
Original Papers

STUDY OF INTERACTIONS AT THE SLAG-BASIC REFRACTORY BOUNDARY

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Interaction at the phase boundary, between molten slag and the refractory was studied on L I and L I H magnesite refractories and L III K and L III HK chrome-magnesite refractories, using silicate and ferritic-calcium slags. Slags of the system $FeO - Fe_2O_3 - CaO$ penetrate more readily into the depth of the refractories than the silicate slags, but show lower chemical aggressivity. In the case of L I H and L III K, the matrix is enriched with Ca, Mg silicates. Periclase in L I H gets enriched with the $MgFe_2O_3$ phase, while periclase grains in L III K tend to dissolve. With the L III HK material, the penetration is not extensive but the boundary is chemically attacked to a higher degree. The ferritic slag enriches the L I material with Fe_2O_3 , forming magnesium-ferritic inclusions around the periclase grains. In the case of L I H, Fe_2O_3 penetrates the periclase grains similarly as it does with L III K, where it also attacks the chrome-spinel grains. A more extensive formation of ferritic interstitial material takes place in L III HK. The effects of ferritic-calcium slags with various CaO contents do not show any substantial differences. The structure in the interaction zone is not significantly affected by changes in the atmosphere.

INTRODUCTION

The non-ferrous metal industry is a relatively small consumer of refractories, and has been traditionally accepting materials originally developed for iron and steel producers. Basic refractory materials have found wide applications in the furnaces for non-ferrous metal production, having replaced the silicate and aluminosilicate refractories used in the past. This change has been brought about by ever more exacting demands on the conditions of furnace operations, in particular those associated with operation temperatures, which required new basic refractories, more resistant to the aggressive effects of slags at high temperatures, to be introduced.

The use of refractories in non-ferrous metal metallurgy is generally characterized by the following aspects:

- (1) A high aggressivity of silicate slags, frequently rich in iron oxides
- (2) Aggressive attack by both metallic and non-metallic oxidic phases
- (3) High temperatures
- (4) Temperature differences
- (5) Mechanical stressing
- (6) Oxidation and reduction conditions
- (7) The conditions of contact with the slag, which vary from highly abrasive to highly turbulent ones.

One has to know precisely the properties of refractories in order to design high-grade and durable furnace linings. The individual materials have to be assessed from the standpoints of technology, power consumption and economy.

The present paper summarizes the results obtained in the study of interactions at the phase boundary between molten slag and the refractory. Various types of magnesite and chrome-magnesite refractories were investigated in this respect. The classical silicate slag and the basic ferritic-calcium slag were tested as the aggressive media. The study had the purpose to compare the effects of the two types of slags on the respective grades of refractories, and to assess the mechanism of interactions at the slag-lining phase boundary during pyrometallurgical production of non-ferrous metals.

EXPERIMENTAL

The static test by the so-called crucible method was chosen for investigating the interaction between liquid slags and the refractories. A hole 33mm or 12mm in diameter was drilled into the respective refractory brick. The hole was filled with the corrosive medium, and the test specimens were placed in a silitite resistance furnace. Having heated the specimens to the required temperature and melted the aggressive medium, the specimens were kept at the temperature for 12 hours, while making up the slag level

during the experiment. Following conclusion of the heating, the specimens were cooled down in the furnace and samples for macroscopic and microscopic analysis were prepared by cutting the specimens with a diamond saw. The interaction tests were carried out in two series. In the first series of experiments, four types of refractories and two types of slags were used as follows:

The refractories:

LI – magnesite refractory:

86–87% MgO, 7.5–8.0% Fe₂O₃, 2.5–3.5% CaO,
1.5–2.5% SiO₂, 0.2–0.5% Al₂O₃,
 $\delta = 2.8\text{--}2.9\text{ g/cm}^3$, AP = 14–16%

LIH – magnesite refractory:

87–89% MgO, 7.8–8.3% Fe₂O₃, 2.3–3.0% CaO,
0.8–1.5% SiO₂, 0.2–0.5% Al₂O₃,
 $\delta = 2.95\text{--}3.1\text{ g/cm}^3$, AP = 14–16%

LIIK – magnesia-chrome refractory:

60–70% MgO, 12–16% Cr₂O₃, 7–11% Fe₂O₃,
1.5–3.0% CaO, 2.5–5.0% SiO₂,
 $\delta = 2.9\text{--}3.0\text{ g/cm}^3$, AP = 18–22%

LIIHK – chrome-magnesite refractory:

41–47% MgO, 28–32% Cr₂O₃, 11–15% Fe₂O₃,
6–7% Al₂O₃, 1–2% CaO, 2.5–5% SiO₂,
 $\delta = 3.0\text{--}3.1\text{ g/cm}^3$, AP = 18–23%

where AP is apparent porosity.

The corrosive media employed:

(a) Silicate slag:

43.62% FeO, 19.27% Fe₂O₃, 5.56% CaO, 30.8% SiO₂

(b) Ferritic-calcium slag:

53.55% FeO, 22.04% Fe₂O₃, 23.95% CaO.

The second series of experiments was carried out on a single type of refractory, the LIIK. Ferritic-calcium slag with three different CaO contents was used as the corrosive media. Both oxidation and reduction atmospheres were employed. The ferritic slags had the following compositions:

(1) 61.97% FeO, 17.07% Fe₂O₃, 20.01% CaO

(2) 50.70% FeO, 19.60% Fe₂O₃, 28.70% CaO

(3) 46.50% FeO, 19.17% Fe₂O₃, 33.13% CaO

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Samples from the first series of corrosion tests on four types of refractories, LI, LIH, LIIK and LIIHK, made with two types of slags, were subjected to macro- and microstructural analyses. Some of the typical microstructures are shown on micrographs made with the NEOFOT 2 microscope under reflected light.

In the case of the LI refractory and both types of slag, slag penetration into the refractory matrix was observed, creating a sharp boundary while corroding the refractory surface in the instance of the silicate slag, which is more aggressive. The content of calcium and magnesium silicates in the refractory in-

creased. The ferritic slag enriches the refractory with Fe₂O₃ and forms magnesite-ferritic inclusions around the periclase grains.

The LIH sample is demonstrated on Figs. 1 and 2. The refractory is of a higher density and the structure of penetration is similar to that of sample LI. Under the effect of the ferritic-calcium slag, Fe₂O₃ can be observed to penetrate the periclase grains and form magnesite-ferritic inclusions. On the other hand, the silicate slag enriches the refractory with Ca and Mg silicates, and the periclase with the MgFe₂O₄ phase.

The corrosion tests of the LIIK chrome-magnesite refractory showed a distinct penetration of the corrosive medium into the refractory and a difference in the appearance of the boundary: while the ferritic-magnesite slag forms a sharp boundary and Fe₂O₃ affects the periclase and chrome-spinel grains, forming enriched layers around the grains, the silicate slag forms Ca and Mg silicates and dissolves periclase grains. The chrome-spinel grains are more resistant. The microstructures of the samples are shown in Figs. 3 and 4.

In the case of the LIIHK refractory material, the penetration of silicate slag into the intergranular space and matrix is well discernible, and the refractory boundary is corroded. The effect of the ferritic-calcium slag is different in character. The slag penetrates periclase and chrome-spinel grains at the boundary. The grains become enriched with Fe₂O₃ and a ferritic interstitial material replacing the silicate material is formed in the matrix. The penetration of the ferritic slag into the matrix is deeper than with the silicate slag. The ferritic-calcium slag impregnates more the refractory, but the boundary remains sharp: Penetration of the silicate slag is not so extensive, but the refractory surface is more corroded than in the case of the ferritic slag. The microstructures of these samples are shown in Figs. 5 and 6. Table I illustrates that contact of the refractories with the silicate slag brings about significantly more extensive dissolution of MgO and Cr₂O₃ than contact with the ferritic-calcium slag.

The tests in the second series of experiments were made on the LIIK refractory, using ferritic-calcium slag with three different CaO contents.

Macroscopic evaluation of the depth of penetration by the ferritic-calcium slag on this group of samples showed that the greatest penetration depth occurred with the slag containing about 28 wt.% CaO in a reduction atmosphere, while the shallowest penetration was found with the slag containing approx. 20 wt.% CaO, also in a reduction atmosphere. This may be explained by a difference in the properties of slag due to the changed CaO content.

The microstructures of these samples are similar in

Table I
Slag composition after the corrosion test

Sample	Slag composition after the corrosion test (wt.%)							Penetration depth (mm)
	MgO	Fe ₂ O ₃	CaO	SiO ₂	MgO	Cr ₂ O ₃	Fe _M e	
LI	5.16	71.29	17.42		3.16	0.18		4-6
LIH	1.37	74.92	20.92		0.78	0.10		8-13
LIIK	1.12	77.38	19.59		0.83	0.21		3-5
LIIHK	1.63	74.60	18.54		5.40	0.37		>14
LI	51.01	9.17	3.43	21.25	6.05	0.51	2.36	2-4
LIH	50.37	9.71	4.62	26.50	5.06	0.07	1.40	3-8
LIIK	53.37	13.37	3.43	20.25	4.48	0.69	0.90	2-6
LIIHK	48.44	12.46	4.06	21.75	8.26	1.84	0.86	1-3

Table II
Initial and final composition of the slags

Sample	Initial composition (wt.%)			Final composition (wt.%)			Penetration depth (mm)
	FeO	Fe ₂ O ₃	CaO	FeO	Fe ₂ O ₃	CaO	
1 A	61.97	17.02	20.01	7.84	76.90	15.26	14-17
1 B	61.97	17.02	20.01	49.33	32.00	18.68	5-9
2 A	50.70	19.60	28.70	13.16	59.15	27.69	23-25
2 B	50.70	19.60	28.70	50.30	23.80	25.90	38-40
3 A	46.50	19.17	33.13	6.92	62.36	30.71	6-16
3 B	46.50	19.17	33.13	-	-	-	22-25

A - oxidation atmosphere, B - reduction atmosphere

character, as shown in Fig. 3, and thus need not be described in more detail.

Table II lists the chemical analyses of slags both before and after the corrosion tests, and the depth of penetration into the matrix.

The microscopic examination showed that the ferritic-calcium slag with various CaO contents underwent no significant changes in its structure in the interaction area, in both oxidation and reduction atmospheres. Structurally, an indistinct effect of reduction was established in the impregnated zone. The slag penetrates the refractory structure and the silicate intergranular phase is replaced by a ferritic one. Also some parts of the grains are subject to changes. The chromo-spinel grains at the edge are en-

riched with Fe₂O₃ which forms a sort of rim around the chromo-spinellitic grains. The periclase grains also become enriched with Fe₂O₃ and there arise magnesio-ferritic inclusions of MgFe₂O₄ separated from the MgO-FeO solid.

CONCLUSION

The results obtained from the first experimental series including four types of refractory materials and two types of slags show that slags of the system FeO-Fe₂O₃-CaO penetrate more the refractory than the silicate ones, this being due to the lower viscosity of the former. However, the ferritic slags are less chemically aggressive. Infiltration of the ferritic-calcium slag into the refractory matrix results in re-

actions between the slag and the refractory components, producing ferrites and enriching the periclase and chromo-spinel grains with Fe_2O_3 , which forms a kind of barrier suppressing further dissolution of the refractory in the slag. This reaction zone can be observed in the microstructures shown in Figs. 1, 2 and 5. The penetration of the silicate slag is more aggressive, the slag-refractory boundary is corroded, and the individual periclase grains are so to speak washed out of the matrix, while at the same time being dissolved in the slag. It should be noted that at the given temperatures, the viscosity of ferrite-calcium slags is lower by an order of magnitude than that of the silicate slags.

The results of the second series of experiments on a single type of refractory, LIIIK, subjected to the effects of ferrite-calcium slags with various contents of CaO, have established no significant differences between the reactions, which were also not affected by the prevailing type of atmosphere. In the specimens, the slag was mostly separated from the refractory by a more-or-less continuous crack, behind which the mutual reactions could be observed.

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ŠTÚDIUM INTERAKCIE NA ROZHRAŇÍ TEKUTÁ TROSKA - ZÁSADITÝ ŽIARUVZDORNÝ MATERIÁL

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V príspevku sú uvedené výsledky štúdia interakcii na fázovom rozhraní trosková tavenina - žiaruvzdorný materiál. Ako žiaruvzdorné materiály boli použité magnezitové staviva LI a LIH a chrómmagnezitové staviva L III K

a L III HK. Pre skúšky bola zvolená statická skúška tzv. tégliková metóda. Ako korózne médium bola použitá silikátová troska s obsahom 45,62% FeO, 20,27% Fe_2O_3 , 6,56% CaO, 30,8% SiO_2 a feriticko-vápenatá troska s obsahom 53,35% FeO, 22,04% Fe_2O_3 , 23,95% CaO. U žiaruvzdorného staviva L III K bola okrem vyššie uvedeních trosiek skúšaná feriticko-vápenatá troska s obsahmi 20,01%, 28,7% a 33,13% CaO.

Vzorky z celej série korózných skúšok bolo podrobené makroštruktúrnej a mikroštruktúrnej analýze.

U žiaruvzdorného materiálu LI trosky prenikajú do staviva, pričom pri použití feriticko-vápenatej trosky je rozhranie ostré, pri silikátovej troske je rozhranie rozrušené, čo odpovedá väčšej chemickej korózii. Pri použití silikátovej trosky zvyšuje sa obsah vápenatých a horechnatých silikátov v stavive. Feritická troska obohacuje stavivo o Fe_2O_3 a okolo zŕn periklasov tvorí magnoferitické inklúzie.

Pôsobením feriticko-vápenatej trosky na stavivo LIH dochádza k preniknutiu Fe_2O_3 do zŕn periklasu a vznikajú magnoferitické inklúzie. Pôsobením silikátovej trosky matrix sa obohacuje o Ca, Mg - kremičitany a periklasy o fázú MgFe_2O_4 .

U staviva L III K pri použití feriticko-vápenatej trosky dochádza k pôsobeniu Fe_2O_3 na zrná periklasu a chróm-spinelu. Pôsobením silikátovej trosky vznikajú Ca Mg kremičitany a dochádza k rozpúšťaniu zŕn periklasu.

U materiálu L III HK pôsobením feriticko-vápenatej trosky dochádza k výraznejšej tvorbe feritovej intergranulárnej výplne, ktorá nahrádza kremičitanovú. Dochádza k väčšej impregnácii staviva troskou. Prienik silikátovej trosky nie je tak intenzívny ale rozhranie je viac rozrušené.

Vyhodnotenie pôsobenia feriticko-vápenatej trosky s rôznym obsahom CaO na stavivo L III K ukázalo, že pri oxidačných a redukčných podmienkach korózie nie sú podstatnejšie zmeny v štruktúre interakčnej oblasti. Chróm-spinelitické zrná na okraji sú obohatené o Fe_2O_3 . Periklasové zrná sa tiež obohacujú o Fe_2O_3 a dochádza k ich obohateniu o magnoferitické inklúzie - MgFe_2O_4 .

Záverom je možné konštatovať, že trosky sústavy FeO - Fe_2O_3 - CaO vo väčšej miere prenikajú do hĺbky žiaruvzdorného materiálu ako trosky silikátové, ale ich chemická korózia je menšia. Pôsobenie feriticko-vápenatých trosiek s rôznym obsahom CaO neukázalo výraznejšiu odlišnosť. Zmena atmosféry nemá podstatný vplyv na štruktúru v interakčnej oblasti.

Obr. 1. Magnéziové stavivo LIH po pôsobení feriticko-vápenatej trosky, zrná periklasu (sivá) - P, inklúzie magnézioferitu (sivobiela) - MF, póry a trhliny (čierna) - O.

Obr. 2. Magnéziové stavivo LIH po pôsobení silikátovej trosky, zrná periklasu (svetlo sivá) - P, medzizrnová silikátová výplň (sivá) - S, póry a trhliny (čierna) - O.

Obr. 3. Magnézió-chromitové stavivo LIIIK po pôsobení feriticko-vápenatej trosky, zrná periklasu (sivá) - P, medzizrnová feritická výplň (tmavo sivá) - F, inklúzie magnézió-feritu (sivobiela) - MF, chróm-spinelitické zrno (biela) - C, póry a trhliny (čierna) - O.

Obr. 4. Magnézió-chromitové stavivo LIIIK po pôsobení silikátovej trosky, zrná periklasu (svetlo sivá) – S, chrómspinelitické zrno (sivo biela) – C, póry a trhliny (čierna) – O.

Obr. 5. Chróm-magnéziové stavivo LIIHK po pôsobení feritickovápenatej trosky, zrno periklasu (sivá) – P, inklúzie magnézió-feritu (sivo biela) – MF, medzizrno-

vá feritická výplň (tmavo sivá) – F, chrómspinel (svetlo sivá) – C, póry a trhliny (čierna) – O.

Obr. 6. Chróm-magnéziové stavivo LIIHK po pôsobení silikátovej trosky, zrno periklasu (svetlo sivá) – P, medzizrnová silikátová výplň (tmavo sivá) – S, chrómspinel (sivobiela) – C, póry a trhliny (čierna) – O.

Conference

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May 8–13, 1994

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The program will attempt to maintain parallel sessions on fundamental and theoretical aspects of chromatography; applications and automation of chromatography and ancillary techniques; and focus topics such as specific detector technology. Something for chromatographers of all levels of experience. Discussion sessions will emphasize how to best use new approaches and technologies for the practitioner as well as theoretical aspects of chromatography.

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Field Flow Fractionation	Supercritical Fluid
Hyphenated Techniques	Thin Layer
(LC/MS, LC/IR, LC/NMR,	Toxicology
LC/Laser Scattering, etc.)	

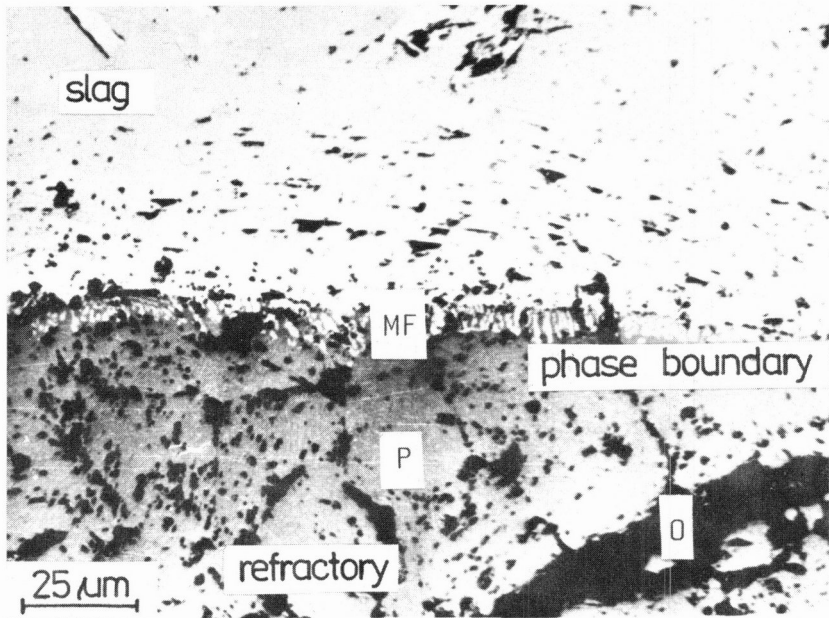


Fig. 1. Magnesite refractory LTH following high-temperature exposure to ferrite-calcium slag. P - periclase grains (grey), MF - magnesite-ferrite inclusions (grey-white), O - pores and cracks (black).

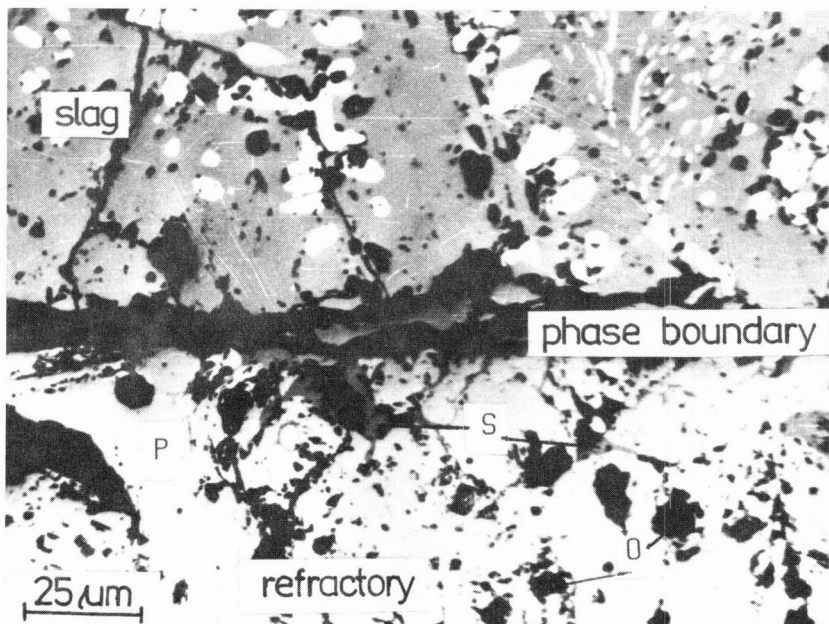


Fig. 2. Magnesite refractory LIH following high-temperature exposure to silicate slag. P - periclase grains (light grey), S - interstitial silicate material (grey), O - pores and cracks (black).

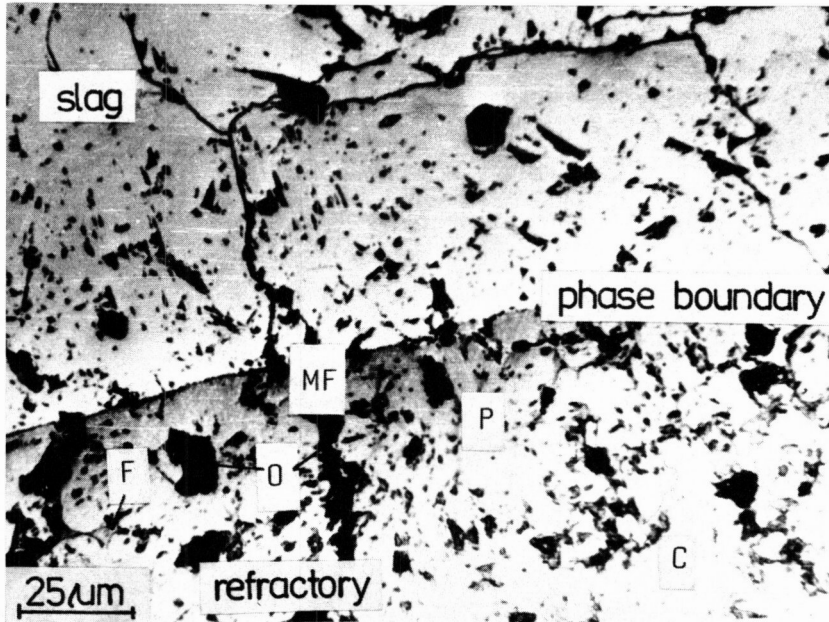


Fig. 3. Magnesite-chromite refractory LIIIK following high-temperature exposure to ferritic-calcium slag. P - periclase grains (grey), F - interstitial ferritic material (dark grey), MF - magnesite-ferrite inclusions (grey-white), C - chrome-spinel grain (white), O - pores and cracks (black).

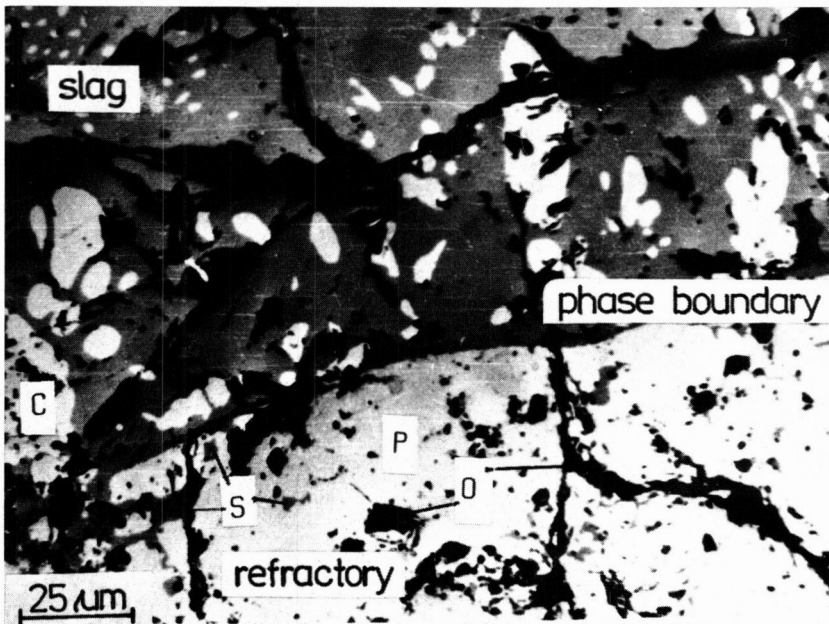


Fig. 4. Magnesite-chromite refractory LIIIK following high-temperature exposure to silicate slag. P - periclase grains (light grey), S - interstitial silicate material (dark grey), C - chromo-spinel grain (grey-white), O - pores and cracks (black).

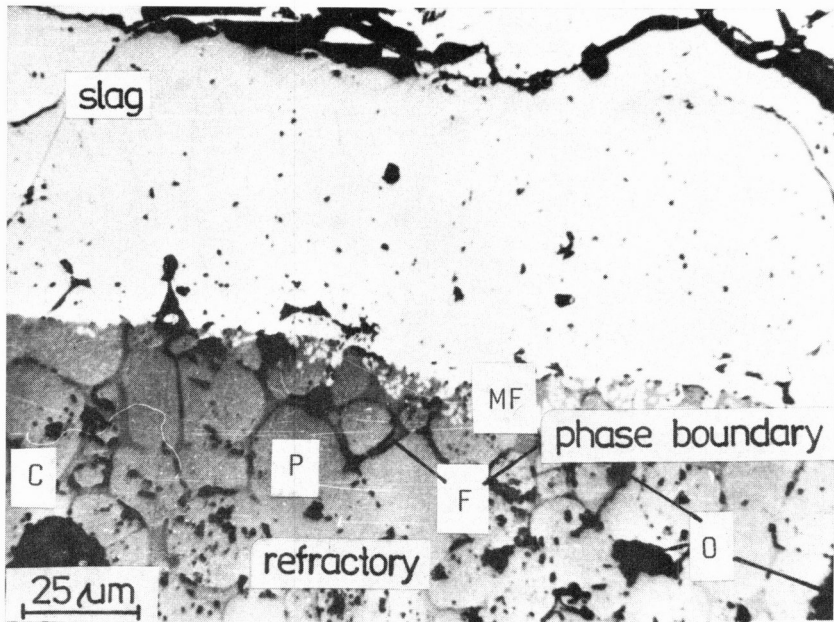


Fig. 5. Chrome-magnesite refractory LIIHK following exposure to ferritic-calcium slag. P – periclase grains (grey), MF – inclusions of magnesite-ferrite (grey-white), F – interstitial ferritic material (dark grey), C – chromo-spinel (light grey), O – pores and cracks (black).

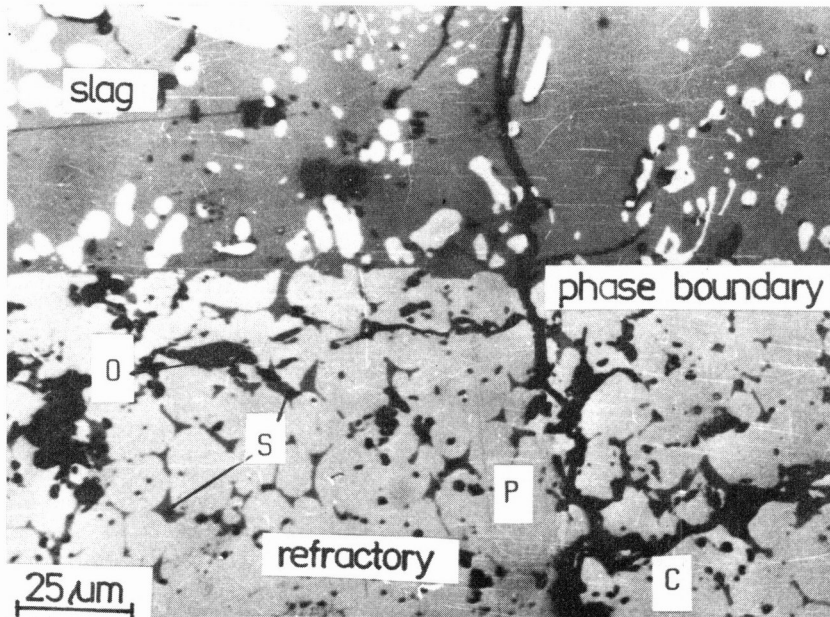


Fig. 6. Chromo-magnesite refractory LIIHK following high-temperature exposure to silicate slag. P – periclase grain, S – interstitial silicate material (dark grey), C – chromo-spinel (grey-white), O – pores and cracks (black).