INTERACTION AT THE PERICLASE – SLAG MELT PHASE BOUNDARY

PAVOL VADÁSZ, ĽUDOVÍT MOLNÁR

Institute of Metallurgy and Materials, Faculty of Metallurgy, Technical University Košice, Park Komenského 3, 043 85 Košice

Received 13. 5. 1991

Corrosion of periclase monocrystals by the ferrite-calcium, silicate and composite slag melts is for the most part caused by diffusion of iron. In silicate and composite slags, periclase is dissolved while at the same time forming magnesium silicates. Diffusion of calcium and silicon into periclase could not be proved by the methods employed.

INTRODUCTION

Refractory lining materials in kilns and furnaces are exposed to chemical and physical effects of the ambient medium. At high temperatures, reactions occur between the solids, the lining and the liquids (slag, metal) and sometimes also gaseous media (flue gases, vapours) existing in the kiln or furnace atmosphere, and the reactions cause corrosion of the refractories. In the given case, corrosive attack by melts represents a complex thermochemical and thermophysical process. Mutual reactions between the components of the refractory material and the aggressive medium constitute the basic chemical phenomenon. The reactions depend on the chemical nature of the refractory and that of the aggressive medium, as well as on its physico-chemical properties.

In [1, 2 and 3], corrosion of basic refractories by slag melts during pyrometallurgical production of copper was studied. Corrosion of the materials was found to proceed in the form of diffusion of iron into periclase and by the formation of soluble or insoluble compounds according to the character of the slag (ferritecalcium, silicate or composite).

During dissociation in slag melts, oxides and silicates form complex anions, the O^{2-} anion and the M^{2+} cations. Free oxygen anions in slag exhibit the highest activity. Orlovskij [4] found that the initial stage of (kinetic) corrosion of the refractory depends directly on the concentration of free oxygen in the melt.

At the Urals Polytechnical Institute, the rotating disk method was used to study the rate of dissolution of refractories in oxidic melts [5]. It was established that fused magnesia dissolved in ferrous oxide melt at a rate of 9.4 mg cm⁻²s⁻¹ and in fayalite melt at a rate of 1.3 mg cm⁻²s⁻¹. In the case of the fayalite melt, the diffusion coefficients $D_{SiO_2} = 3.2 \times 10^{-5}$ cm²s⁻¹ and $D_{MgO} = 9.3 \times 10^{-6}$ cm²s⁻¹ were determined.

The physico-chemical interaction between a spinelitic-periclase refractory and a slag melt represents reactions in which the iron contained in the slag is absorbed by periclase and spinel, producing solid solutions. The calcium silicate components of the melt combine with periclase or spinel, forming metasilicates or orthosilicates and calcium compounds [6].

Hatfield et al. [7] studied the system CaO-MgO-SiO₂ at 1550-1700°C and found that the solubility of silica in periclase amounts to about 0.2% and that of calcium oxide is still poorer. The solubility depends on the CaO/SiO₂ (C/S) ratio in the melt.

The corrosive aggressivity of slag towards all types of basic refractories decreases with increasing C/S ratio and increases with increasing content of iron oxides in both the refractory and the slag [8]. With C/S rising up to 2.5, the aggressivity of slag at 1600°C increases. At C/S exceeding 2.5, dicalcium silicate (2CaO.SiO₂; t_t = 2130°C) is formed and crystallizes, rapidly increasing the melt viscosity and thus suppressing the aggressivity of the slag.

Pánek and Danēk [9] studied the mechanism by which a protective periclase layer is formed in the course of corrosion of dolomagnesia refractories by steelmaking slags and found that during the interaction, CaO was dissolved in slag producing dicalcium silicate and causing MgO grains to grow in the presence of the melt, the rate of growth being controlled by diffusion of Mg^{2+} cations through the liquid phase.

EXPERIMENTAL

The pellet corrosion test [10] was chosen for studying the aggressive effects of slags on the periclase grain. The periclase (MgO) specimens were obtained from electrofused magnesite sinter (SMZ Lovinobaña). The periclase crystals were cut and ground into the form of plates about $5 \times 10 \times 15$ mm in size. The respective slag in pellet form was placed onto the pads obtained in this way. The slags were prepared from A.R. purity chemicals Fe₂O₃, CaO and SiO₂ in iron or platinum crucibles by melting in an electric resistance furnace. Table I shows the chemical analysis corresponding to the initial compositions of slags employed in the corrosion tests, and specifies the test conditions.

The samples prepared in this way were introduced into the Leitz-Wetzlar high-temperature microscope and heated to the respective temperature in protec-

Sample design	Chemica	l composi	tion of slag	g [wt.%]	Slag melting temperature [°C]	Time of exposure [h]	Temperature of exposure [°C]
	FeO	Fe2O3	CaO	SiO ₂			
A1	6.50	75.40	18.2	_	1190	0.5	1300
A2	6.50	75.40	18.2	-	1190	1	1300
A3	49.68	20.75	28.12	-	1230	2	1300
A4	55.65	28.21	16.17	-	1180	2	1300
A5	54.89	23.95	21.76	-	-	1	1300
A6	5.83	75.05	16.44	-	1240	1	1300
A7	55.65	28.21	16.17	-	1180	1 ·	1300
B 1	58.19	16.39	17.14	5.35	1205	1	1300
B2	65.99	11.01	7.28	16.25	1420	1	1480
B 3	66.33	3.00	4.17	25.00	1115	1	1300
C1	67.87	3.25	-	26.5	1200	1	1400
C2	73.81	9.49	-	14.25	1200	1	1300
C3	61.93	7.28	-	31.5	1250	1	1400

Table I

Chemical composition of the aggressive media and the conditions of the corrosion tests

tive nitrogen atmosphere (gas flow arrangement). Following the respective time of exposure (0.5, 1 or 2 hours) the samples were cooled down, cut transversally and prepared for microstructural and electronmicroscope analysis, aimed at determining the penetration of the individual components of the aggressive media into the periclase monocrystals.

The microstructural analysis was carried out on the NEOFOT 2 microscope, and the electron-microscope one on the JEOL 35 CF electron microscope fitted with the LINK analyzer.

The following symbols are used to describe the microstructures: C_x - semiquantitative concentration, h- distance, T - slag, P - periclase, R - boundary.

EXPERIMENTAL RESULTS AND THEIR ANALYSIS

All the samples listed in Table I were subjected to optical microscopic analysis, and selected ones also to electron microscopic analysis. Only some samples from the individual series are shown for illustration. The figures show the slag-periclase monocrystal boundary. The semiquantitative concentration does not correspond to the actual concentration of the elements in the sample, solely indicating the concentration course along one line of the microstructure. In view of this, it is impossible to compare the sizes of peaks corresponding to the individual elements.

Figs. 1 through 4 demonstrate the corrosion of a periclase monocrystal by ferrite-calcium slag. Fig. 2 (sample A1) allows the diffusion of Fe and Ca into MgO, and the dissolution of Mg in slag to be followed along one line of the microstructure. The Fe concentrations fall abruptly at the slag-periclase boundary, the further decrease of iron concentration being slow and gradual. The microstructural analysis indicates that the reaction zone comprises magnesium ferrite



Fig. 2. Semiquantitative concentration of Fe, Ca and Mg along a line of the microstructure of sample A1.





Fig. 4. Semiquantitative concentration of Fe, Ca and Mg along a line of the microstructure of sample A2.



Fig. 6. Semiquantitative concentration of Fe, Ca, Si and Mg along a line of the microstructure of sample B1.

and periclase. The magnesium content in the slag is low, rising slowly towards the boundary where its concentration shows a sharp increase. The increase in magnesium content in the periclase grain is terminated in the region where the iron content falls to a minimum. The depth of this region corresponds to the diffusion zone of iron in the periclase monocrystal under the respective conditions of the corrosion. No diffusion of calcium into periclase was established under the given conditions. A similar course of corrosion can also be seen on sample A2 (Fig. 4), the only difference being the greater depth to which iron has diffused into the periclase monocrystal.

Another series of samples was used to investigate the effect of composite slags containing both calcium oxide and silica in various proportions. The case is illustrated by sample B1 in Figs. 5 and 6. The diffusion of iron into the periclase monocrystal was deeper at a higher SiO_2 content in the slag (B3 in Fig. 6). The dicalcium silicate being formed is concentrated at the periclase-slag boundary, providing an additional obstacle to the diffusion of iron into periclase. Increasing concentration of SiO₂ changes the character of slag, reducing the amount of 2CaO.SiO₂ and promoting the chemical corrosion of periclase. These findings are in good agreement with the results of the studies by Strelov [6] as well as those by Pánek and Danek [9]. Diffusion of calcium and silicon into the periclase monocrystal was not established with this type of slag either.

The third series of corrosion experiments is demonstrated on sample C2 in Figs. 7 and 8, where the effect of a silicate slag on the corrosion of periclase was studied. A reaction zone of magnesium ferrite and MgO was likewise formed in these instances. The diffusion of iron into the periclase monocrystal (Fig. 8) was almost continuous without any distinct abrupt changes at the silicate slag-periclase boundary. The content of iron in the diffusion region decreased gradually while



Fig. 8. Semiquantitative concentrations of Fe, Si and Mg along a line of the microstructure of sample C2.

Table 1	Ι
---------	---

Spot analysis of the content of Fe, Ca and Mg along a line of the microstructure of samples A1 and A2

Sample designation	Distance from	Spot and	alysis, elen	Note	
	boundary [µm]	Fe	Ca	Mg	
A1-1	-25	93.89	4.84	1.27	The percent
A1-2	-15	95.3	3.49	1.21	listed
A1-3	0	53.37	0.39	46.23	correspond
A1-4	+100	18.87	0.27	80.27	to areas
A1-5	+230	2.76	0.23	97.01	below spot
A1-6	+360	1.61	0.32	98.08	analysis curves
A2-1	-20	39.81	59.98	0.2	
A2-2	-10	40.8	58.97	0.23	
A2-3	0	55.82	41.31	2.87	
A2-4	+35	38.53	11.32	50.15	
A2-5	+60	22.76	1.51	75.73	
A2-6	+120	14.27	1.52	83.93	
A2-7	+190	6.64	1.0	92.07	
A2-8	+240	3.77	2.21	93.59	
A2-9	+375	3.92	1.67	94.15	
A2-10	+500	3.89	1.7	94.15	

that of magnesium increased. At the point of crossing the boundary, the magnesium concentration shows a gradual course, and even the dissolution of Mg in slag can be observed. The depth of Fe diffusion into periclase is approximately identical with that in the case of the ferrite-calcium slag. No diffusion of silicon into the periclase monocrystal was established. The microstructural analysis indicates that an increase in silica content in slag promotes slag penetration into the periclase grain. It is assumed that this fact is due to more extensive chemical effects of silica on the reaction zone, producing soluble silicates, as well as to a change in the physico-chemical properties of silicate slags over the respective range of composition and temperatures.

To be able to access more reliably the aggressive effects of iron oxides on periclase monocrystals, the authors carried out spot analyses of elements in terms of the distance from the boundary; the results obtained with samples A1 and A2 are listed in Table II. The results were used to calculate graphically the thickness of the diffusion layer for iron, $h_{\rm Fe} = 113 \ \mu m/0.5$ h, and $h_{\rm Fe} = 212 \ \mu m/h$. In view of the small thickness of the diffusion layer, the short exposure and additional simplifying assumptions, the results were only used to supplement the results of microstructural analyses.

On the basis of the experiments described above, the depth of diffusion of iron into periclase grains with both ferrite-calcium and silicate slags can be said to be roughly identical (samples A2 and C2). However, it should be taken into account that in the case of silicate and composite slags the semiquantitative concentrations of magnesium show different courses. There is no abrupt increase in Mg concentration at the boundary, as is the case of ferrite-calcium slags. The change in the concentration of magnesium has a more gradual course, and a higher magnesium concentration in slag beyond the boundary can also be observed.

The effect of ferrite-calcium slag on periclase grains produces a thin surface layer of magnesium ferrite which forms a barrier restricting direct contant of the slag with the periclase grain. The corrosion of the periclase grains then already proceeds through this reaction zone containing $(MgO + MgFe_2O_4)$.

Dissolution of refractory materials in viscous melts is controlled by diffusion which depends on the concentration gradient [11]. For this reason, the corrosion process is retarded by the formation of the barrier mentioned above. It may be pointed out that in the case of ferrite-calcium slags, the corrosion of periclase is essentially due only to diffusion of iron into the periclase grain, and the formation of $MgFe_2O_4$.

The effect of silicate slags on basic refractories also results in diffusion of iron into the periclase; however, the arising magnesium ferrite is being disturbed and does not meet the criteria of an efficient stable protective layer preventing dissolution of MgO in slag. In addition to the diffusion of iron into periclase, these slags also cause dissolution of periclase and formation of magnesium silicates. Their presence was established also by analyses of silicate slags following corrosion tests on basic refractory materials [1, 2, 3, 5].

The corrosive behaviour of composite slags can be characterized as a combination of the two mechanisms described above. In dependence on the C/S ratio in slag, calcium silicates are formed (particularly $2CaO.SiO_2$), which concentrate at the boundary with the periclase grain and constitute an additional obstacle to the diffusion of iron into periclase, as well as to its dissolution. A comparison of the depth to which Fe had penetrated into periclase in samples B1 and B3 showed that an increase in Si content in slag promoted diffusion of iron into the periclase grain. This is due to the fact that the arising 2CaO.SiO₂ $(t_t = 2130^{\circ}C)$ raises strongly the slag viscosity at the periclase-slag boundary, thus slowing down diffusion of iron into periclase. These findings are in agreement with those by Pánek, Daněk [9] and Strelov [8]. Following solidification of the dicalcium silicate, it undergoes changes in volume and cracks. The fissures were also found in our samples.

CONCLUSION

Corrosion of basic refractories by ferrite-calcium, silicate and composite slags results from diffusion of iron into periclase grains. In the case of silicate and composite slags, the process is combined with dissolution of periclase by silica, producing magnesium silicates. With composite slags, the diffusion of iron is also retarded by dicalcium silicate which concentrates at the slag-periclase boundary and whose amount depends on the slag composition and its C/S ratio.

The mechanism involved in the corrosion of real basic refractory materials can be described on the basis of the results given above and on that of conclusions reported in the literature [1, 2, 3]. Infiltration of ferrite-calcium slags into the matrix of the refractory material is deeper than in the case of silicate slags, particularly owing to the physical properties of the former type, such as low viscosity, a very good wetting ability of the given surfaces, etc. On the other hand, it should be emphasized that in spite of more extensive penetration into the refractory, its erosion is not distinctly more serious. The corrosion boundary is sharp, a magnesium ferrite layer is formed on the periclase grains and the intergranular silicate substance is replaced by a ferritic one. The corrosive attack by silicate slags has a much more pronounced course. The corrosion of periclase grains, i.e. diffusion of iron into the grain interior, is combined with simultaneous dissolution of periclase, producing soluble magnesium silicates. The intergranular space expands and the periclase grains are eluted from the matrix.

The thickness of the diffusion layer of iron in periclase is approximately identical for ferrite-calcium and silicate slags.

From the standpoint of corrosion of basic refractory materials, the composite slags appear to be the most suitable ones, because in their case the diffusion of iron into periclase is retarded by the formation of dicalcium silicate at the slag-periclase boundary. The precipitation of 2CaO.SiO₂ also changes quite significantly the physical properties of the slag at the boundary.

The results of the present studies have contributed to elucidating the mechanism involved in the corrosion of basic refractory materials by slag melts, and thus provided conditions for selecting a suitable slag composition in pyrometallurgical production of nonferrous metals.

References

- Bobok Ľ. et al.: Study of Physico-Chemical Processes in Pyrometallurgical Production of Non-Ferrous Metals (in Slovak). Research Report ŠPVZ ČÚ III, VST VPKM Košice, 1988.
- [2] Bobok L., Vadász P., Molnár L., Fedor J.: Determination of Physico-Chemical Interactions in the Slag Melt – Lining System (in Slovak). Research Report ŠPZV ČÚ III-1-7/02, VŠT VPKM Košice, 1989.
- [3] Molnár L., Vadász P.: Laboratory Study of Interactions at the Liquid Slag – Basic Refractory Boundary, in press.
- [4] Orlovskij J. A.: Chermetinformacia 5, 15 (1975).
- [5] Babkin V. G., Carevskij B. V., Popel S. I. et al.: Ogneupory 12, 37 (1974).
- [6] Kuznecov J. D., Suvorov S. A., Melnikov A. D.: Ogneupory 3, 35 (1975).
- [7] Hatfild T., Richmond C., Ford W. F. and White J.: Trans. Brit. Ceram. Soc. 2, 53 (1970).
- [8] Strelov K. K.: Structure and Properties of Refractories (in Russian), 2nd Ed., Metallurgia, Moscow 1982.
- [9] Pánek Z., Daněk V.: Mechanism of Formation of a Protective Periclase Layer in the Corrosion of Dolomagnesia Refractories by Steelmaking Slags (in Slovak). Research Report, Inst. of Inorg. Chemistry, Slovak Academy of Sciences, Bratislava 1984.
- [10] Crescent R., Rigand M.: Refractories Testing, Refractories for the Metallurgical Industries, pp. 235-250.
- [11] Strelov K. K.: Theoretical Principles of the Technology of Refractories (in Russian), Metallurgia, Moscow 1985.
- [12] Staroň J.: Refractories (in Slovak), textbook, VUHK Bratislava, 1987.

203

[13] Tomšu F.: Refractories I (in Slovak), textbook, VUHK Bratislava, 1987.

INTERAKCIE NA FÁZOVOM ROZHRANÍ PERIKLAS – TROSKOVÁ TAVENINA

PAVOL VADÁSZ, ĽUDOVÍT MOLNÁR

Ústav metalurgie a materiálov, Hutnícka fakulta, Technická univerzita Košice, Park Komenského 3, 043 85 Košice

V tomto príspevku sú uvedené výsledky skúšok korózneho pôsobenia troskových tavenín na zrno periklasu. Pre sledovanie sa zvolila tabletková korózna skúška, kde podložka bola tvorená elektrotaveným magnéziovým slinkom. Na tieto plátky sa umiestnila tabletka trosky a celá vzorka sa vyhrievala vo vysokoteplotnom mikroskope pod ochrannou atmosférou (N_2) na príslušnú teplotu a po stanovenú dobu. Po vyhladnutí sa vzorky priečne rozrezali a pripravili sa preparáty pre optickú a elektrónovú mikroskópiu.

Vyhodnocovala sa mikroštruktúra vzoriek a sledoval sa prienik prvkov (Fe, Ca Si) do zrna periklasu ako aj rozpúšťanie Mg v troskovej tavenine. korózia sa robila s tromi druhmi trosiek t.j. feritickovápenatou, silikátovou a kombinovanou. Východzie chemické zloženie trosiek a podmienky experimentov sú uvedené v tabulke I.

Na obrázkoch 1 až 4 je dokumentovaná korózia monokryštalu periklasu feritickovápenatou troskou. Môžeme tu sledovať difúziu železa do periklasu za tvorby reakčnej (difúznej) zóny, ktorá je tvorená s MgFe₂O₄ a MgO. V tabulke II sú výsledky bodovej analýzy prvkov Fe, Ca a Mg na jednej línii mikroštruktúry vzoriek A1 a A2. Z týchto výsledkov sa vypočítali hrúbky difúznych vrstiev železa v závislosti na čase $h_{Fe} = 113 \ \mu m/0.5$ hod. resp. 212 $\mu m/1$ hod.

Korózia kombinovaných trosiek je uvedená na obrázkoch 5 a 6. Tu tiež dochádza k difúzii železa do periklasu za tvorby reakčnej zóny a je možno sledovať zmenu hl'bky difúzie v závislosti od pomeru oxidu vápenatého k oxidu kremičitému (C/S) v troske. Zvyšovanie koncentrácie SiO₂ spôsobuje zväčšovanie hl'bky difúzie Fe do periklasu.

Tretia séria skúšok odpovedá korózii silikátovou troskou a je dokumentovaná na obrázkoch 7 a 8. Hl'bka difúzie železa do zrna periklasu je rovnaká ako pri feritickovápenatej troske. Vzniknutá reakčná zóna je rozrušovná taveninou obsahujúcou oxid kremičitý za tvorby rozpustných kremičitanov horečnatých.

Záverom môžem povedať, že korózia zŕn periklasu vo všetkých prípadoch je vprevažnej miere spôsobená difúziou železa. Dochádza k tvorbe reakčnej zóny (Fe₂MgO₄ + MgO), ktorá ale v prípade silikátovej resp. kombinovanej trosky je sprevádzaná aj chemickou koróziou periklasu oxidom kremičitým. V prípade kombinovaných trosiek je táto chemická korózia brzdená tvorbou dikalciumsilikátu na rozhraní troska – periklas.

Difúzia vápnika a kremíka do zrna periklasu pri daných podmienkach korózie nebola pozorovaná ani na jednej vzorke.

- Obr. 1. a) Mikroštruktúra vz. A1, b) Distribúcia prvkov Fe, Ca a Mg na ploche mikroštruktúry vz. A1.
- Obr. 2. Semikvantitatívna koncentrácia prvkov Fe, Ca a Mg na jednej línii mikroštruktúry vz. A1.
- Obr. 3. a) Mikroštruktúra vz. A2, b) Distribúcia prvkov Fe, Ca a Mg na ploche mikroštruktúry vz. A2.
- Obr. 4. Semikvantitatívna koncentrácia prvkov Fe, Ca a Mg na jednej línii mikroštruktúry vz. A2.
- Obr. 5. a) Mikroštruktúra vz. B1, b) Distribúcia prvkov Fe, Ca a Si a Mg na ploche mikroštruktúry vz. B1.
- Obr. 6. Semikvantitatívna koncentrácia prvkov Fe, Ca, Si a Mg na jednej línii mikroštruktúry vz. B1.
- Obr. 7. a) Mikroštruktúra vz. C2, b) Distribúcia prvkov Fe, Si a Mg na ploche mikroštruktúry vz. C2.
- Obr. 8. Semikvantitatívna koncentrácia prvkov Fe, Si a Mg na jednej línii mikroštruktúry vz. C2.

P. Vadász, Ľ. Molnár: Interaction at the Periclase





Fig. 1. a) Microstructure of sample A1, b) Distribution of Fe, Ca and Mg over the microstructure of sample A1.





Fig. 3. a) Microstructure of sample A2, b) Distribution of Fe, Ca and Mg over the area of the microstructure of sample A2.





Fig. 5. a) Microstructure of sample B1, b) Distribution of Fe, Ca, Si and Mg over the area of the microstructure of sample B1.



Fig. 7. a) Microstructure of sample C2, b) Distribution of Fe, Si and Mg over the area of the microstructure of sample C2.