	86 – 89	2 – 3	–	Olivine, cordierite	8 – 12

of which differences were revealed in the microstructure, chemical and mineral-phase compositions, and behavior at high temperature.

Features of the test chromite ores are given below:

Indian:

- grains mainly with a monolithic microstructure;
- presence of chromium spinellide grains with a cracked microstructure, in cracks and over the periphery of which there are developed veins of gibbsite and haematite (confirmed by thermal analysis and x-ray phase analysis data) and during firing of chromite ore they are transferred into the chromium spinellide composition;
- according to chemical analysis data (see Table 1) the ore only contains Fe_2O_3, FeO is entirely absent, in view of which according to the results of thermal analysis there is no weight increase on TG-curve. The Fe_2O_3 content in the ore is close to the overall content of iron oxide (Fe_2O_3 + FeO) in Iranian and Turkish ore (~14%, see Table 1);
- with high-temperature firing in chromite grains there is crystallization of two solid solutions: trivalent oxides of iron and chromium $Fe_2O_3 \cdot Cr_2O_3$ in the form of acicular crystals and spinellide $FeO \cdot Cr_2O_3$ in the form irregular shaped crystals;

Iranian:

- chromite grains of cracked microstructure which subsequently may favorably affect an increase in PC-object heat resistance;
- content of a significant amount of serpentine impurity (in coarse fractions 300 – 0 mm, 12 – 15%) in the form of veins within chromite grains. According to thermal analysis data at 480 – 720°C there is breakdown of the serpentine structure with formation of new mineral phases, i.e. forsterite and enstatite. Presence of serpentine is a negative factor for chromite ore since with loss of water it disintegrates, and at 1350 – 1450°C it breaks down into clinoenstatite (decomposition temperature 1557°C) and forsterite (melting temperature 1890°C) with an increase in volume. Due to presence in the ore of iron oxides together with forsterite olivine is formed (iron forsterite) which is confirmed by studies of fired chromite ore (see Table 5);
- according to chemical analysis data the FeO content in this ore is 9.46%, that compared with South African and Turkish ores is the least. In view of this according to thermal analysis data the weight increase with oxidation of FeO is the least (see Tables 1 and 4) that leads to a smaller increase in volume;
- with high-temperature firing there is crystallization of one solid solution of oxides of trivalent iron and chromium $Fe_2O_3 \cdot Cr_2O_3$ in the form of acicular crystals;

South African (*concentrate CM AFS-50*):

- chromite grains with a monolithic microstructure almost without inclusions, that is a favorable factor for PC-objects for domestic purposes based on high-purity minerals;
- it contains the minimum amount of impurity components (not more than 2 – 3%);
- according to the results of chemical and microprobe analyses (see Tables 1 and 2) there is the greatest overall content of iron oxides (Fe_2O_3 + FeO) compared with the other ores, and it is 25 – 30%. In addition, the FeO content is the greatest, which correspondingly affects the results of thermal analysis: in the range 350 – 800°C with oxidation of FeO to Fe_2O_3 there is the greatest weight increase, in contrast to Iranian and Turkish chromite ores (see Table 3). As a result of this no overall weight loss is observed, but an increase of it that in turn is connected with absence of impurities, containing structural water. The lower the weight loss, the less dense is the microstructure formed in objects; with high-temperature firing, as in grains of Iranian chromite ore, there is crystallization of one solid solution of oxides of trivalent iron and chromium;

Turkish:

- chromite grains with a cracked microstructure;
- 8 – 12% of chromite grains contain up to 50% of serpentine or aluminoserpentine. According to thermal analysis data at 600 – 942°C there is breakdown of the aluminoserpentine structure with simultaneous removal of OH groups with formation of new mineral phases. In contrast to Indian chromite ore, in Turkish ore the temperature for breakdown of serpentine is somewhat higher, which is connected with an increase in the Al_2O_3 content within it. Therefore during firing, in contrast to Iranian chromite ore, in the silicate phase apart from forsterite and olivine, there is formation of cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ with a low decomposition temperature (1450°C);
- according to chemical analysis data the overall content of iron oxides (Fe_2O_3 + FeO) in this ore is close to the overall content in Indian, Iranian, and Turkish ores (see Table 1). The FeO content in this ore is 13.3%, that is greater than in the Iranian and less than in the south African ores. Correspondingly, according to thermal analysis data the weight increase with oxidation of FeO is between the indices for the change in weight for Iranian and South African Chromite ores;
- with high-temperature firing there is crystallization of one solid solution of oxides of trivalent iron and chromium.

Microstructural Features of PC-Refractories Caused by the Effect of Chromite Ores

In order to evaluate the effect of different chromites on the microstructure and properties of PC-refractories a study was made of objects within which as the granular filler, apart from chromite, in one case sintered periclase, and in another fuzed periclase-chromite were added.

As is well known, during firing in all PC-objects there is counter (reciprocal) diffusion of components between periclase and chromite [6]. The rate of ion migration of chromium and iron from chromite grains is different in relation to the features of the chromite ore (chemical composition, amount and nature of impurity components, etc.). As a result of mass transfer of periclase there is intense impregnation with chromite decomposition products forming grains of periclase with secondary chromium spinellide crystallized by inclusions. The chemical composition of the original chromite grains changes, as a result of which there is formation of regenerated grains of chromium spinellide around which as a rule there are circular and(or) semicircular pores. The study of PC-objects prepared using different chromite ores makes it possible to see the difference in ore behavior.

PC-objects prepared on the basis sintered periclase using the test chromite ores:

Indian (*2 – 0 mm*):

- chromite grains of irregular round shape, monolithic microstructure with corroded edges, and rounded micropores within grains;
- the chromite grain size is less compared with the size of the original grains by about a factor of 1.5 – 2 (up to 600 μm, 100 – 400 μm predominate);
- around chromite grains there are semicircular chains of discontinuous pores with a width up to 100 μm, and up to 50 μm predominate, that affects the reduction in heat resistance of an object. These pores distinguish PC-objects, prepared using Indian chromite ore, from PC-objects with other chromite ores within which pores are mainly circular and width is at a minimum;
- bonding of chromite grains with the finely-ground component is good;
- in grains of chromium spinellide in PC-objects according to microprobe analysis data there is a reduction in the amount of Fe_2O_3 from the periphery towards the center (Table 6), and in the peripheral area the content of Fe_2O_3 grains compared with the original grains of chromium spinellide is about the same. This is connected with the content in the ore only of the trivalent ion and presence of a haematite impurity phase, and consequently the occurrence

TABLE 6. Average Content of Main Oxides in the Original Chromite Grains and in Grains of Chromite in Fired PC-Objects (SEM), wt.%

Chromite ore	MgO	Al_2O_3	Cr_2O_3	Fe_2O_3 + FeO
PC-objects based on sintered periclase				
Indian:				
original	12 – 14	8 – 11	63 – 66	11 – 12
grain in PC-object:				
central part of grain	16 – 18	9 – 10	67 – 69	4 – 7
periphery	17 – 20	11 – 13	59 – 60	9 – 11
Iranian:				
original	12 – 13	9 – 10	62 – 63	14 – 16
grain in PC-object:				
central part of grain	15 – 16	9 – 10	64 – 65	10 – 11
periphery	19 – 20	8 – 9	63 – 64	8 – 9
South African (concentrate CM AFS-50)::				
original	7 – 9	13 – 15	47 – 49	28 – 30
grain in PC-object:				
central part of grain	20 – 21	12 – 13	56 – 57	10 – 11
periphery	16 – 17	9 – 10	67 – 68	5 – 6
Turkish:				
original	14 – 15	8 – 9	61 – 62	14 – 15
grain in PC-object:				
central part of grain	13 – 14	8 – 9	66 – 67	11 – 13
periphery	16 – 18	8 – 9	67 – 69	6 – 9
PC-objects based on fuzed periclase chromite*[1]				
Indian:				
grain in PC-object:				
central part of grain	16 – 18	8 – 10	67 – 69	4 – 7
periphery	18 – 20	12 – 15	57 – 59	6 – 8
Iranian:				
central part of a grain*[2] in PC-objects	20 – 22	10 – 11	61 – 62	6 – 7
South African (concentrate CM AFS-50):				
grain in PC-object:				
central part of grain	19 – 20	14 – 15	54 – 55	10 – 11
periphery	22 – 23	14 – 15	54 – 55	7 – 8

*[1] Original chromite ore the same as for objects based on sintered periclase.

*[2] In view of the small size of grains their composition is about the same throughout the whole volume of a grain.

of some other processes of mass transfer in intensity compared with other ores;

Iranian (3 – 0.5 mm):

- chromite grains of angular-oval rarely elongated shape (1:1.5), cracked microstructure, monticellite observed in cracks. Some grains of chromium spinellide uncrystallized;
- size of chromite grains up to 2400 μm, predominant 100 – 800 μm. Cracking of chromite grains may have an effect on reducing the strength of an object;
- around chromite grains there are semicircular, mainly circular pores with a width up to 170 μm, they predominate with a width up to 80 μm that affects an increase in heat resistance;
- bonding of chromite grains with the finely-ground component is good, satisfactory in some areas;
- according to the results of microprobe analysis it is seen that the overall content of iron oxides (Fe_2O_3 + FeO) in chromium spinellide grains compared with the original grains decreases by about a factor of 1.5, and from the center to the periphery in contrast to Indian chromite, or the MgO content correspondingly increases from the center to the periphery (see Table 6), which is connected with counter diffusion of components, i.e. periclase is impregnated with chromium spinellide decomposition products, and chromium spinellide in turn dissolves MgO;

South African (*concentrate CM AFS-50, 0.5 – 0 mm*):

- grains of chromite of irregular rounded shape, monolithic structure;
- chromite grain size up to 400 μm, 100 – 300 μm predominate, compared with original grains the reduction is insignificant;
- around chromite grains there are circular, rarely semicircular, pores with a width up to 100 μm, a width of 30 – 70 μm predominates;
- bonding of chromite grains with the finely-ground component is satisfactory, and in some areas it is good;
- microprobe analysis data shows that the content of iron oxides (Fe_2O_3 + FeO) in chromium spinellide grains compared with the original grains decreases from the center towards the periphery as in the Iranian and Turkish ores, but MgO correspondingly increases. From the chemical composition of chromium spinellide grains (see Table 6) it can be seen that the content of iron oxides decreases by a factor of 3 – 5 with respect tot her original chromium spinellide grains. Compared with other test ores diffusion of iron ions from this ore into the periclase proceeds rapidly, that in turn is connected with the greater content of FeO in the South African ore (see Table 1);

Turkish (*3 – 0.5 mm*):

- chromite grains of angular-oval shape, cracked microstructure, in some cracks there is cordierite, and close to the periphery of grains there is monticellite. Uncrystallized grains are rarely encountered;
- chromite grain size up to 2600 μm, 400 – 1200 μm predominate;
- around chromite there are circular pores with a width up to 200 μm, a width of 40 – 100 μm predominates. The size of circular pores is greater than in PC-objects based on Iranian chromite ore introduced in the same fraction (3 – 0.5 mm), which is connected with the greater FeO content in the original ore than in the Iranian ore. Consequently the heat resistance of objects based on Turkish ore should be somewhat higher;
- bonding of chromite grains with the finely-ground component is satisfactory;
- according to microprobe analysis data (SEM) the content of iron oxides (Fe_2O_3 + FeO) in chromium spinellide grains compared with the original grains decreases by about a factor of 1.5 – 2 from the center towards the periphery, but MgO increases (see Table 6);
- single grains of forsterite are encountered with a size up to 2000 μm, with circular pores around 200 – 400 μm wide forming from serpentine impurity.

The microstructure of PC-objects based on sintered periclase is presented Fig. 6.

PC-objects prepared on the basis of fuzed periclase with use of the test chromite ores:

Indian:

- chromite grains of irregular angular-oval shape with corroded edges, with rare inclusions of silicate merwinite;
- chromite grain size reaches 1600 mm, 100 – 400 mm predominate, as in objects based on sintered periclase there is a reduction compared with the original grains by about a factor of 1.5 – 2;
- around chromite grains there are semicircular, rarely circular, pores with a width up to 100 μm, and up to 50 μm predominate;
- bonding of chromite grains with the finely-ground component is satisfactory;
- similar to chromium spinellide grains in objects based on sintered periclase, in chromium spinellide according to microprobe analysis data there is a reduction in the iron oxide content from the periphery towards the center (see Table 6);

Iranian:

- chromite grains are very rarely encountered;
- chromite grains markedly reduced in size compared with the initial sizes (maximum size 100 μm) as a result of almost total solid phase diffusion interaction with fuzed periclase-chromite in finely-ground component and in a grain with formation of chromium spinellide films and diffused inclusions of chromium spinellide;
- as a result of total reaction of chromite with periclase grains there is no chromite, there are no circular or semicircular pores, typical for chromium-containing objects, and consequently there is a significant reduction in object heat resistance. In an area of diffused chromite grains there are porous areas of irregular circular shape containing crystals of secondary chromium spinellide and particles of periclase-chromite;
- according to microprobe analysis data the iron oxide content (Fe_2O_3 + FeO) in the rarely remaining grains of chromium spinellide compared with the original grains decreases by about a factor of two, but MgO increases (see Table 6);

South African (*concentrate CM AFS-50*):

- chromite grains of irregular round shape, monolithic microstructure;
- chromite grains with a size up to 500 μm, 200 – 400 mm predominate. Chromite grain size, as in objects based on sintered periclase, decrease markedly compared with the initial grains;
- around chromite grains there are circular, rarely semicircular, pores with a width up to 100 μm, and a width of 20 – 80 μm predominates;
- bonding of chromite grains with the finely-ground component is satisfactory;
- according to microprobe analysis data the content of iron oxides in chromium spinellide grains, the same as in objects based on sintered periclase, decreases from the center towards the periphery by a factor of 3 – 4 with respect to the original grains, and the MgO content correspondingly increases (see Table 6).

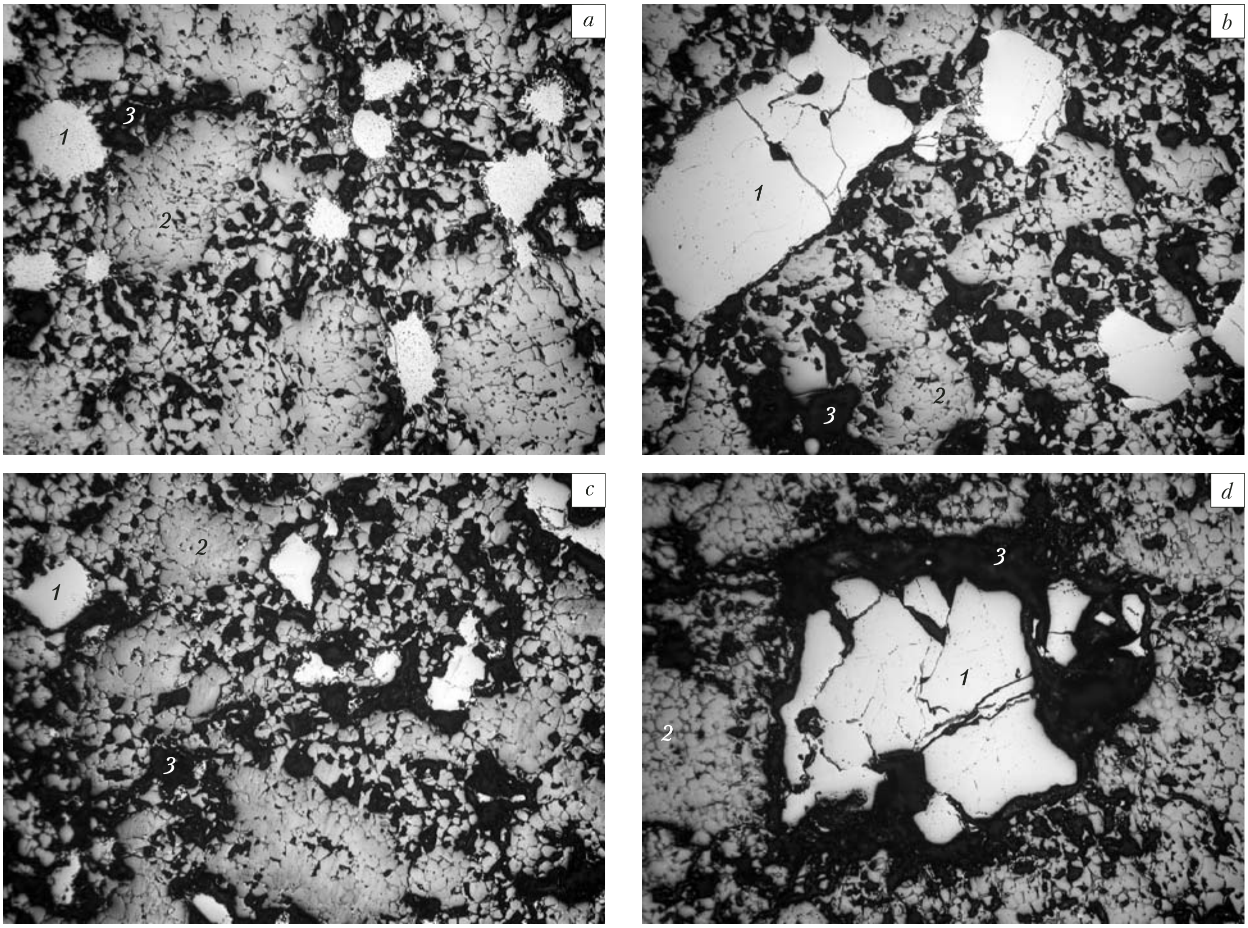

Fig. 6. Microstructure of PC-objects based on sintered periclase prepared with different chromite ores: *a*) Indian (fraction 2 – 0 mm); *b*) Iranian (3 – 0.5 mm); *c*) South African (0.5 – 0 mm); *d*) Turkish (3 – 0.5 mm); *1*) chromium spinellide; *2*) sintered periclase; *3*) pores (dark).

TABLE 7. Physicomechanical Properties of PC-Objects Prepared Using Different Chromite Ores

Chromite ore	Fraction, mm	Apparent density, g/cm^3	Open porosity, %	Ultimate strength in compression, MPa	Heat resistance (1300°C – water), thermal cycling
PC-objects based on sintered periclase					
Indian	2 – 0	3.06	18.47	61.13	6
Iranian	3 – 0.5	3.03	17.7	60.97	7
South African (concentrate CM AFS-50)	0.5 – 0	3.07	17.23	72.8	7
Turkish	3 – 0.5	3.04	17.4	71.0	8
PC-objects based on fuzed periclase-chromite					
Indian	2 – 0	3.09	16.5	39.9	3
Iranian	0.5 – 0	3.11	16.6	42.3	2
South African (concentrate CM AFS-50)	0.5 – 0	3.17	14.5	63.5	5

TABLE 8. Comparative Properties of Structural Elements of PC-Objects Prepared Using the Test Chromite Ores

Index	PC-objects based on sintered periclase				PC-objects based on sintered periclase-chromite		
	Indian (2 – 0 mm)	Iranian (3 – 0.5 mm)	South African (0.5 – 0 mm)	Turkish (3 – 0.5 mm)	Indian (2 – 0 mm)	Iranian (0.5 – 0 mm)	South African (0.5 – 0 mm)
Chromite grain size*1, μm	$\frac{\le 600}{100 - 400}$	$\frac{\le 2400}{100 - 800}$	$\frac{\le 400}{100 - 300}$	$\frac{\le 2600}{400 - 1200}$	$\frac{\le 1600}{100 - 400}$	Particles < 100	$\frac{\le 500}{200 - 40}$
Chromium spinellide grain size in periclase, μm:							
granular	$\frac{\le 3}{\le 1}$	$\frac{\le 2}{\le 1}$	$\frac{\le 3}{\le 1}$	$\frac{\le 2}{\le 1}$	$\frac{\le 3}{1 - 2}$	$\frac{\le 3 \text{ (rarely 10)}}{1 - 2}$	$\frac{\le 3 \text{ (rarely 5)}}{1 - 2}$
finely ground	$\frac{\le 5}{1 - 3}$	$\frac{\le 3}{1 - 2}$	$\frac{\le 5}{1 - 3}$	$\frac{\le 3}{1 - 2}$	$\frac{\le 5}{1 - 3}$	$\frac{\le 7}{1 - 4}$	$\frac{\le 3}{1 - 2}$
Chromium spinellide film size in finely ground component	$\frac{\le 20}{\le 10}$	$\frac{\le 10}{\le 5}$	$\frac{\le 30}{\le 20}$	$\frac{\le 10}{\le 5}$	$\frac{\le 70}{\le 30}$	$\frac{\le 70}{\le 30}$	$\frac{\le 20}{\le 10}$
Pore shapes and sizes, μm:							
fine closed	$\frac{\le 70}{20 - 50}$	$\frac{\le 100}{20 - 50}$	$\frac{\le 80}{20 - 50}$	$\frac{\le 80}{20 - 50}$	$\frac{\le 100}{20 - 60}$	$\frac{\le 100}{20 - 80}$	$\frac{\le 100}{20 - 80}$
grouped communicating	$\frac{\le 80}{20 - 50}$	$\frac{\le 100}{20 - 80}$	$\frac{\le 100}{20 - 60}$	$\frac{\le 200}{20 - 100}$	$\frac{\le 200}{40 - 100}$	$\frac{\le 100}{20 - 50}$	$\frac{\le 200}{40 - 100}$
coarse	$\frac{\le 400}{100 - 300}$	$\frac{\le 400}{100 - 300}$	$\frac{\le 600}{100 - 400}$	$\frac{\le 400}{100 - 300}$	$\frac{\le 600}{100 - 300}$	$\frac{\le 400}{100 - 300}$	$\frac{\le 600}{100 - 400}$
circular, semicircular around chromite	$\frac{\le 100}{30 - 50}$	$\frac{\le 200}{\le 80}$	$\frac{\le 100}{30 - 70}$	$\frac{\le 200}{40 - 100}$	$\frac{\le 100}{10 - 50}$	No	$\frac{\le 100}{20 - 80}$
Nature of bond*2 between chromite and finely ground component	Good		Satisfactory			–*3	Satisfactory

*1 Maximum sizes in the numerator, predominant in the denominator.

*2 In all cases the bond of periclase with finely ground component and between particles in finely ground component is good.

*3 Chromite grains absent as a result of total reaction of the latter with periclase.

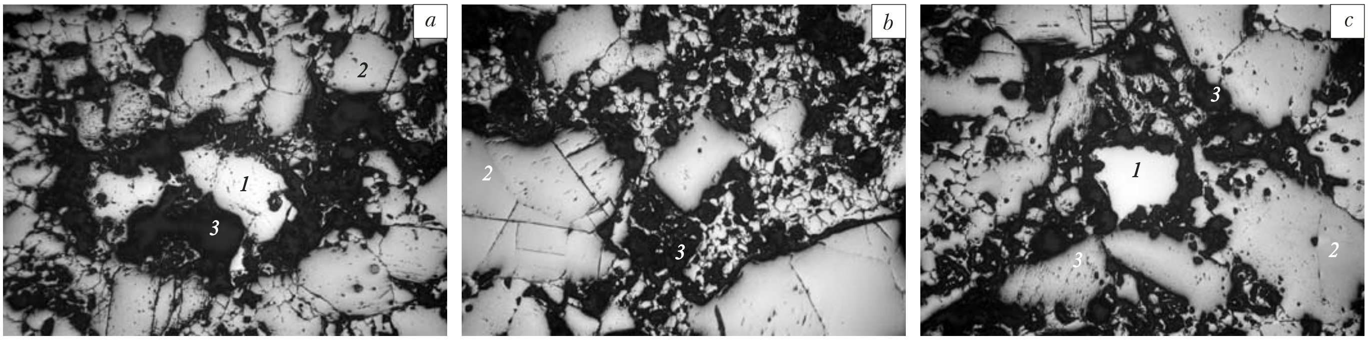

Fig. 7. Microstructure of PC-objects based on periclase-chromite prepared with different chromite ores: *a*) Indian (fraction 2 – 0 mm); *b*) Iranian (fraction 0.5 – 0 mm); *c*) South African (fraction 0.5 – 0 mm); *1*) chromium spinellide; *2*) fuzed periclase-chromite; *3*) pores (dark).

The physicomechanical properties of PC-objects are presented in Table 7, and comparative characteristics of these structural elements are given in Table 8. The microstructure of PC-objects based on fuzed periclase is shown in Fig. 7.

In grains of chromium spinellide in PC-objects based on Iranian, South African and Turkish chromite ores as a result of reciprocal diffusion of chromite with periclase there is as a rule a reduction in the iron oxide content (from the central part of a grain towards the periphery) and an increase in MgO content in the reverse direction, but with different intensity (see Table 6). In grains of chromium spinellide of Indian ore, conversely the iron oxide content increases from the periphery towards the center, which is connected with crystallization of high- chromium spinellide, and this is one of the features of this ore.

Correlation Analysis Between Physicomechanical Indices, Microstructural Features of Objects and Properties of the Original Chromite Ore

In order to determine the interconnection of thermomechanical indices (apparent density, open porosity, ultimate strength in compression and heat resistance) with the microstructure of objects and the composition of the original chromite ores correlation analysis was performed for the results of studies and physicomechanical tests.

The following parameters were used for the original chromite ores:

- content of FeO, Fe_2O_3 and Cr_2O_3;
- overall content of iron oxides (Fe_2O_3 + FeO);
- amount of impurities (silicates);
- degree of chromite grain cracking (evaluated visually in the range from 0 to 1; 0 is all grains monolithic, not cracked; 1 is all cracked);

For characteristics of the PC-object microstructure the following parameters were used:

- average width of circular pores around chromite grains;
- average value of the reduction in chromite grain size after firing an object calculated by the equation

$$Y = ((L_{\text{orig}} - L_{\text{fir}})/L_{\text{orig}})\cdot 100\%,$$

where L_{orig} is the average grain size for the original chromite; L_{fir} is the average chromite grain size in an object after firing;

- nature of chromite grain bonding with particles of finely-ground component (evaluated by a nominal five-point scale);
- average size of chromium spinellide films in films-ground component of objects.

Calculated dependences are presented in Table 9 and in the form of block schemes (Fig. 8) from which the following mathematical relationships proceed:

- *apparent density* of objects increases with a reduction in impurity content (correlation coefficient $k = -0.97$), the degree of chromite grain cracking (–0.93), an increase in the spinellide film dimensions in finely-ground component (0.90, the content of Fe_2O_3 (0.76), the overall content of iron oxide (0.74) and bonding capacity for chromite grains with periclase (0.71). On the rest of the parameters: the apparent density of objects does not depend on the content of Cr_2O_3, width of circular pores, reduction in chromite grain size and FeO content (Fig. 8*a*).
- *open porosity* of articles increases with a reduction in FeO content ($k = -0.99$) and an increase in Cr_2O_3 content (0.84); open porosity decreases with a reduction in chromite grain size (0.90). To a lesser extent open porosity depends on

TABLE 9. Correlation Coefficients*[1] Between Physicomechanical Indices, Microstructural Features of Objects and Properties of the Original Chromite Ore*[2]

	Ultimate strength in compression	Open porosity	Apparent density	Heat resistance	Width of circular pores around chromite grains	Reduction in chromite grain size	Nature of chromite grain bonds	Size of chromium spinellide film	Content of FeO	Content of Fe_2O_3	Overall iron oxide content	Content of Cr_2O_3	Amount of impurities	Degree of chromite grain cracking
Ultimate strength in compression	1.00*[1]													
Open porosity	–0.81	1.00												
Apparent density	0.40	0.04	1.00											
Heat resistance	0.64	–0.80	–0.45	1.00										
Width of circular pores around chromite grains	0.60	–0.66	–0.44	0.97	1.00									
Reduction in chromite grain size	–0.97	0.90	–0.35	–0.63	–0.54	1.00								
Nature of chromite grain bonds	–0.36	0.64	0.71	–0.95	–0.92	0.37	1.00							
Size of chromium spinellide film	0.51	–0.27	0.90	–0.29	–0.37	–0.56	0.55	1.00						
Content of FeO	0.84	–0.99	0.09	0.71	0.57	–0.94	–0.53	0.41	1.00					
Content of Fe_2O_3	–0.29	0.64	0.76	–0.91	–0.87	0.32	0.99	0.57	–0.51	1.00				
Overall iron oxide content	0.71	–0.59	0.74	0.04	–0.08	–0.79	0.23	0.94	0.70	0.25	1.00			
Content of Cr_2O_3	–0.86	0.84	–0.48	–0.40	–0.26	0.95	0.15	–0.75	–0.91	0.12	–0.93	1.00		
Amount of impurities	–0.19	–0.20	–0.97	0.64	0.64	0.17	–0.85	–0.88	0.05	–0.88	–0.67	0.36	1.00	
Degree of chromite grain cracking	–0.04	—0.33	–0.93	0.75	0.74	0.02	–0.92	–0.81	0.19	–0.94	–0.57	0.22	0.99	1.00

*[1] Values of correlation coefficient: more than 0.7 high; 0.5 – 0.7 average and 0 – 0.5 low.

*[2] ☐ physicomechanical indices of objects; ▒ microstructural features of objects; ▓ properties of original chromite ore.

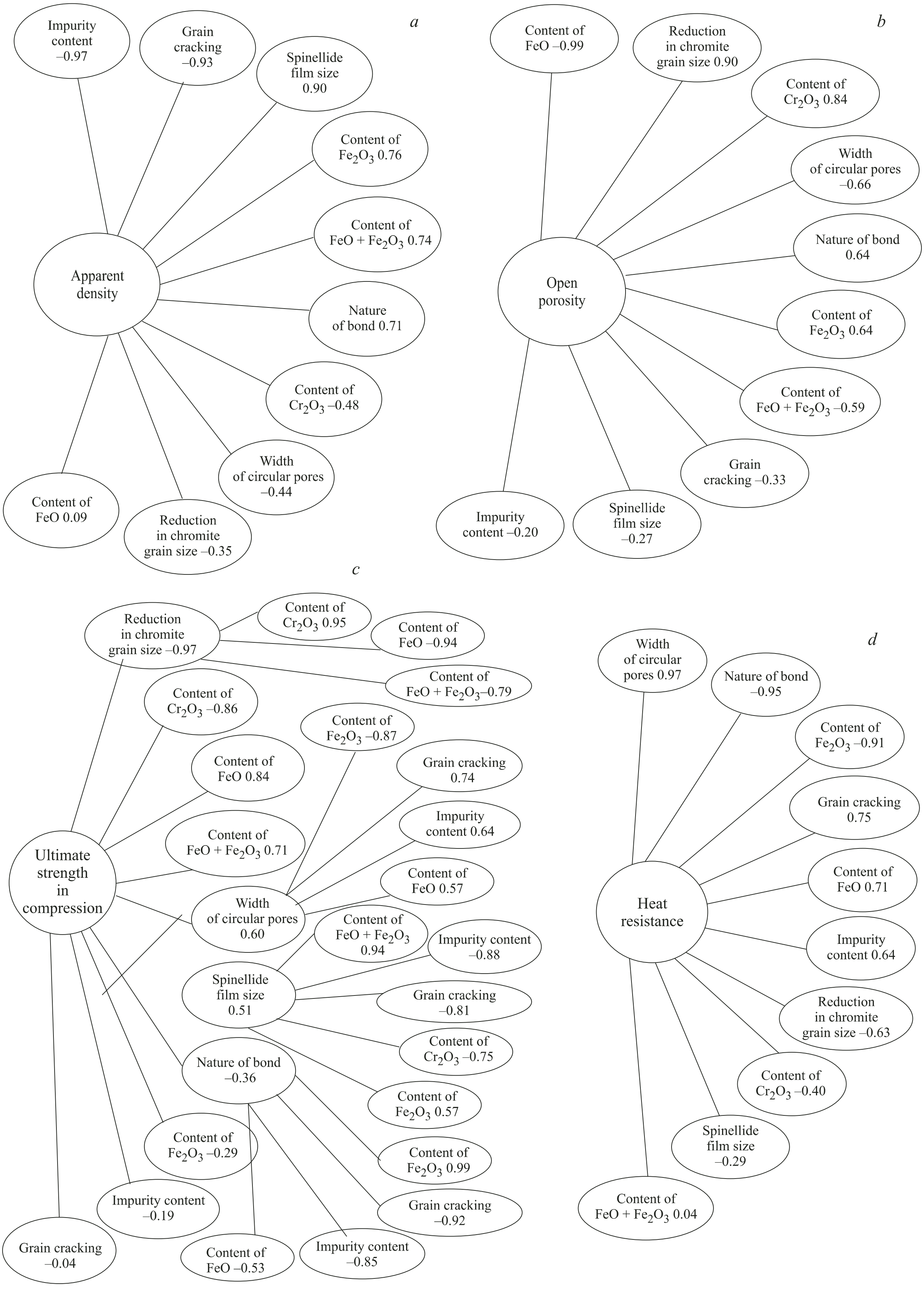

Fig. 8. Correlation dependences of apparent density (*a*), open porosity (*b*), ultimate strength in compression (*c*) and heat resistance (*d*) on microstructural features of PC-objects and properties of the original chromite ore (numbers in ovals are correlation coefficient *k*).

the width of circular pores (-0.66), Fe_2O_3 content (0.64), overall iron content (–0.59). On the rest of the parameters: open porosity of objects does not depend on chromite grain cracking, spinellide film size, amount of impurities (Fig. 8*b*);

- *ultimate strength in compression* for PC-objects increases with a reduction in chromite grain size ($k = –0.97$) and Cr_2O_3 content in the original chromite ore (–0.86) and also with an increase in FeO content (0.84) and overall iron content in the ore (0.71). To a lesser extent the ultimate strength in compression depends on the width of circular pores around chromite grains (0.60) and the size of spinellide films in the finely ground component (0.51). the rest of the parameters analyzed do not affect object strength (,0.5, see Fig. 8*c*);
- *heat resistance* of articles increases with an increase in the width of circular pores around chromite grains ($k = 0.97$), cracking of grains (0.75), FeO content (0.71), and also with an increase in bonding of chromite grains with finely ground component (-0.95) and Fe_2O_3 content in the original chromite ore (–0.91). To a lesser extent heat resistance of objects depends on the amount of impurities in the ore (0.64) and a reduction in chromite grain size (–0.63). The heat resistance of objects does not depend on the rest of the parameters: Cr_2O_3 content, spinellide film size, overall iron content (Fig. 8*d*).

In turn, parameters of the original ores affect the microsctructural features of objects (see Fig. 8*c*):

- the width of circular pores increases with an increase in chromite grain cracking ($k = 0.74$), an increase in FeO content (0.57), and the amount of silicate impurities (0.64) and also with a reduction in Fe_2O_3 content (–0.87); only the more significant parameters are presented;
- a reduction in chromite grain size decreases with an increase in the content of FeO ($k = –0.940$ and Cr_2O_3 (0.95);
- the bond of chromite grains with finely ground component increases with an increase in Fe_2O_3 content in the original ore ($k = 0.99$) and a reduction in the amount of silicates (–0.085) and chromite grain cracking (–0.92);
- the size of chromium spinellide films in finely ground component increases with an increase in the overall iron oxide content ($k = 0.94$) and a reduction in chromium oxide content (–0.75).

Thus, in order to increase the strength of articles it is necessary to use ore with an increased iron content (particularly FeO). In order to increase heat resistance it is necessary to use ore with the minimum Fe_2O_3 content, and increased FeO content, and also with presence of cracked grains containing impurity components (silicates).

DISCUSSION OF RESULTS

In the course of studies it has been revealed that features of the structure of original chromite ores from different deposits (nature and amount of impurity and basic components, grain structure and shape), the behavior of ores during heating, are important in forming the microstructure of PC-refractories. In turn, the results of comparing the microstructural features with thermomechanical indices of PC-objects based on these ores (apparent density, open porosity, ultimate strength in compression, heat resistance) make it possible to propose some recommendations for production solutions of their application.

PC-objects based on Indian chromite ore. Chromite grains exhibit a monolithic microstructure not containing FeO. During firing there is no oxidation of iron oxide, and this means no intense volumetric changes for grains. Consequently around chromite grains interrupted semicircular pores form and their width is at a minimum. In view of this objects based on Indian chromite ore do not exhibit high heat resistance, in contrast to objects based on other chromite ores. In addition, total absence of bivalent iron oxides leads to less intense mass transfer in objects and the overall strength of objects is reduced. Finally, Indian chromite ore is recommended for use in manufacturing PC-objects with increased resistance to infiltration of molten metal-slag into a volume, not requiring high heat resistance, for example at the level of molten metal for the working area of pouring ladles of the nonferrous metallurgy industry.

Recommendations for use of Indian chromite ore are of a rough nature since at this time there are no results of service tests for finished objects.

PC-objects based on Iranian and Turkish chromite ores. Chromite grains in these ores have a cracked microstructure, they contain bivalent iron, that during oxidation leads to additional volumetric changes of the chromite grains and consequently to formation of circular pores around them, which increases the heat resistance of objects. The FeO content in Turkish ore is higher than in Iranian ore, and consequently the heat resistance of objects based on Turkish ore is somewhat higher. Also due to the lower FeO content in Iranian chromite ore the reduction in chromite grain in size is greater than in PC-objects based on Turkish chromite ore (see Table 8). Introduction in the form of a fine fraction (0.5 – 0 mm) of chromite grains into PC-objects based on fuzed periclase-chromite are almost entirely dissolved. In view of the significant content of serpentine impurity in these ores they are desirable for use combined with high purity fuzed materials. Thus, use of these ores is possible for producing PC-objects intended for units not subject to the corrosive action of metal and slag, but experiencing sharp temperature drops, i.e. requiring high heat resistance, for example for lining rotary cement furnaces, steel pouring ladles and arches of steel smelting units.

Objects of grade KhPT based on Iranian ore showed good results in testing in converters for producing copper and nickel and rotary cement furnaces. The Turkish ore is used especially for preparing a large assortment of production of OAO Kombinat Magnezit: articles of grades PKhTs, PKhK, KhPT, KhP, that have stable service properties and are used for lining various industrial units.

PC-objects based on South African chromite ore (*concentrate CM AFS-50*). Grains have a high iron oxide content, particularly FeO. Oxidation of bivalent iron during firing leads to formation of circular pores and as a consequence an increase in object heat resistance. A high content of iron oxides (Fe_2O_3 + FeO) promotes rapid mass transfer between refractory phases, it increases the size of spinellide films on the finely ground component, and in addition the South African chromite ore has a monolithic grain microstructure. These factors promote an increase in the strength of objects. Thus, in using South African ore it is possible to prepare objects with a high ultimate strength in compression and heat resistance. The minimum content of impurity components in the ore makes it possible to use for preparing PC-objects for critical purposes based on high purity raw material, i.e. fuzed periclase, for use in areas with a high slag-corrosion, for example for vacuum degassing units, i.e. bottoms, connections, and for tuyere zones of copper and nickel converters, and also slag belts of steel pouring ladles [1]. This is confirmed by the good results of testing objects grade PKhP during service in degassing units.

CONCLUSION

The test performed make it possible to give precise properties for the original chromite ores and PC-objects based on them. Correlation dependences have been constructed between physicomechanical indices, microstructural features of PC-refractories and the properties of the original chromite ores, that makes it possible depending on features of the original chromite ores, and also their behavior on heating, to propose practical recommendations for use one or other form of ore in order to prepare PC-objects with the desired thermomechanical properties. This in turn is suitable both from an economic point of view and from the point of view of increasing PC-refractory quality. The accumulated experience for studying different chromite ores will be used for developing new forms of PC-objects with prescribed improved production property indices taking account of the interests of refractory production users.

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