

HOT CORROSION BEHAVIOR OF MAGNESITE – CHROMITE REFRACTORIES USED IN REVERBERATORY FURNACES AT SARCHESHMEH COPPER COMPLEX

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Abstract Iran's Sarcheshmeh copper industries with an annual production of 120,000 tones are the biggest of its kind in South Asia. The main method of production is pyrometallurgical matte making in two reverberatory furnaces which use direct-bond magnesite-chromite refractories supplied by German and Austrian companies. Following a recent major overhaul, bricks in contact with slag, matte and furnace atmosphere were collected and used for evaluation of the hot corrosion mechanisms of MgO-Cr₂O₃ refractories using OM, Chemical-Analysis, XRD, SEM, EDS techniques. Furthermore, Iranian produced refractories were assessed in the light of the present results for the possibility of replacement. A substitutional diffusion mechanism based on replacement of Fe S and Si compounds with MgO-Cr₂O₃ and is proposed to account for the changes observed in the chemical analysis of refractories.

Key Words Refractories, Refractory Corrosion, MgO-Cr₂O₃ Refractory, Copper Extraction, Reverberatory Furnace

چکیده مجتمع مس سرچشمه در ایران با تولید سالانه ۱۲۰ هزار تن مس کاتدی بزرگترین مجتمع تولید مس در خاورمیانه است. روش اصلی تولید به صورت پیرومتالورژی می باشد. مات مس در دو کوره انعکاس که از آجرهای نسوز اتصال مستقیم منیزیت و منیزیت - کرومیتی تولید شرکت های خارجی (آلمان - اتریش) ساخته شده اند، تهیه می شود. پس از تعمیرات اساسی اخیر کوره شماره ۲، نمونه های اولیه آجر نسوز محصول ایران و تولیدکنندگان خارجی و همچنین نمونه هایی نسوز مستهلک جمع آوری شده از مناطق مختلف کوره مانند نقاط در تماس با سرباره، مات و اتمسفر گازی کوره جمع آوری و برای شناسایی رفتارهای خوردگی نسوز، ارائه مکانیزم و برآورد مقاومت به خوردگی نسبی مورد بررسی های ویژه ساختاری و آنالیز شیمیایی قرار گرفتند.

1. INTRODUCTION

Sarcheshmeh copper complex producing some 120,000 tones of copper annually is the biggest of its kind in South Asia. The major share of production is pyrometallurgical matte making using two reverberatory furnaces with magnesite or magnesite-chromite direct bond refractories. During the previous decade a quarter of all refractory used in the smelting unit has gone to these furnaces, resulting in above normal

refractory consumption per unit production. The factors causing refractory deterioration can be mechanical, thermal and chemical or a combination of these [1]. Apart from two complicating factors in such furnaces i.e. side bulging and the excessive furnace floor build up, the intrinsically quiet nature of furnace operations, causes thermo-mechanical factors to be the basis of the hot corrosion mechanism. In this research the mechanism of refractory corrosion in furnace No.2 was investigated.

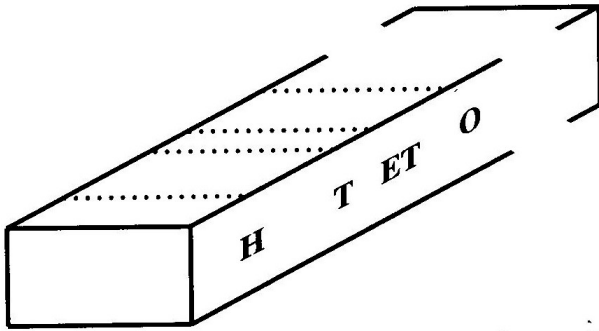


Figure 1. Deteriorated refractory sampling regime.

2. LITERATURE REVIEW

Refractory corrosion is not necessarily an electrochemical phenomenon based on redox reactions but more often is chemical in nature controlled by one of diffusion, intergranular, stress and inter-dissolution mechanisms. In a reverberatory furnace at different localities refractors come into direct contact with each other, furnace atmosphere, charging material, melt and slag. The corrosive environment experiences heterogeneous reaction whose rate determining step (rds) usually is the transfer of reactants or the rate of chemical reaction on the refractory surface [2]. Slag attack is the main cause of corrosion in the melt zone while gaseous furnace products cause the corrosion in the furnace ceiling [3]. The major factors in the refractory corrosion can be divided into two main groups:

- (a). Matte smelting operational conditions reflected in properties such as chemical composition, phase analysis, viscosity, temperature, surface tension etc. as related to the charging material, matte, slag and the furnace atmosphere.
- (b). Factors pertaining to the refractory brick material such as chemical composition, phase analysis, porosity, permeability, and production technique.

The refractory dissolution being a topochemical phenomenon explains the kinetics of the process in terms of primary dissolution of brick into refractory slag interface followed by the transfer of reaction products from this layer [4]. Research also suggests mechanisms based on diffusion and phase transformation and as such postulates direct

TABLE 1. Chemical Analysis of Furnace Gas (Wt %).

Constituent	N ₂	CO ₂	SO ₂	O ₂	H ₂ O
Wt %	68.6	11.8	2.6	1.5	15.5

TABLE 2. Chemical Analysis of Typical Charge, Slag, Matte and Dust of The Furnace (Wt %).

Wt%	Cu	Fe	CaO	Al ₂ O ₃	SiO ₂	S
Charge	30.0	20.9	5.0	4.7	6.9	26.9
Slag	0.6	33.6	8.7	8.8	32.3	0.7
Matte	41.4	30.1	---	---	1.2	0.2
Dust	25.0	20.0	6.0	6.0	8.7	13.3

influence of microstructure on hot corrosion resistance of magnesite-chromite refractories used in the reverberatory furnaces [5].

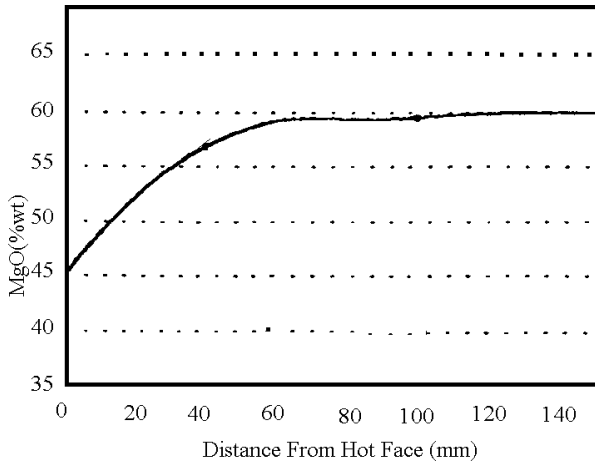
3. EXPERIMENTAL METHODS

Following main overhaul in furnace No. 2 in a systematic sampling program, bricks from different parts of the furnace were collected. Chemical analysis was carried out on the furnace's charge, slag, matte and dust-rich atmosphere as well as refractories used.

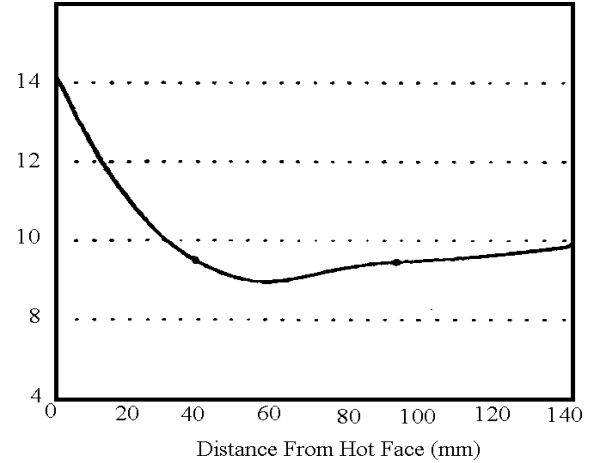
Figure 1 shows the four main domains in any one of the bricks i.e., hot, transition, end of transition and ordinary brick zones, on which chemical and XRD analysis were carried out. X-ray Diffractometry on 200 mesh powdered samples were performed using Jeol-JDX 8030 while for the SEM, EDS and BSE studies a Lecia Cambridge Stereo Scan 3600, EDS EXL link was used. All the samples were cold mounted and to avoid hydration were polished using alcohol.

4. RESULTS AND DISCUSSION

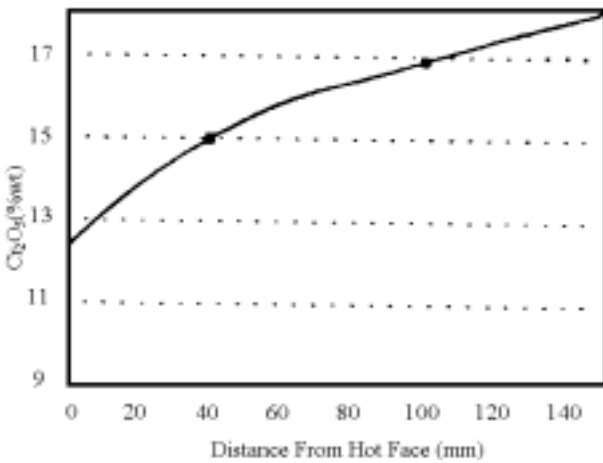
The build up of the furnace floor brings the magnesite-chromite bricks at higher parts of



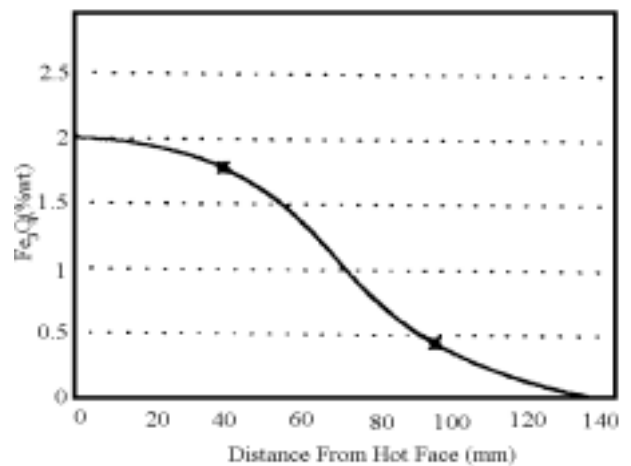
(a)



(a)



(b)



(b)

Figure 2. (a)- MgO and (b)- Cr₂O₃ concentration profiles within bricks in contact with the melt.

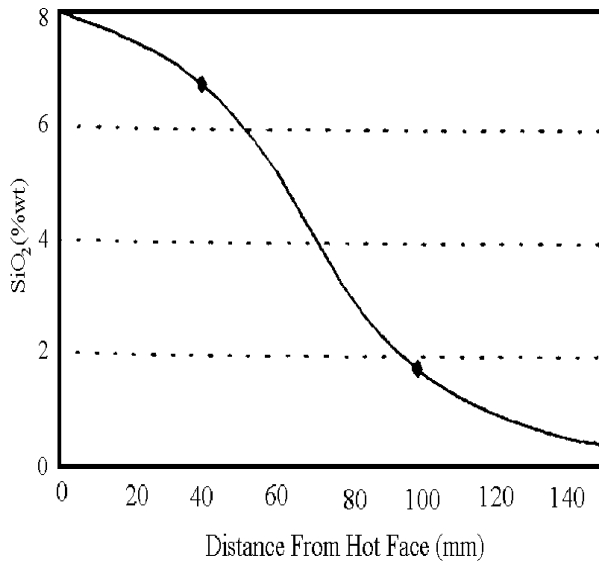
Figure 3. (a) Fe (total) and (b) Fe₃O₄ concentration profiles in deteriorated refractories.

the walls into direct contact with the molten matte. Table 1 shows the analysis of the furnace gas atmosphere while Table 2 demonstrates the chemical composition of charge, slag, matte and the furnace dust, all of which contain a wide range of potentially corrosive compounds when in contact with such refractories.

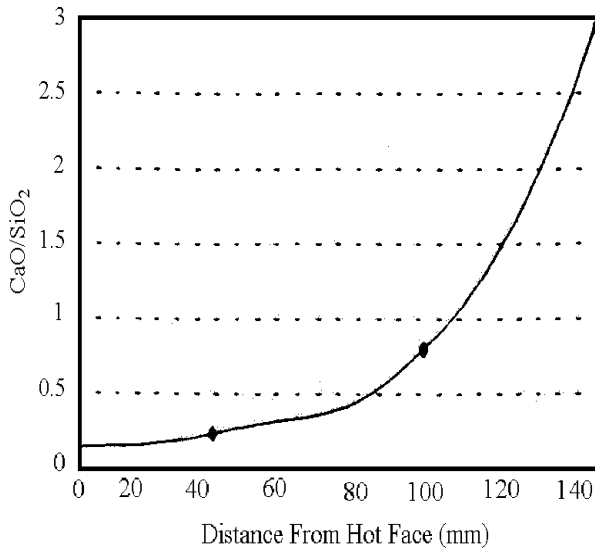
Typical analysis of magnesite- chromite bricks was 60% MgO, 18% Cr₂O₃, 14% Fe₂O₃, 6.5% Al₂O₃, 1.5% CaO and 0.5% SiO₂. Figure 2 shows

the change in concentration of Cr₂O₃ and MgO within bricks in contact with the melt.

Displacement of main refractory oxides leads to the depletion of bricks causing their eventual destruction. No such displacement was observed in bricks in contact with the furnace atmosphere. Figure 3 exhibits the penetration of molten iron and magnetite deep inside refractories when experiencing different conditions in the furnace.



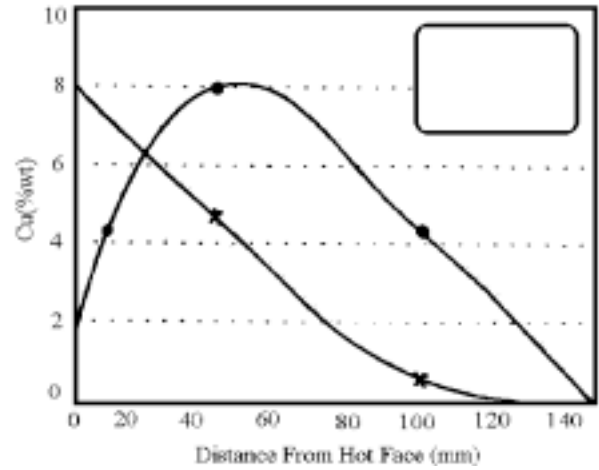
(a)



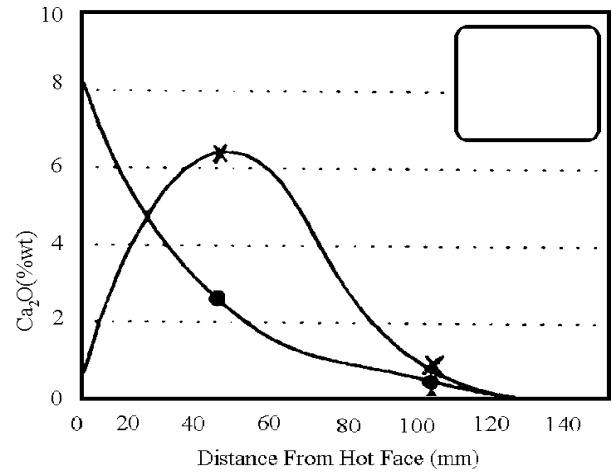
(b)

Figure 4. (a) SiO_2 diffusion into the fettling zone brick, (b) CaO/SiO_2 ratio change in bricks.

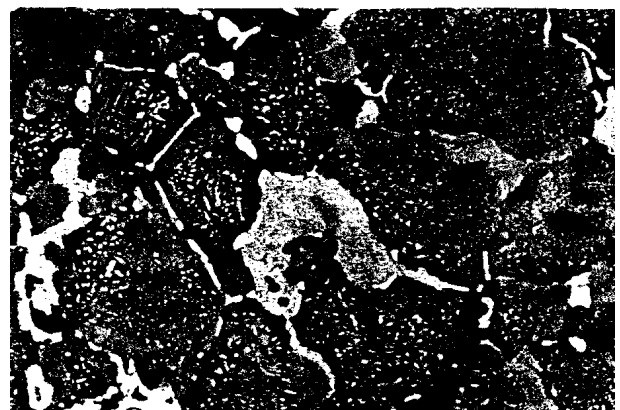
This is in accord with the data in Table 2 showing high levels of iron in all the phases affecting refractories due to variations in the furnace atmosphere. The reversible change between FeO and Fe_2O_3 occurs regularly. This can cause



(a)



(b)



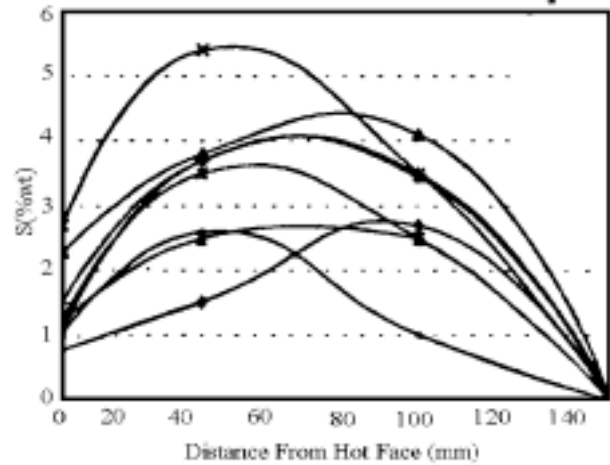
(c)

Figure 5. (a) Cu and (b) Cu_2O diffusion patterns, (c) SEM picture of refractories exhibiting copper containing phases; (500 \times).

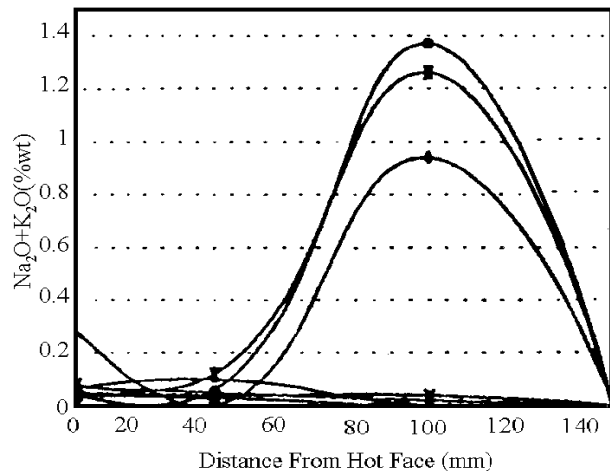
chemical fatigue and spalling as a result of the periodic volume expansion and contraction and the Kirkendall effect. The operational reasons behind such changes in the furnace atmosphere could be the imbalance in the burners, causing oxidizing conditions for diffusing elements and compounds inside refractories. For instance Fe_3O_4 was detected in the slag line bricks due to the very high activity of iron there. While the original silica level of refractories is negligible, according to the Figure 4 considerable amounts of SiO_2 and silicates was detected in all samples. This partly comes about through charging coarse grade SiO_2 pieces close to the furnace walls; a practice known as fettling and at the same time silicate rich slag causes SiO_2 to diffuse into the adjacent bricks.

This changes the important CaO/SiO_2 ratio through the years. The above ratio in bricks shows the propensity to form silicates whose low melting point predetermines the mechanical strength. It is worth mentioning that the SiO_2 penetration will not cease as a result of a protective layer formed on the surface. A solid-state diffusion mechanism activated by furnace heat will take over once such layer is formed. Changes of this ratio as shown in Figure 4-b demonstrates the near zero values encountered in distances close to the hot face where the silica activity is quite high, restored to the original values when moving away from this end. The penetration profiles of copper and copper compounds deep inside the refractories are demonstrated in Figure 5. Figure 5-a represents the copper ingress from the melt and furnace atmosphere while 5-b exhibits changes in Cu_2O concentration resulting from contact with matte slag and the furnace atmosphere.

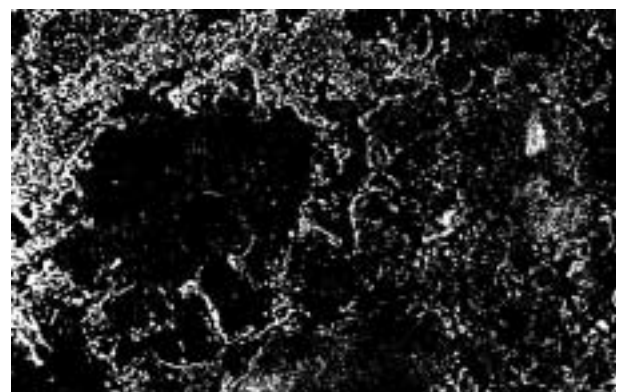
According to the SEM and EDS results (Figure 5-c), the diffusion of copper and formation of copper oxides leads to complex microstructures, in matrices of periclase and $(\text{Mg}(\text{Cr},\text{Fe})_2\text{O}_4)$, the secondary spinel. Metallic copper can cause slabbing or parting while Cu_2O reduces the brick's interfacial energy with slag and matte [6]. This results in an activated surface ready to be wetted by molten phases thus facilitating the diffusion of constituents from the melt and slag into brick. The main mechanism for this is the surface diffusion and capillary effect of existing narrow cracks or small porosities. The formation of sulfur containing copper and other low melting



(a)



(b)



(c)

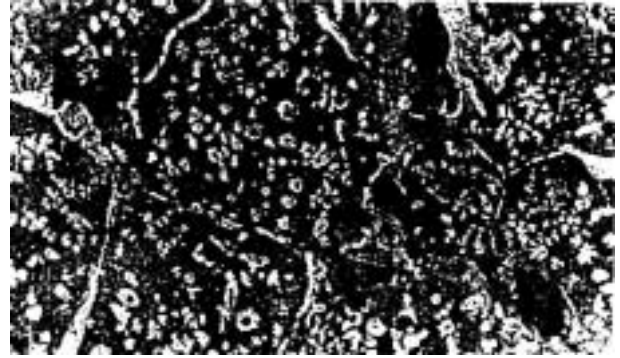
Figure 6. Diffusion patterns of (a) S and (b) $\text{Na}_2\text{O}+\text{K}_2\text{O}$. SEM showing the diffusion patterns of S and K (250 ×) (c).

TABLE 3. Chemical Analysis of MgO-Cr₂O₃ Refractories.

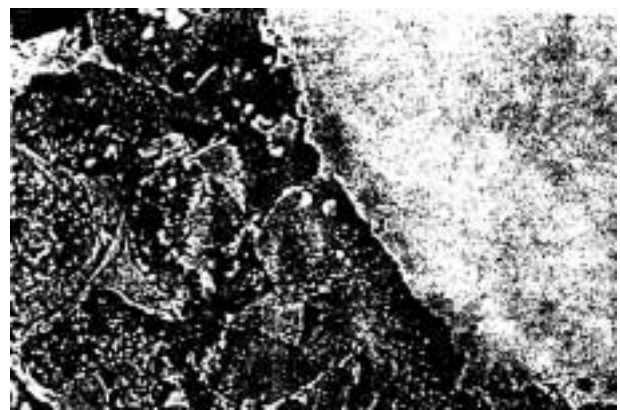
Wt% Sample	MgO	Cr ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO
No.1 (Germany)	58.9	18.1	14.1	6.5	0.5	1.4
No.2 (Germany)	62.2	13.5	9.3	8.8	2.0	1.0
No.3 (Iran)	70.9	14.1	6.3	6.5	1.9	0.7

compounds will cause slopping and float out. Sulfur concentration profiles for bricks from different parts are demonstrated in Figure 6-a. Sulfur exercises a twofold deleterious effect on refractories. Its intrinsic acid nature and affinity towards basic oxides, converts the silicate bonding phases into CaSO₄ and MgSO₄ in reversible chemical reactions. SEM and EDS studies confirm the formation of such compounds well inside bricks even at the end of transitional zone. Volume change accompanying sulfate conversion weakens the bonds deteriorating the microstructure turns refractories to powder.

Sulfur also acts as wetting agent for MgO-Cr₂O₃ bricks by copper containing matte in effect encouraging inward diffusion. Figure 6-b shows the diffusion of alkali oxides. Since these are all concentrated in the slag, only bricks in direct contact are affected. The deteriorating effect of these compounds comes from phase changes in the chromite grains. The CrO₃ gas formed by (Mg(Cr,Fe,Al)₂O₄) conversion, moves towards the cold end of brick causing microstructural change and embrittlement. The overall picture emerging from the collated data identifies the compounds moving inward and those traversing the refractories outward and establishes a mechanism according to which in the melt zone, hot corrosion is governed by the substitutional counter diffusion in the brick. The corrosive agents such as Fe and Si, S, Cu and alkali elements' compounds enter the refractory driving periclase and chromite out. The driving forces behind these movements are thermal and concentration gradients. Although fettling leads to formation of a protective layer between the



(a)



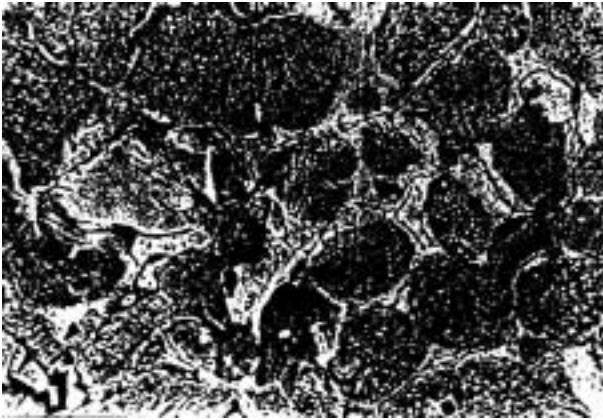
(b)

Figure 7. SEM results for sample No.1. (a) direct periclase-periclase contact, intergranular and grain boundary secondary spinels (400×), (b) direct periclase-chromite contact (400×).

corrosive environment and the refractories, the solid-state diffusion mechanism never ceases and a dynamic equilibrium between the brick dissolution and the growth mechanism of the protective layer is established.

In the ceiling region, degradation of the bricks is based on the inward diffusion of the sulfur and copper compounds. This coupled with the prevailing temperatures of up to 1550°C cause thermal shocks and spalling.

According to Table 3, which shows the



(a)



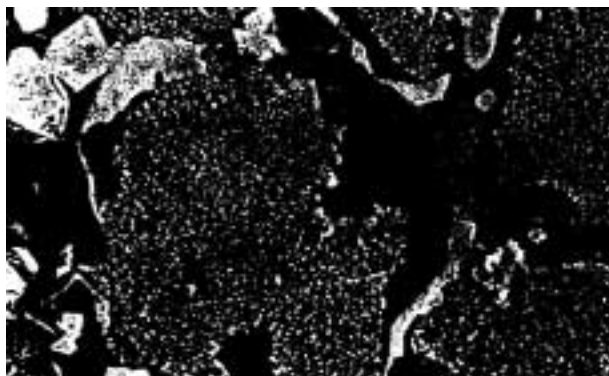
(b)

Figure 8. SEM results for sample Number 3 showing, (a) direct and silicate periclase – periclase contact as well as intergranular and grain boundary secondary spinels (300×) and (b) direct periclase – chromite contact (510×).

chemical analysis of different refractories tested, the highest MgO content belongs to the specimen No. 3 while maximum chromite and iron were detected in specimen No. 1. SEM and EDS studies established the presence and distribution of various phases formed under the special chemical and thermal conditions prevailing during the manufacturing of each refractory.

Direct bonded magnesite–chromite refractories as the name implies are characterized by conspicuous contact between periclase grains

themselves and periclase–chromite phases. Formation of large amounts of secondary spinels, which are a major source of high temperature strength, is another characteristic of these refractories. Free silicates found between periclase grains could act as a bonding agent, but generally due to their low melting points, reduce the overall performance of the refractory. The secondary spinels have different formation mechanism [5]. Flake and balled up flakes that precipitate out during cooling from a MgO–Cr₂O₃ solid solution within periclase grains are common and is encountered frequently in the present study. The iron content of the spinel dictates the shape of grains. This is done by affecting the compatibility of periclase lattice parameters with spinel being formed. The higher iron content refractories form rounded up spinels in the periclase grains as a result of closeness of lattice parameters in the two phases. As the iron content decreases the compatibility diminishes and preferential growth of certain crystal planes is encouraged. This uneven growth results in flake like structures inside periclase grains. The second group of spinels distributed throughout the microstructure is mixed with silicates and are polyhedral in shape while the final group is characterized by precipitating along the periclase grain boundaries. Figure 7 exhibits the bond formation of the original chromite grains (white) with periclase and also internal spheroidal spinels, as well as distinct grain boundary precipitates in specimen Number 1. The growth of small spheroidal spinels within the periclase grains of specimen Number 3, is well illustrated in Figure 9. It also shows an abundance of primary and secondary spinels precipitated in the boundary areas. The EDS analysis of this sample confirmed the presence of silicates MS₂ and C₃MS₂ occupying intergranular spaces. Overall, direct MgO–MgO and MgO–Cr₂O₃, bonding as well as silicate bonding is evident, however, no polyhedral spinel was detected here. The result of SEM and EDS analysis for specimen Number 2 is shown in Figure 9. Suitable growth of polyhedral secondary spinels within the periclase grains and at grain boundaries contrasts with previous specimen. The above observation leads to the



(a)



(b)

Figure 9. SEM results for sample Number 2 showing, (a) – intergranular and grain boundary secondary spinels (700×) and (b) direct periclase – chromite contact (200×).

conclusion that ore processing with the aim of enhancing raw material purity and temperature control during the firing of specimen Number 3 needs further refinement.

EDS analysis of secondary spinels formed in sample No. 2 periclase grains indicates a lower iron content.

This further confirms the hypothesis forwarded earlier as the reason for polyhedral morphology of spinel phases in such refractories. Although the iron content positively influences the hot strength of a refractory, the atmosphere of furnace and the subsequent volume change leads to thermal

fatigue and spalling counter balancing this advantage. Therefore, it is correct to assume that magnesite–chromite refractories with high iron content perform poorly under redox conditions which due to difficulty in flame control is prevailing in the reverberatory furnaces and as such the use of such bricks especially in the ceiling area has to be restricted.

5. CONCLUSIONS

Substitutional counter diffusion between elements of the environment such as Cu, S, Si, Fe and alkali element and the refractory's main constituents is the main mechanism of refractory degradation in the Sarcheshmeh reverberatory furnace No.2. This is greatly aggravated by undue growth of the furnace floor mainly as a result of the oxidizing nature of the furnace atmosphere. Fettle practice causes the formation of a protective layer but this does not stop the solid state diffusion of the detrimental elements and compounds the final thickness of the layer is reached when a dynamic equilibrium between the growth and the dissolution processes is established. The diffusion of detrimental elements such as S and Cu and the high temperature experienced at the furnace ceiling as well as furnace atmosphere changes are the main reasons for intense corrosion rates encountered in this area. Hot corrosion resistance of magnesite-chromite refractories used in the reverberatory copper smelting furnaces is directly influenced by microstructure. Although the importance of a high chromite content for better refractory performance could not be understated, the baking regime and firing temperatures seem to have overriding effect on brick quality.

6. REFERENCES

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