

Surface Interactions between Fayalite Slags and Synthetic Spinel and Solid Solutions

J.R. DONALD, J.M. TOGURI, and C. DOYLE

To obtain a better understanding of the complex corrosion mechanisms occurring at the interface, the surface and interfacial properties between fayalite-type slags and homogeneous, synthetic spinels and solid solutions of these spinels were investigated. These oxides represent the conventional refractory components. The sessile drop technique incorporating high-temperature X-ray radiography was employed for this purpose. The experimental temperature was 1200 °C and the oxygen potential was 10^{-9} atm controlled by CO/CO₂ gas mixture. The contact angles between the solid substrates and molten silica-rich fayalite slag ranged from 0 deg for MgFe₂O₄ to 23 deg for MgAl₂O₄. When iron-rich slags were employed, the contact angles ranged from 15 deg for MgCr₂O₄ to 22 deg for MgAl₂O₄. The interfacial reactions between the slags and the various spinel materials and the dissolution of the solids into the slags are discussed.

I. INTRODUCTION

CURRENTLY, the refractory bricks employed by copper and nickel producers contain a mixture of magnesia in the form of periclase and chromite ore in varying ratios. Overall, the general composition of the refractory bricks involves MgO, Cr₂O₃, Al₂O₃, FeO, and Fe₂O₃. Figure 1 illustrates the quaternary system of interest and indicates the average compositions of some commercially available refractory bricks. The compositions are situated in a region enclosed by MgO and the magnesia based spinels, namely, spinel (MgAl₂O₄), picrochromite (MgCr₂O₄), and magnesium ferrite (MgFe₂O₄). The mineralogy of the bricks is such that magnesia exists in its pure state, but the other oxides and spinels exist in solid solution with each other and with the magnesia.^[1]

Periclase has a relatively high thermal expansion coefficient (α), which, in a high-temperature furnace environment, makes the material very susceptible to thermal shock. Spinel, in the form of chromite ore, are mixed with the periclase to reduce the thermal expansion coefficient and to "prestress" the structure by adding cracks that, during operation, will assist in the prevention of large crack propagation. However, there are several problems associated with the use of chromite ore in refractory bricks. First, it is very expensive and must be imported, since the major copper producing regions have no chromite ore reserves. Second, although the chromium in the bricks is associated with stable, complex solid solutions, increasingly stringent environmental dumping legislation could soon target disposed refractory bricks. Possible alternatives for the addition of chromite ore to the refractory include MgAl₂O₄ and Fe₃O₄, both of which are economically available. These spinel ad-

ditives may provide significant cost savings if the performance of these bricks is comparable to the chromite additives.

The erosion mechanism of refractory bricks in nonferrous operations is becoming increasingly important due to globalized competition and the need to minimize all operational expenditures. Refractories are eroded by both mechanical and chemical means. Mechanical erosion includes spalling, when the inherent turbulence of the melt causes small pieces of the brick to break off. Other causes of mechanical erosion include internal cycles due to furnace rotation, charging, and pouring. Chemical corrosion involves the dissolution of the solid refractory into the melt. In addition, the reaction product between the melt and the refractory may lack the strength of the original solid or crack due to a reaction volume change, thus increasing the susceptibility to spalling.

Several articles are available on the interaction of slag and the Mag-Chrome refractory brick^[2-10] dating back about 35 years. Recent literature includes Barthel,^[5] reporting that above the slag line in the converter, periclase (MgO) dissolution into the slag was the dominant factor in refractory erosion. The wear by crack formation was, in comparison, less important. In addition, the fayalite-type slag was oxidized to form magnetite and cristobalite and tridymite (both are phases of SiO₂).

Slag corrosion has been independently investigated as an important consideration in refractory loss.^[6,7,8] By employing the dynamic slag drip test, a process that involves dripping hot slag onto the refractory face for extended periods of time, it has been found that bricks with a relatively high chrome ore content will resist chemical corrosion by fayalite-type slags. However, it was also observed that an increased chrome ore content will also increase the slag penetration into the brick.

The conventional finger test^[9] was employed to investigate the effect of oxygen potential on the reaction between fayalite slag and Mag-Chrome refractory materials.^[10] The study indicated that the rate of refractory dissolution into fayalite slag was highly dependent on the oxygen potential of the melt and the magnetite activity in particular. At lower oxygen activities, the magnesia was easily dissolved by the

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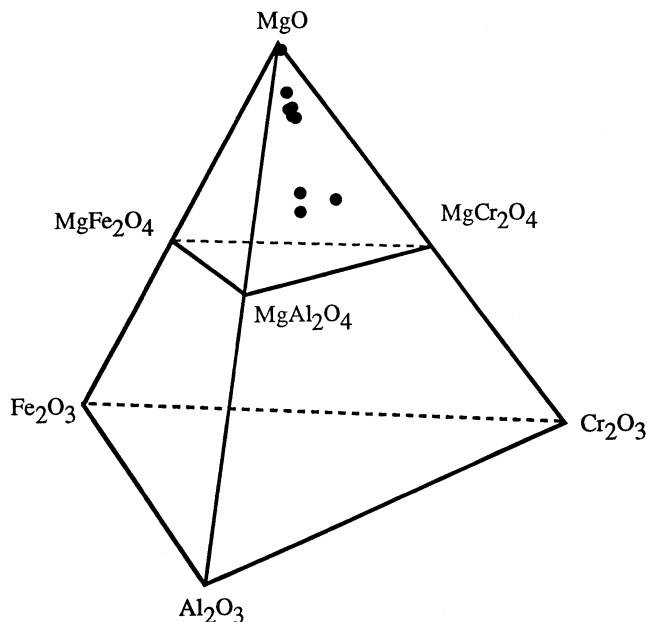


Fig. 1—The solid circles represent the average chemical compositions of the magnesia-chrome refractories on the molar scale.

slag. At higher oxygen partial pressures, the magnesia combined with the dissolved magnetite to form insoluble, solid magnesioferrites.

Previous fundamental research has focused on the interfacial phenomena between fayalite-type slag and pure single oxide materials. The interfacial reaction product between the fayalite slag and the single crystal of MgO was determined to be magnesioferrite and olivine. The contact angle between the solid and liquid phases varied between 16 and 30 deg and decreased with time. The increased wettability as a function of time was attributed to the change in the solid MgO surface.^[11,12] An alumina substrate reacted with the slag to produce hercynite, FeAl_2O_4 . The contact angle was found to range from 17 to 20 deg, depending upon the experimental conditions.^[13]

In the present work, the synthetic spinels MgFe_2O_4 , MgCr_2O_4 , and MgAl_2O_4 , and solid solutions of these spinels which comprise the conventional Mag-Chrome brick, were employed as solid substrates to investigate the surface and interfacial interactions with fayalite-type slags.

II. EXPERIMENTAL

The sessile drop technique was employed to measure the contact angles. The experimental apparatus, which consisted of a high-temperature furnace equipped with an X-ray fluoroscope, has been described in detail in previous publications.^[14] The fayalite-type slags were prepared synthetically by melting a mixture of iron, silica, and hematite in an iron crucible at 1300 °C, while argon gas was passed over the system. The silica contents of the slags employed were determined to be 27.5 and 35.2 mass pct, which correspond to iron-to-silica (Fe/SiO_2) ratios of 2.05 and 1.44, respectively.

The solid spinel materials were synthetically prepared by first mechanically mixing the powders of the single oxides (e.g., MgO and Fe_2O_3) for 24 hours. The powders were then pressed into cylindrical briquettes by compacting the pow-

der in a 25-mm-i.d. mold under a load of 700 kg/cm². The briquette was then fired in air at 1300 °C for 48 hours, ground, rebriquetted, and refired at 1300 °C for an additional 24 hours. This sample was ground to a fine powder and a sintered briquette was obtained by employing a hot press. The sample was then cut into discs of 2- to 3-mm thickness and 20-mm diameter. The solid substrates were polished to a mirror finish with a 1- μm diamond paste and cleaned ultrasonically with ethanol. The solid solutions of the spinels were obtained by mechanically mixing the powders of the spinels (taken after the second firing) in the desired mass ratio, then briquetting and firing at 1300 °C to 1450 °C (depending on composition) for at least 72 hours. X-ray diffraction and electron probe microanalysis (EPMA) were employed to confirm that the reactions were complete. These briquettes were then ground and hot pressed. The apparent density of the substrates was greater than 98 pct in all cases.

In the experiments, a small fragment of fayalite-type slag, having an approximate mass of 0.15 g, was carefully positioned onto the center of the substrate material. The substrate and slag were then placed onto a boron nitride cradle, which was suspended by a hollow quartz rod containing a type-R thermocouple. The cradle and rod were placed into a quartz reaction tube within the furnace hot zone, and the open end of the quartz tube was sealed with a brass cap. The atmosphere within the reaction tube was carefully controlled by a CO/CO₂ gas mixture such that the oxygen potential was 10⁻⁹ atm. After the sample was properly aligned with the X-ray path, the specimen was heated to 1200 °C under controlled atmosphere at a rate of 6 deg/min. Eight radiographs were taken at 5-minute intervals beginning at the moment the furnace temperature reached 1200 °C (i.e., $t = 0$), for a total experimental time of 40 minutes. The X-ray images were obtained on high resolution KODAK* X-Omat TL film, and the exposure time was

*KODAK is a trademark of Eastman Kodak Corporation, Rochester, NY.

12 seconds. At the conclusion of the experiment, the cradle was removed from the hot furnace and the sample was quenched in water.

To determine the contact angles and the surface tensions, the computer program developed by Rotenberg *et al.*^[15] was employed. Profile points required by this program for the calculations were digitized with a computer program.^[16] Based on previous work with the sessile drop technique, the contact angles over 20 deg have a reproducibility of ± 2 deg.

III. RESULTS AND DISCUSSION

A. Contact Angles

Figures 2(a) through (c) show photographs of typical drop images on the spinel substrates MgFe_2O_4 , MgCr_2O_4 , and MgAl_2O_4 , respectively. The photographs in Figure 2 were taken at $t = 0$, which was the time when the furnace reached a temperature of 1200 °C. The iron-to-silica (Fe/SiO_2) ratio of the slag was 2.05. The contact angle values of the spinels were all relatively similar, ranging from 15 deg for MgCr_2O_4 to 22 deg for MgAl_2O_4 .

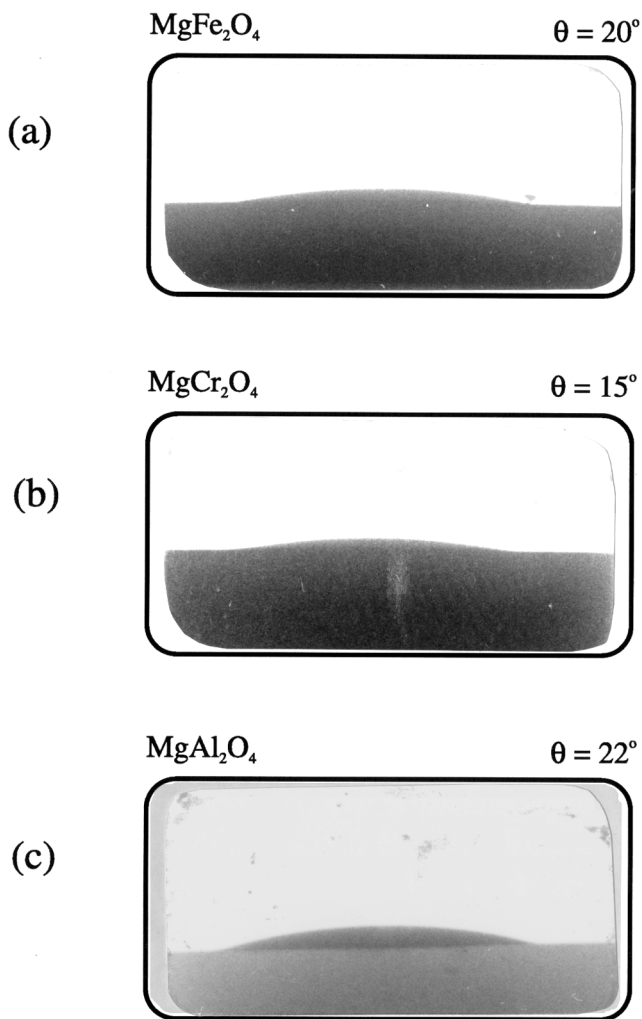


Fig. 2—(a) through (c) Images of the contact angles between the solid spinel substrates and the iron-rich fayalite slag.

Figures 3(a) and (b) present the contact angle results for the ternary system of the spinels for slag iron-to-silica ratios (Fe/SiO_2) of 2.05 and 1.44, respectively. In Figure 3(a), the difference in contact angle value was very small between the MgFe_2O_4 and the MgAl_2O_4 . The wettability of the substrate increased as the composition of the solid tended toward MgCr_2O_4 . This effect was the most pronounced between the MgAl_2O_4 and the MgCr_2O_4 , where the contact angle decreased from 22 to 18 deg with just 33 mass pct MgCr_2O_4 in the solution. The contact angle values for the silica-rich slag presented in Figure 3(b) are similar, with the exception of the wettability of MgFe_2O_4 . In both the initial experiment and a replica run, the silica-rich slag completely wetted the MgFe_2O_4 substrate. In the solid solution sample containing 33 mass pct MgCr_2O_4 and the balance MgFe_2O_4 , the contact angle was too low to be measured accurately by the sessile drop method; however, the angle was estimated to be between 5 and 10 deg. Of the substrates, MgAl_2O_4 was found to be the least wetted, and a solution containing this solid and 33 mass pct MgFe_2O_4 was observed to behave in a manner similar to the pure MgAl_2O_4 . The contact angle of the slag on the MgCr_2O_4 substrate was 17 deg, and it was 15 deg in a replicate experiment.

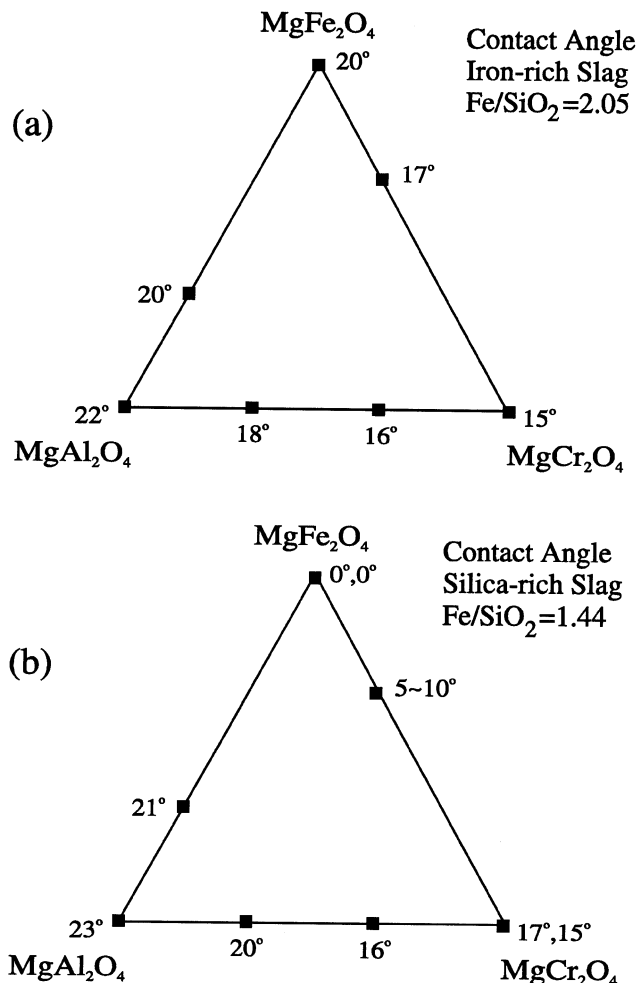


Fig. 3—(a) and (b). The contact angles between the solid substrates and the fayalite-type slags.

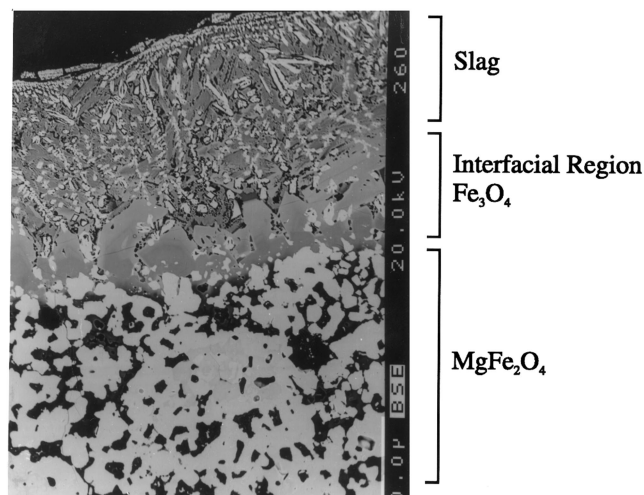


Fig. 4—A backscattered image with a magnification factor of 260 times, showing the interfacial product (Fe_3O_4) between the solid MgFe_2O_4 and the fayalite slag.

B. Interfacial Reactions

Figure 4 presents a backscattered micrograph obtained by EPMA of the interfacial reaction zone of the fayalite-

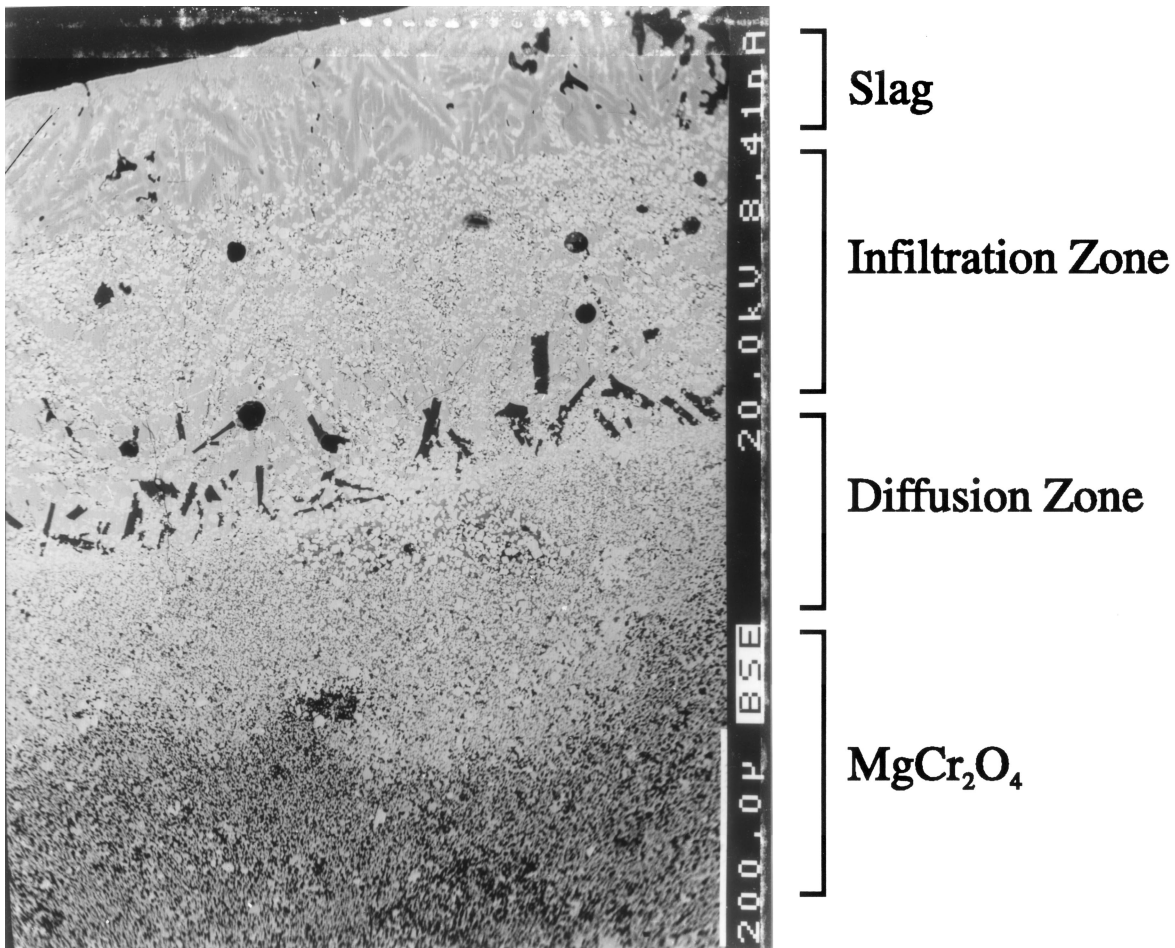
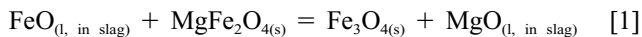


Fig. 5—A backscattered image with a magnification factor of 130 times showing the interfacial region between the solid MgCr_2O_4 and the fayalite slag.

type slag ($\text{Fe}/\text{SiO}_2 = 2.05$) and the MgFe_2O_4 substrate. The phase between the slag and the spinel was determined to be magnetite, Fe_3O_4 . The magnetite phase contained only trace amounts of silica and magnesia. The interfacial reaction and corresponding standard free energy change can be described as in Eqs. [1] and [2].



$$\Delta G_{1473 \text{ K}}^0 = -191 \text{ kJ/mol}^{[17]} \quad [2]$$

As the iron oxide in the slag reacted with the spinel to form the magnetite, the magnesium oxide in the solid was liberated and dissolved in the slag. The magnitude of this dissolution is discussed in section C. These results indicate that from a chemical potential viewpoint, magnetite has good potential as an additive to the MgO based refractory brick. Since the magnetite was a reaction product between an important component of the refractory and the slag, employing magnetite as a spinel additive may reduce the chemical potential between the fayalite slag and the brick.

The interfacial reaction between MgCr_2O_4 and the fayalite-type slag ($\text{Fe}/\text{SiO}_2 = 1.44$) is presented in a backscattered EPMA micrograph in Figure 5. The area displayed in Figure 5 has four distinct sections: the slag, the infiltration zone, the diffusion zone, and the unchanged MgCr_2O_4 . Figure 6 presents an enlarged view of the infiltration and dif-

fusion zones. The slag was observed to infiltrate approximately $200 \mu\text{m}$ into the substrate, and the iron was observed to diffuse a further $200 \mu\text{m}$ into the substrate. In the infiltration zone, the particles were determined to be FeCr_2O_4 , while in the diffusion zone, the particles were found to be $(\text{Mg,Fe})\text{Cr}_2\text{O}_4$ with the outer edges richer in iron than the interior of the particles. This indicates that the reaction took place in the solid state, as described by Reactions [3] and [4], as opposed to the particle precipitating from the dissolved components.



$$\Delta G_{1473 \text{ K}}^0 = -138 \text{ kJ/mol}^{[17]} \quad [4]$$

The dark particles, which indicate low atomic mass (low Z) in backscattered micrographs, were determined to be quartz with very low impurities. The solid quartz appeared only in the experiment involving the initially silica-rich slag. As the iron reacted with the MgCr_2O_4 , the slag rapidly became oversaturated with silica, and thus, the quartz precipitated out of the solution. In the experiments employing the iron-rich slag, the saturation point was not reached.

A backscattered micrograph of the interfacial region between the fayalite-type slag and the MgAl_2O_4 is presented in Figure 7. The region situated between the slag and the MgAl_2O_4 was determined to be $(\text{Mg, Fe})\text{Al}_2\text{O}_4$, and the reaction can be described as

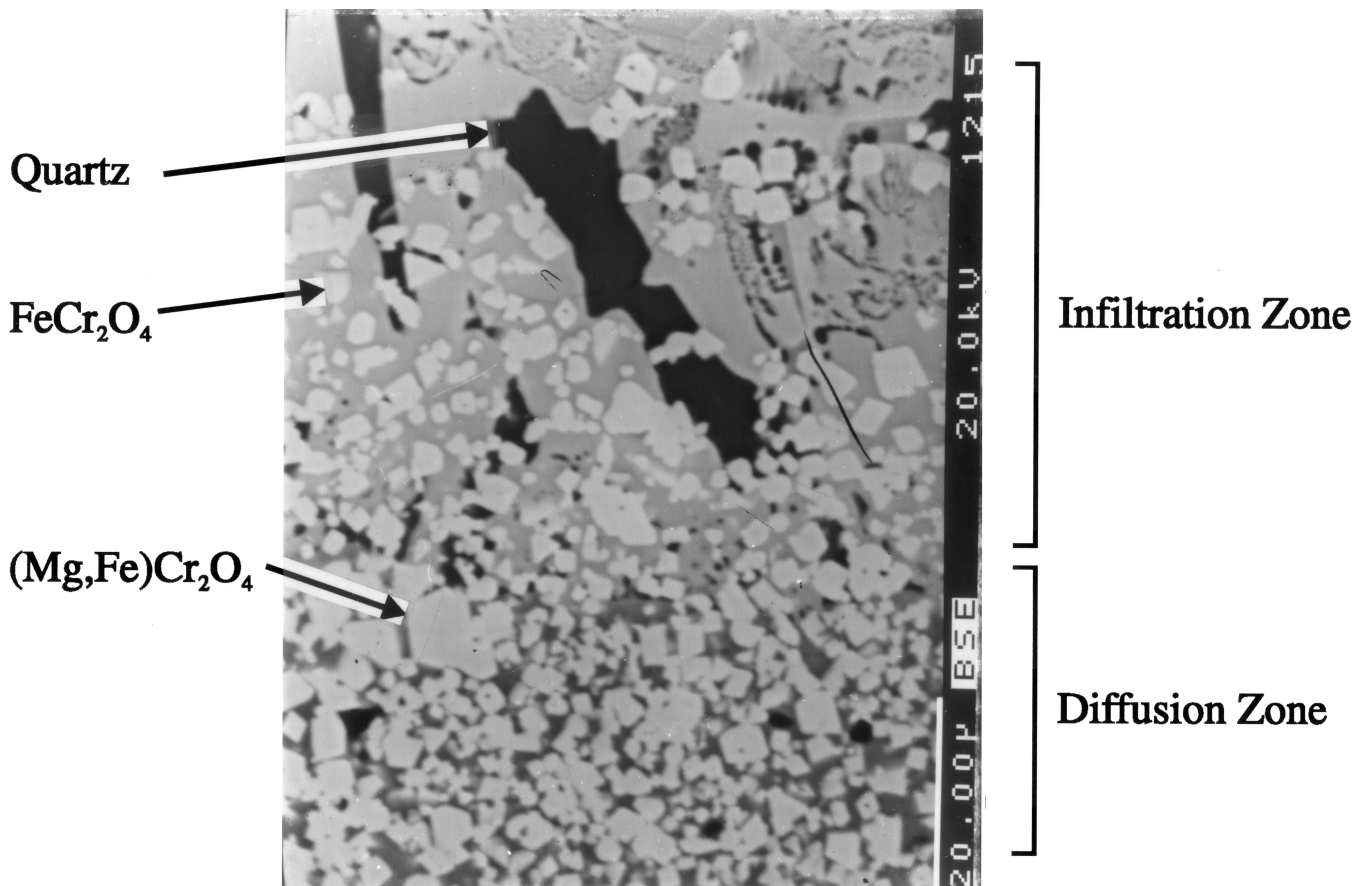


Fig. 6—A backscattered image with a magnification factor of 1300 times showing the interface between the infiltration zone and the diffusion zone of the MgCr_2O_4 sample.

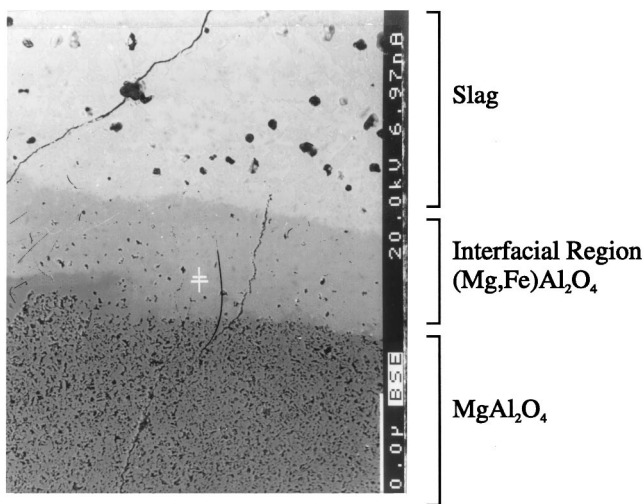
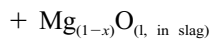
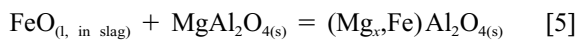


Fig. 7—A backscattered image with a magnification factor of 280 times showing the interfacial product ($(\text{Mg,Fe})\text{Al}_2\text{O}_4$) between the solid MgAl_2O_4 and the fayalite slag.



$$\Delta G_{1473 \text{ K}}^0 = -128 \text{ kJ/mol}^{[17]} \quad [6]$$

Iron from the fayalite-type slag diffused into the substrate as the magnesia dissolved into the slag. The concentration profile of iron across the interfacial reaction region for the

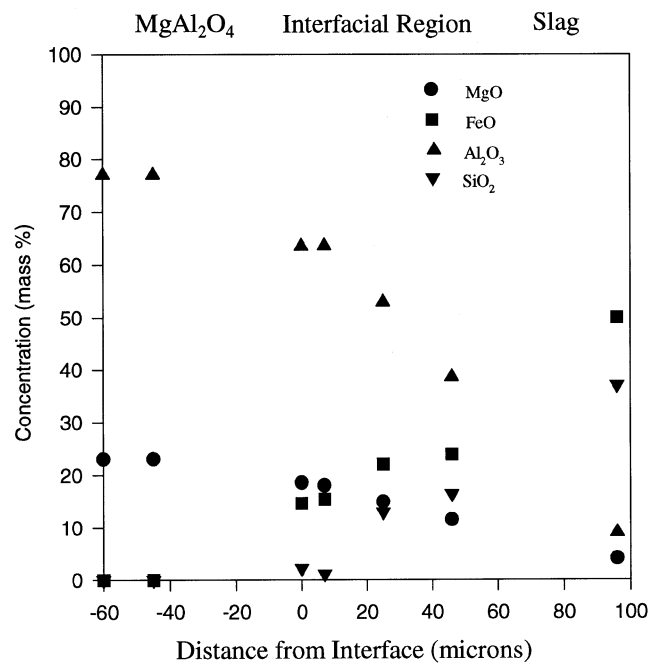


Fig. 8—The concentration profile of the various oxides over the interfacial reaction zone between the MgAl_2O_4 and the fayalite slag.

experiment involving the iron-rich slag ($\text{Fe}/\text{SiO}_2 = 2.05$), as determined by EPMA, is shown in Figure 8. No silica or iron were observed to be present near the interface in

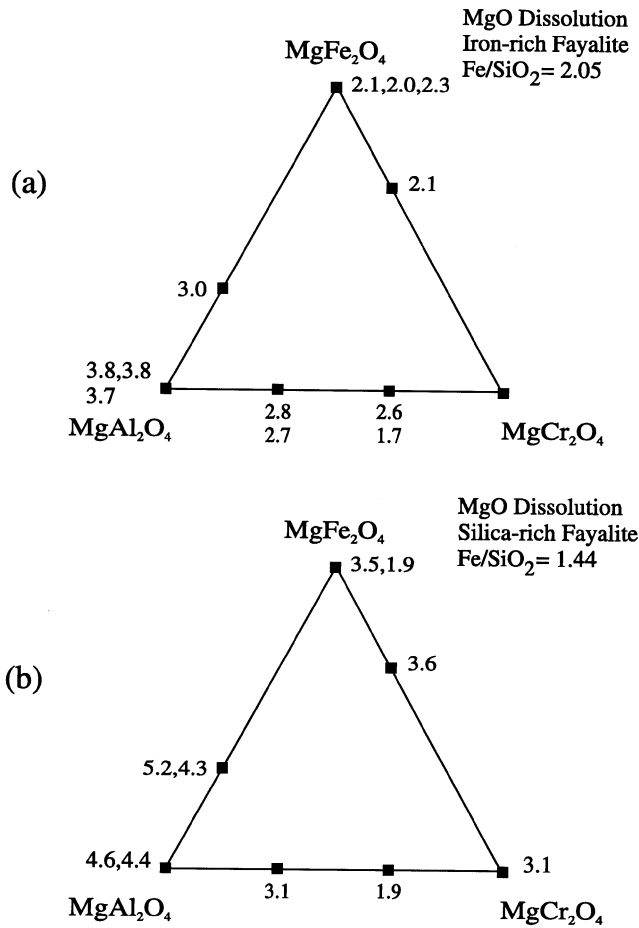


Fig. 9—(a) and (b) The MgO dissolution (mass percent) into the slag phase over the solid substrate compositions. The temperature was 1200 °C, the oxygen potential was 10⁻⁹ atm, and the experimental time was 40 min. Multiple values represent replicate EDX quantitative analysis of the slag.

the MgAl₂O₄ phase. The concentration of alumina drops dramatically over the interfacial region toward the slag phase as the iron and the silica increase. The magnesia concentration decreases moderately and consistently over this range. The silica was observed to be present in the interfacial region until near the MgAl₂O₄/interface boundary, while the iron was present throughout the middle phase. This indicates that both infiltration and diffusion are mechanisms of the formation of the reaction product region. The interfacial phase was 90 and 65 μm in thickness for the Fe/SiO₂ ratios of 1.44 and 2.05, respectively. As will be discussed in section C, the dissolution of Mg and Al into the silica-rich slag was greater for the silica-rich slag, which facilitated the diffusion of iron into the spinel matrix. Hence, the interfacial region in the experiments employing silica-rich slag yielded the thicker reaction zone. These results indicate that MgAl₂O₄ is a good candidate to replace chromite ore as a MgO based refractory additive.

C. Dissolution of Elements into the Slag

Figures 9(a) and (b) illustrate the mass percent of MgO dissolved into the slag at Fe/SiO₂ ratios of 2.05 and 1.44, respectively. The experimental time was 40 minutes. Multiple values on the figure represent replicate energy-disper-

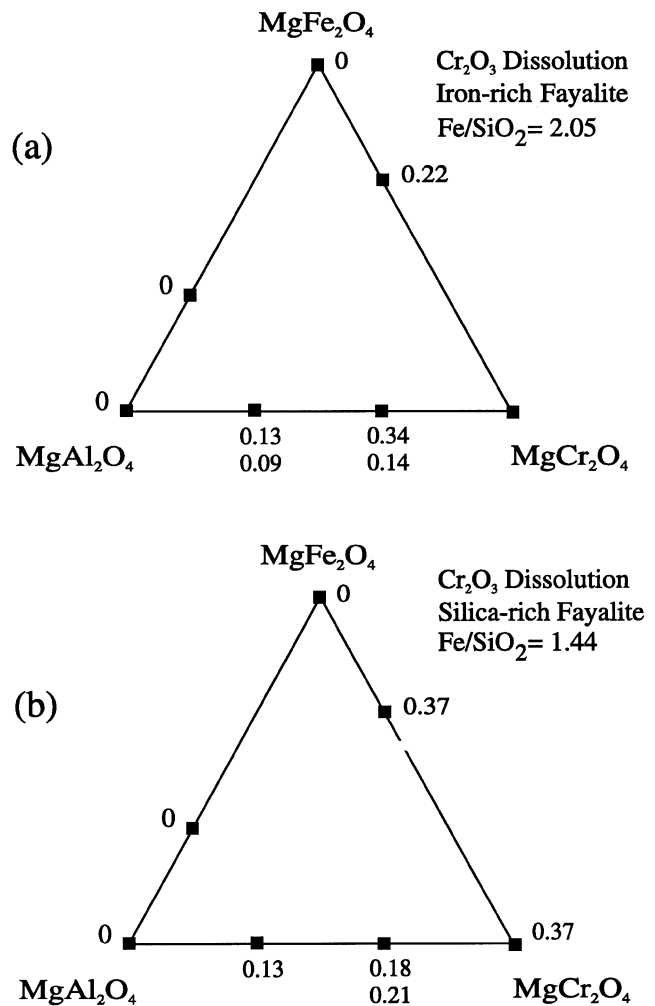


Fig. 10—(a) and (b) The Cr₂O₃ dissolution (mass percent) into the slag phase over the solid substrate compositions. The temperature was 1200 °C, the oxygen potential was 10⁻⁹ atm, and the experimental time was 40 min. Multiple values represent replicate EDX quantitative analysis of the slag.

sive X-ray (EDX) quantitative analysis of the slag. The highest concentration of MgO in the slags was found in the samples that employed a MgAl₂O₄ substrate. Overall, the MgO dissolution was found to be greater in the silica-rich fayalite slag. In previous research involving a MgO substrate, the MgO dissolution was reported to be 7 mass pct for both the fayalite slag types.^[11,12]

The amounts of Cr₂O₃ that dissolved into the slag during the 40-minute experiment are shown in Figures 10(a) and (b). The Cr₂O₃ dissolution was relatively low and did not change substantially over the range of substrate compositions. As was observed with the Mg dissolution, the quantity of Cr₂O₃ in the silica-rich slag was higher.

Figures 11(a) and (b) present the data of Al₂O₃ dissolution into the fayalite-type slags. The quantity of Al in the slags was higher than that of the Cr₂O₃ and the MgO. The amount of Al observed was highest in the experiment involving the MgAl₂O₄ substrate and progressively decreased as the amount of alumina in the solid solution substrate decreased. In contrast to the results of MgO and Cr₂O₃, the Al₂O₃ content was determined to be slightly higher in the iron-rich slag. Previous work involving the same slags on a pure alumina substrate concluded that the alumina content

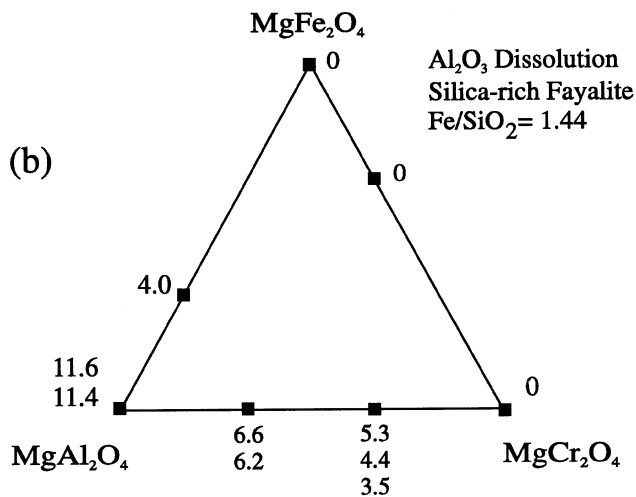
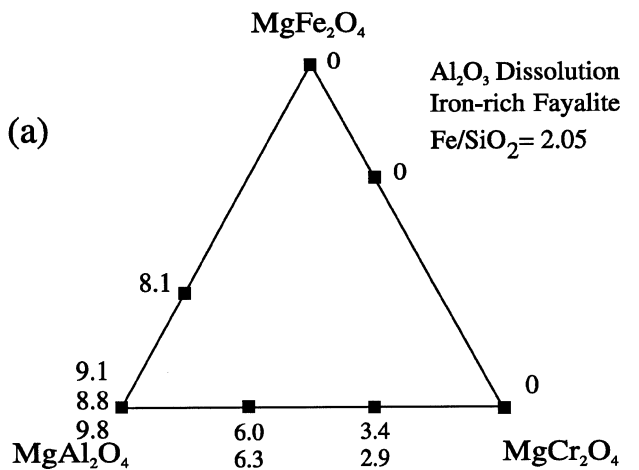


Fig. 11—(a) and (b) The Al_2O_3 dissolution (mass pct) into the slag phase over the solid substrate compositions. The temperature was 1200 °C, the oxygen potential was 10^{-9} atm, and the experimental time was 40 min. Multiple values represent replicate EDX quantitative analysis of the slag.

in the slags was 8.8 and 15.8 mass pct for Fe/SiO_2 ratios of 2.05 and 1.44, respectively.^[13] Dissolution of significant amounts of both magnesia and alumina into the slag is a major consideration concerning the addition of MgAl_2O_4 to the periclase bricks.

IV. SUMMARY

The wettability of synthetic refractory materials, which represent the components of the Mag-Chrome refractory brick, by fayalite-type slags was determined. The contact angles did not vary significantly in the experiments employing the iron-rich fayalite slag and were found to range from 15 deg for the MgCr_2O_4 substrate to 22 deg for the MgAl_2O_4 . The values of the contact angle using the silica-rich fayalite slag were similar with the exception of the MgFe_2O_4 substrate, which was completely wetted (*i.e.*, $\theta = 0$ deg).

The interfacial reaction products were determined by EPMA. The MgFe_2O_4 substrate reacted with the slag to produce magnetite (Fe_3O_4). The interfacial reaction when the MgAl_2O_4 was employed was determined to be a solid solution of (Mg,Fe) Al_2O_4 with the iron both infiltrating and diffusing into the solid. The reaction product involving MgCr_2O_4 with the fayalite-type slags was determined to be FeCr_2O_4 .

The dissolution of the various refractory compounds into the slags was obtained by quantitative EDX analysis. Both MgO and Al_2O_3 were observed to be present in the slag phase in the highest quantities when the MgAl_2O_4 substrate was employed. The MgO content in the slag ranged from 2 to 5 mass pct, while the Al_2O_3 was observed in higher quantities, 3 to 11 mass pct. Less than 1 mass pct Cr_2O_3 was found in the slag phase after the 40-minute experiment.

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