

urgent task in the investigation of the porous structure of refractories.

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INTERACTION BETWEEN CHROMITE AND MAGNESIUM OXIDE WHEN HEATED

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A study was made earlier of the reactions in the solid state between Akkarga chromite ore and magnesium oxide in chrome-magnesite mixtures of the heat-resistant type (1-3).

When these mixtures are fixed, complex diffusion processes develop at the contact points between the chromite and periclase grains and form reaction edges (4).

The peculiar zonality of the structure of the heat-resistant chrome-magnesite refractory (5), which shows up as the alternation of the phase composition typical of chromite, chrome-magnesite and magnesite compositions, must be taken into account when evaluating and studying its chemical-mineralogical composition. In minealogical composition this refractory should be regarded as a combination of chromite, chrome-magnesite and magnesite brick.

As initial raw material for the investigation we used Saranov and Kimpersay chromite ores and chemically pure magnesium oxide. The latter was pre-pressed into compacts, fired at 1600° and ground down into two fractions 1-0 and 0.06-0 mm.

The chemical composition of the initial materials is given in Table 1. The weight composition of the charge was 50% chromite ore 1-3 mm and 50% periclase powder 1-0 mm. For purposes of comparison we also prepared a charge from fine-ground materials with a grain size less than 0.06 mm.

The results of the investigation of the finely-ground mixtures may be important for the development of technology in the production of periclase-spinel brick.

The mixtures were moistened with sulfite alkali with a density 1.12 and allowed to stand for a day. Specimens were pressed at 1000 kg/cm², fired at 1680° for four hours in a mildly oxidizing medium.

To gain an idea of the degree of variation in the chrome spinel composition during firing, the powders with a fraction finer than 30 microns were examined through a microscope against the light, and the number of translucent and non-translucent crystals counted.

In the coarse-ground mixtures, the chromite grains were not firmly linked with the periclase, which made it possible to separate them and examine them independently. The thoroughness with which the chromite grains had been separated from the periclase grains surrounding them was checked under the microscope.

The results of the chemical analysis, microscopic and x-ray investigation of the chrome-magnesite specimens, and the chromite and periclase grains separated from the coarse-ground mixtures are given in Tables 2 and 3.

When coarse-ground chrome-magnesite mixtures are

TABLE 1
 CHEMICAL COMPOSITION OF INITIAL MATERIALS*

Material	Fraction, mm	Content, %						
		SiO ₂	Al ₂ O ₃	CaO	MgO	FeO+Fe ₂ O ₃	Cr ₂ O ₃	Ignition Loss
Saranov chromite	3—1	6,28	16,70	0,98	15,11	19,04	39,62	2,28
Saranov chromite	0,06—0	8,40	15,12	1,78	17,54	17,60	35,57	4,00
Kimpersay chromite	3—1	4,39	8,48	0,89	16,81	13,92	55,31	1,95
Kimpersay chromite	0,06—0	8,48	8,38	1,36	18,74	12,32	47,56	4,37
Magnesium oxide fired at 1600°	1—0	0,20	0,40	1,18	98,35	Traces	None	None
Magnesium oxide fired at 1600°	0,06—0	0,22	0,48	1,12	98,25	Traces	None	None

fired, the chromite grains are predominantly enriched with chromium and magnesium oxide, and become deficient in iron and calcium oxides, SiO₂ and sometimes aluminum oxide. The Fe₂O₃:FeO ratio for Saranov ore increases from 0.22 to 4.42, and for Kimpersay ore from 0.34 to 3.40.

The periclase grains are mainly enriched with iron oxides, and to a lesser extent chrome and calcium oxide SiO₂, and are depleted in magnesium oxide. The number of oxides migrating in them (CaO, SiO₂, FeO + Fe₂O₃, Cr₂O₃, Al₂O₃) is 20.02% for Saranov ore, and 10.61% for Kimpersay ore.

The variation in chemical composition of the chromite-periclase grains when the chromite magnesite mixtures are fired is due, on the one hand, to oxidation of the chrome-spinel iron oxide into ferric oxide, and, on the other to dif-

fusion processes of an exchange nature at the separation boundaries of the components.

The active diffusion of Fe₂O₃ into the periclase from the chromite is apparently not only due to the reaction involving substitution of magnesium oxide for chrome spinel ferrous oxide, and oxidation of ferrous into ferric oxide, but also to the strange behavior of iron oxides at high temperatures. At 1385° and constant oxygen pressure, the pure ferric oxide dissociates and is turned into Fe₃O₄ (8).

As distinct from certain other spinels, magnetite contains free electrons. The Fe³⁺ ion may diffuse as a bivalent ion, and then be reconverted to the original state by attracting one electron. The iron ions are able to occupy a tetrahedral position as well as an octahedral position in the

 TABLE 2
 CHEMICAL COMPOSITION OF CHROMITE AND PERICLASE GRAINS, %*

Materials	Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	SiO ₂	CaO
Saranov chromite grains:							
after firing	57,63	10,89	7,00	1,56	20,12	2,55	0,25
natural ore	41,62	14,49	3,72	16,27	15,97	6,70	1,23
Difference	+16,01	-3,60	+3,28	-14,71	+4,15	+4,15	-0,98
Periclase grains:							
after firing	3,89	2,64	8,40		79,94	3,29	1,84
before firing	0,00	0,57	0,00		98,08	0,22	1,13
Difference	+3,89	+2,07	+8,40		-18,14	+3,07	+0,71
Kimpersay chromite grains:							
after firing	59,19	8,68	8,11	2,38	20,11	0,88	0,65
natural ore	54,99	8,58	3,66	10,35	17,01	4,43	0,90
Difference	+4,20	+0,10	+4,45	-7,97	+3,10	-3,55	-0,25
Periclase grains:							
after firing	1,30	0,70	1,51	0,70	89,47	2,16	2,17
before firing	0,00	0,57	0,00	0,00	98,08	0,22	1,13
Difference	+1,30	+0,13	+1,51	+0,70	-8,61	+1,94	+1,04

* All commas are equivalent to a decimal point.

TABLE 3

PHASE COMPOSITION OF FIRED CHROME MAGNESITE MIXTURES

No. of mixture	Composition of mixtures	Results of microscopic and x-ray investigation
1	Saranov chromite grains separated from coarse-ground mixture (50% chromite 3-2 mm and 50% magnesium oxide 1-0 mm)	<p>Altered chrome spinel crystals; forsterite and glass (2-3%) present in bond. Judging by color, chrome spinel crystals have heterogeneous composition; substantial development of magnesium spinels, while ferrichrome picatite (about 20%) is secondary.</p> <p>Optic constants of forsterite normal, grain size 5-20 microns. Glass is colorless with $N = 1.537$ or brown in color with $N = 1.552 - 1.574$.</p> <p>X-ray photographs show altered chrome picatite* and hematite lines.</p>
2	<p>Periclase grains in contact with chromite (mixture 1)</p> <p>Periclase grains after treatment in 20% NH_4Cl**</p> <p>Periclase grains after treatment in 20% HCL.</p>	<p>Periclase of non-uniform color, from dark brown (52% grains) to light yellow and colorless with $N = 1.737$ (20% grains).</p> <p>Mean periclase crystal size 40 microns, 20 microns predominating.</p> <p>Individual periclase grains contain magnesioferrite crystals from 1-5 microns.</p> <p>Forsterite and glass present in proportion 5-7%. Forsterite crystals from 5-30 microns, 20 microns predominating.</p> <p>X-ray photographs show periclase with lattice parameter 4.20 \AA and spinel.</p> <p>62.6% magnesium oxide lixiviated; two types of spinel, forsterite and glass present in extract residue. One spinel reminiscent of magnesio-ferrite in color and crystal shape, the other more complex in composition and possibly has formula $(\text{Mg}, \text{Fe}^{2+})(\text{Fe}, \text{Cr}, \text{Al}^{3+})_2\text{O}_4$; crystal size 1-3 microns.</p> <p>X-ray photographs shows spinel and silicates with $\text{MgO} \cdot n \cdot \text{SiO}_2$.</p> <p>Spinel with different crystal coloring. X-rays showed two types of spinel.</p>
3	Kimpersay chromite and periclase grains***, separated from coarse-ground mixture.	<p>Mineralogical composition and microstructure to great degree similar to mixture 1. 63% translucent grains in chrome spinel compared with 31% in natural ore. Forsterite and glass in chromite grains 2-3%, forsterite crystal size 5-30 microns, 15 microns predominating. Periclase part forms 5-6% forsterite and glass, forsterite crystal size 5-15 microns. When treated with 20% $\text{NH}_4\text{Cl} + \text{NH}_3\text{H}_2\text{O}$, 70.1% magnesium oxide lixiviated from periclase grains.</p>
4	50% Saranov chromite, 50% periclase $\leq 0.06 \text{ mm}$.	<p>Mixture mainly consists of altered chrome spinel and different colored periclase. Secondary spinel and forsterite considerably developed as new minerals. Most chrome spinel (83% grains) translucent, coloring varies (from ruby-red to light yellow) and non-uniform even in fine crystals. Non-homogeneous periclase with coloring from dark brown to light yellow and more rarely colorless. Periclase crystals size 30-50 microns, 40 microns predominating. Secondary spinel has peculiar dark yellow coloring with $N > 1.78$, and irregularly shaped crystals from 2 to 3 microns. Forsterite predominates and glass present (10-13%). Forsterite crystals are colorless with normal refractive indices. Forsterite crystal size 5-40 microns, 20 microns predominating. Not more than 1% monticellite discovered with normal crystallo-optic constants and merwinite with $\omega = 1.718$, $\gamma = 1.708$. For glass $N = 1.522 - 1.552$.</p>

* There is a certain shift in the lines in the powder patterns compared with natural chromite ore.

** By the Gladysheva and Zubakov method (7).

*** Degree of regeneration of chrome spinel during firing and structure of reaction edges in periclase was studied from specimens of chemically pure magnesium oxide, into which individual chromite grains were pressed. These specimens were used after firing to make polished and transparent sections.

TABLE 3

PHASE COMPOSITION OF FIRED CHROME MAGNESITE MIXTURES (Cont'd)

No. of mixture	Composition of mixtures	Results of microscopic and x-ray investigation
5	Periclase grains after treatment with 20% NH ₄ CL. Periclase grains after treatment with 20% HCL. The same as mixture 4 but with addition to Kimpersay ore.	X-rays show periclase and spinel. 31.5% periclase lixivates, 18% binds during firing into magnesian compounds. Amount of forsterite and glass about 30%. X-ray shows spinel, related by us to (Mg, Fe ²⁺) (Cr, Al, Fe ³⁺) ₂ O ₄ . Mineralogical composition and microstructure to great extent similar to mixture 4. Amount of non-translucent grains of chrome spinel kept up to 26%, forsterite and glass 9-11%.

spinel, whereas the Cr₃₊ ion, for example, is usually restricted to an octahedral position. This behavior on the part of the components on the separation surface is apparently one of the chief reasons for uneven diffusion of the oxides in the "chromite-periclase" system.

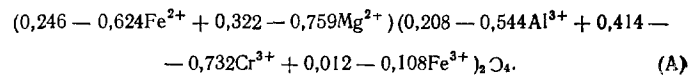
Different kinds of diffusion by oxides in chrome-magnesite refractories, mixtures of chrome spinel and magnesium oxide, and spinels have also been established by other research work (9, 12, 13).

When heated in the systems MgCr₂O₄ - Fe₃O₄, the Fe³⁺ ions diffuse more rapidly than the Cr³⁺ ions, and in the

spinel, its composition can be described by the formula (Mg²⁺) (Cr, Al, Fe³⁺)₂O₄, in which molecules of the two spinels MgCr₂O₄ and MgAl₂O₄ will predominate. The magnesio-ferrite here is secondary.

These changes in the chemical-mineralogical composition of the chrome spinel have an effect on its coloring, and a shift in the chrome picatite lines can be noted in the Debye powder patterns.

Just as for most natural chromite ores, the composition of the chrome spinel solid solution in the chrome-magnesite mixtures after they have been fired can be described by the

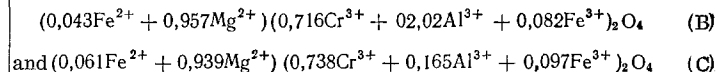


system FeAl₂O₄ - Al₂O₃ the Al³⁺ ions move more rapidly than the Fe³⁺ ions (14).

In chrome spinel the elements Mg - Fe²⁺ and Al - Cr - Fe³⁺ are liable to very extensive isomorphic replacement in view of the nearness of their ionic radii, similarity in parameters and crystal lattice structure of the spinels in them (9, 10, and 11).

According to Rait (9), the composition of chrome spinel in most chromite ores from the largest deposits in the world can be described by the general formula RO · R₂O₃ and the following molecular values:

After the mixtures have been fired, the chrome spinel composition of the Saranov and Kimpersay chromite ores investigated by the author can be described by the following molecular formulae²:



From comparison of formulae A, B and C it is clear that when coarse-ground chrome magnesite mixtures are fired, the chrome spinel is considerably enriched with magnesium and chromium oxides and becomes depleted in ferrous oxide. Discounting the small ferrous oxide content in the chrome

formula RO · R₂O₃. In order to verify whether or not the ratio R₂O₃:RO is constant in chrome spinel for chrome-magnesite compositions alone, we studied the variation in chemical composition of Kimpersay chromite grains when fired in different forms of chromite-containing mixtures: chrome-spinel, chrome-oxide and chrome-silicate.

The data in Table 4 show that when all the chromite-containing mixtures are fired there is a considerable variation in the chemical composition of the chrome spinel. Nevertheless as distinct from chrome-magnesite compositions, the R₂O₃:RO ratio in the spinel does not remain close to unity, but rises from 1.169 to 1.777. On account of an excess of sesquioxides, the chrome spinel composition of these mixtures can be described by the formula n · RO · R₂O₃ · m · R₂O₃. It should be pointed out that the greatest amount of R₂O₃ accumulates in the chromite grains in con-

tact with the oxides (Al₂O₃, Cr₂O₃, Fe₂O₃), and the least quantity in those in contact with the magnesium minerals (MgCr₂O₄, MgAl₂O₄ and Mg₂SiO₄).

In the mixture made from chromite and Fe₂O₃, the ferric oxide content in the chrome-spinel reaches 25.2 mole %, which is not found in natural chromite ores from the world's largest deposits. The author's data tally with Sokolov's conclusions (6) that the maximum iron-oxide content in

² Calculated from data in Table 2.

TABLE 4

CHEMICAL COMPOSITION OF KIMPERSAYI CHROMITE GRAINS
IN DIFFERENT MIXTURES, MOLE, %*

Material in contact with chromite	Chromite grains							Chrome spinel substance					
	Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	SiO ₂	CaO	Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	R ₂ O ₃ RO
MgAl ₂ O ₃	35,7	8,3	7,0	3,0	42,1	2,6	1,3	39,0	9,0	7,6	3,2	41,2	1,252
Al ₂ O ₃	36,5	10,6	7,1	2,4	40,1	2,5	0,9	39,5	11,5	7,8	2,6	38,6	1,427
MgCr ₂ O ₄	38,5	6,3	5,4	2,0	44,5	2,0	1,3	41,3	6,8	5,8	2,2	43,9	1,169
Cr ₂ O ₃	47,1	3,6	6,2	2,7	35,3	3,6	1,5	53,0	4,0	7,0	3,0	33,0	1,777
Fe ₂ O ₃	22,6	4,6	21,7	3,6	41,1	4,7	1,7	26,1	5,4	25,2	4,3	39,0	1,561
SiO ₂	33,7	7,2	7,2	5,5	37,4	8,0	1,0	43,0	9,2	9,2	6,9	31,7	1,590
Mg ₂ SiO ₄	32,5	8,2	6,1	3,7	43,1	5,2	1,2	39,0	9,8	7,3	6,2	37,7	1,278
MgO	35,7	7,8	4,6	3,0	46,2	1,4	1,3	36,3	8,1	4,7	3,1	47,8	0,960

* All commas are equivalent to a decimal point.

chrome-spinel may reach 25 mole %. Sokolov considers that in the cation part all the chrome and alumina are isomorphically replaced by Fe³⁺ and the formula takes the form R²⁺ Fe³⁺ · [(Cr, Al)₂O₄]⁻⁵. In the author's opinion, Fe³⁺ can not be part of the complex anion composition since the complex Fe³⁺ ion has an excellent form (Fe³⁺ O₂)⁻¹, for example magnetite Fe²⁺(Fe³⁺ O₂)₂⁻¹.

The diffusion processes and the reactions taking place when coarse-ground chrome-magnesite mixtures are fired lead to the formation of a number of new phases in the periclase reaction zone, to wit: magnesio-ferrite MgFe₂O₄, spinel (Mg, Fe²⁺)(Fe³⁺, Cr, Al)₂O₄, forsterite with 20 micron crystals, and glass.

The formation of forsterite and two types of spinel in the reaction edges is confirmed by microscopic and x-ray analysis. The magnesio-ferrite crystals are detected under large magnification within the large periclase grains; the total amount of magnesio-ferrite in the mixtures is not more than 8 - 10%.

Apart from the iron oxides, a small quantity of chrome and aluminum oxides diffuse to the periclase from the Sarany and Kimpersayi chrome spinel, and these oxides probably dissolve in the magnesio-ferrite and form a more composite spinel.

It should be taken into account that the principal molecule in this spinel is MgFe₂O₄, and the MgCr₂O₄ and MgAl₂O₄ are of secondary importance.

When chrome-magnesite mixtures are fired, the process of recrystallization in the periclase is apparently speeded up on account of diffusion of the iron oxides from the chromite into the periclase, the formation of magnesioferrite and solid solutions of it with the periclase. Thus, in the coarse-ground mixture made of Sarany chromite, the mean periclase grain size increases from 8 to 40 microns, compared with control specimens made of pure magnesium oxide. In fine-ground chrome-magnesite mixtures the mean periclase grain size increases within more or less the same limits as in the reaction edge of the coarse-ground mixtures.

As the grain size increases, the specific surface increases and so does the imperfection of the crystal structure in the surface layers, which creates more favorable conditions on the separation borders for material to be transferred.

As opposed to coarse-ground chrome-magnesite mixtures, fine-ground mixtures lack free iron oxides, there is less unbonded magnesium oxide, the periclase coloring is more uniform on account of more even distribution of iron oxides

in it, and the chrome spinel grains are lighter in color.

The active occurrence of diffusion processes and reactions in fine-ground mixtures leads to the formation of a more uniform phase composition of the chrome-magnesite refractories, and this fact must have a substantial effect on their technological properties.

CONCLUSIONS

The results obtained from the study of processes occurring when chromite ores from the Sarany and Kimpersayi deposits react with magnesium oxide in coarse-ground and fine-ground mixtures fired up to 1700° and slowly cooled suggest the following.

In the coarse-ground mixtures (chromite with 1 - 3 mm grain size and periclase 1 - 0 mm) diffusion processes of an exchange nature occur at high temperatures. First of all, iron oxides and silicates diffuse from the chromite grains into the periclase, and then magnesium oxide diffuses from the periclase into the chromite.

The variation in chemical composition of chrome spinel when fired is accompanied by a change toward lighter color and a considerable shift in the Debye power patterns on account of incipient rearrangement of the chrome picatite crystal structure. The chrome spinel composition is described by the formula RO · R₂O₃.

More important changes in the composition are observed with it is fired in mixtures of chromite and spinel, oxides and silicates, in which the spinel has the formula n · RO · R₂O₃ · m · R₂O₃, and ratio R₂O₃:RO varies from 1.169 to 1.777.

The diffusion of oxides from the large chromite grains to the periclase leads to the formation of new compounds in the reaction zone: magnesioferrite, composite spinel, forsterite and glass.

As the periclase moves away from the chromite grains it changes its color from dark brown to colorless, and the refractive index correspondingly drops from N > 1.78 to normal.

In fine-ground mixtures (chromite and periclase less than 0.06 mm) the reactions are more complete and sintered material of more homogeneous chemico-mineralogical composition is formed compared with heat-resistant chrome-magnesite parts, for which a peculiar zonality of structure

and sharp heterogeneous in composition are natural.

The principal phases are: Altered chrome spinel with heterogeneous crystals; magnesian spinels predominating ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$, and $\text{MgO} \cdot \text{Al}_2\text{O}_3$), and ferruginous spinels $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ and $\text{FeO} \cdot \text{R}_2\text{O}_3$ being present in very small quantities.

Periclase with normal cubic crystal lattice parameters and variable refractive index.

The new compounds formed are secondary spinel with the formula $(\text{Mg}, \text{Fe}^{2+}) \text{Fe}^{3+} \text{Cr}, \text{Al})_2\text{O}_4$; the $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ in it is considerably more developed than $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and $\text{MgO} \cdot \text{Al}_2\text{O}_3$, which are the basis of the altered chrome spinel during firing; forsterite and glass with single monticellite and merwinite crystals.

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SPINEL-BONDED MAGNESITE BRICK WITH INCREASED REFRACTORINESS-UNDER-LOAD

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The standard magnesite brick made by the "Magnezit" plant has low heat resistance and refractoriness-under-load which means that its life in metallurgical furnaces is reduced.

Research carried out by the Ukrainian Institute of Refractories has shown the possibility of increasing the refractoriness-under-load by adding or using magnesite containing up to 3% SiO_2 and 2% CaO (1). Refractories manufactured from this magnesite show high density, constant volume at high temperatures and high refractoriness-under-load (above 1800°), but are not spalling resistant.

Research has shown that if alumina is added to magnesite mixtures a spinel bond is obtained during firing which increases the thermal resistance of the brick (2).

The spinel is formed more completely at high temperatures and also depends on the dispersed state of the alumina used. Microscopic investigation of commercial alumina after prolonged grinding in a ball mill shows that it consists of large aggregates of the nature of tens of microns in size. Hence the normal practice of adding alumina to the charge, grinding it together with magnesite to a grain size of less than 60 microns and firing the parts at 1650° for six hours, did not produce the required effect. The refractory became friable and the refractoriness-under-load decreased.

Taking it into account that the reaction rate in the solid phase increases as the reacting component grain size decreases (3, 4), when developing technology for the manufacture of magnesite refractories with a spinel bond and increased refractoriness-under-load and thermal resistance we used a vibration-crushed alumina with a grain size of

less than 2 microns. The crushed alumina was added to the fine-ground charge component with joint grinding (in the given case mixing) with magnesite of the chemical composition in %: 2.94 SiO_2 , 1.07 Al_2O_3 , 1.5 Fe_2O_3 , 2.00 CaO , 91.83 MgO , and 0.56 other impurities.

The joint grinding (mixing) was conducted in a ball mill until the residue on a 0.06 mm mesh was not more than 10%. The mixture was moistened with sulfite-cellulose liquor in the proportion of 1% dry weight. For the laboratory tests the moisture content of the mixtures was 3-3.5% and the grain size as follows: 20% 1-0.5 mm, 80% finer than 0.5 mm, including 40% less than 0.060 mm.

Cylinder shaped-specimens 36 mm in diameter and 50 mm long were pressed on a hydraulic press at 1000 kg/cm^2 , dried until a residual moisture content of 0.5% and fired in an oil-fired kiln at 1650° for six hours.

The properties of the fired specimens are given in Table 1. For purposes of comparison we give the figures for specimens made without pregrinding of the alumina. The heat resistance was determined for the specimens by heating in a muffle kiln up to 900° for 15 minutes and then cooling them in running water.

Petrographic investigation showed that specimen No. 2 consisted of maximum size periclase grains - 0.25 mm grains 0.08 - 0.12 mm predominated. Here and there they were combined into irregularly-shaped aggregates 0.4 - 1.8 mm in size. Most of the periclase grains showed pronounced cubic cleavage. The refractive index was 1.740 - 1.750 for periclase. The bond between the periclase grains was rep-