Corrosion Behavior of MgO–C Refractory in Ferromanganese Slags

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The corrosion behavior of MgO–C refractory used in oxygen blowing process in the manufacture of ferromanganese was investigated for different slag compositions. Finger Rotating Test (FRT) was introduced to observe the dependence of the corrosion behavior on various conditions: rotation speed, immersion time, slag, basicity, temperature and slag composition. As a result, the corrosion rate of MgO–C refractory increases with increasing time and rotation speed. Also, the strong corrosion of MgO–C refractory occurred when MnO is included in the slag composition. A kinetic study has been carried out with different slag contents.

KEY WORDS: MgO–C; refractory; ferromanganese; molten slag; corrosion.

1. Introduction

Magnesia-carbon (MgO–C) refractories have been one of the most important composite materials used in various steelmaking process.^{1,2)} Meanwhile, the MgO–C refractory is used in oxygen blowing process for decarburization of ferromanganese.

Magnesia in MgO–C refractory has the characteristics such as high melting point and high refractoriness. Carbon has the characteristics such as high thermal conductivity, low thermal expansion and low wettability of slag. When these two are combined, excellent resistances against thermal shock and corrosion are obtained.^{3,4)} However, the defect of the MgO–C refractory, when in contact with the molten slag, essentially causes the corrosion of refractory. One of the corrosion factors of the MgO–C refractory has been shown that carbon is oxidized by MgO according to the following reaction when the temperature increases and pressure decreases.¹⁾

Carbon of the MgO–C refractory has properties of improved resistance to slag penetration into brick, but the susceptibility to oxidation is major weakness, leading to degradation of the MgO–C refractory.⁵⁾

A. Watanabe *et al.*^{6–8)} have studied the formation of a decarburized layer due to oxidation of graphite by FeO in the slag or oxygen in the furnace atmosphere. The dissolution of the oxide is caused by the infiltration of slag into the decarburized layer and the reduction of oxide grain by high temperature reaction with carbon.

According to Cooper,⁹⁾ the corrosion of oxides occurs by the penetration of the species in the fluid into the solid. When a liquid phase in contact with refractory, the liquid phase penetrates into the pores of the refractory by capillary force and the species in the fluid are diffused into the refrac-

tory through the grain boundaries. Then, the degradation of the refractory is resulted by the expansion or contraction of solid, or by change in the properties due to the diffusion of slag species into refractory.

Jansson *et al.*¹⁰⁾ showed in their experiments with a method similar to FRT that the corrosion rate of MgO–C refractory increased with an increase in time, temperature and rod rotation speed. The observation was explained in terms of the dissolution of MgO, which showed that the mass transfer of MgO into the slag is the rate-controlling process in the corrosion. The corrosion rate of the MgO–C refractory decreased with the increase of MgO content in the slag because of the lower driving force for the dissolution of MgO and the higher slag viscosity.

Recently, the various corrosion mechanisms of the MgO–C refractory due to the slag such as erosion, penetration and chemical decomposition have been studied. However, the corrosion mechanism of MgO–C refractory used in the manufacture of ferromanganese has not been fully understood.

In this study, the corrosion behavior of the MgO–C refractory used in the manufacture of ferromanganese was investigated through the FRT and the analysis of the kinetics of the corrosion behavior was presented.

2. Experimental Procedure

2.1. Materials Preparation

The MgO–C refractories were cut from commercial refractory brick and processed to a cylindrical specimen of 50 mm in height and 20 mm in diameter. **Table 1** shows the chemical composition of the MgO–C refractory.

The synthetic slags were prepared by mixing CaO, SiO₂, Al₂O₃, and MnO melted in high frequency induction furnace. The chemical composition of the slags is specified in **Table 2**. The basicity was fixed to 0.8.

Table 1. Chemical composition of MgO–C refractory (wt%).

Composition (wt%)				
MgO	SiO ₂	Fe ₂ O ₃	CaO	C
82.18	0.26	0.02	0.54	17

Table 2. Chemical composition of the slag (wt%).

Composition (wt%)					Basicity (C/S)
No.	CaO	SiO ₂	Al ₂ O ₃	MnO	
1	34	66			0.5
2	45	55			0.8
3	52	48			1.1
4	40	50	10		0.8
5	36	44	20		0.8
6	27	33	40		0.8
7	27	33	10	30	0.8

Fig. 1. Experimental apparatus.

2.2. Finger Rotation Test

Figure 1 schematically illustrates the experimental apparatus used to study the corrosion behavior of MgO–C refractory and molten slag system.

The synthetic slag of 130 g was filled in a graphite crucible (diameter 50 mm, height 150 mm) and heated in a high-temperature vertical tube furnace under an Ar atmosphere. The MgO–C refractory specimen was glued to a 6-mm diameter Mo rod using ceramic adhesive. When the temperature reached a desired value, the specimen was fully immersed into the molten slag and rotated for a determined time. The experimental conditions are summarized in **Table 3**.

2.3. Corrosion Index Analysis Techniques

Two different corrosion indexes were used: 1) reaction area when the radius of the specimen is not significantly damaged, 2) radius reduction when the specimen is significantly damaged. The change in the appearance of the MgO–C refractory specimen immersed in CaO–SiO₂ slag is shown in **Fig. 2**. It can be seen that changes in appearance and weight are not significant. Horizontal cross-section of react-

Table 3. Test parameters.

Temperature °C	Immersion time (min)	Rotation speed (rpm)
1 450–1 525–1 600	60–120–240–360	200–400–600

Fig. 2. The surface of the MgO–C refractory specimen (a) before and (b) after immersed in CaO–SiO₂ slag at 1 600°C for 360 min.

Fig. 3. Images showing the reaction area of the degraded MgO–C refractory immersed in CaO–SiO₂ slag: (a) actual reaction cross-section, (b) reaction area extracted by Image J.

Fig. 4. Appearance of MgO–C refractory specimens immersed (a) in CaO–SiO₂–Al₂O₃ slag at 1 600°C for 360 min (b) in CaO–SiO₂–Al₂O₃–MnO slag at 1 600°C for 360 min.

ed MgO–C refractory cut at 1 cm from the bottom was observed using an optical microscope (**Fig. 3(a)**). The reaction area as a corrosion index was measured using the image processing software Image J (**Fig. 3(b)**).

The surface of the MgO–C refractory specimens immersed in CaO–SiO₂–Al₂O₃ slag and CaO–SiO₂–Al₂O₃–MnO slag are shown in **Figs. 4(a)** and **4(b)** respectively. It can be seen that the degradation of the MgO–C refractory in these cases is very intense compared with the one immersed in CaO–SiO₂ slag (**Fig. 2(b)**). However, the observation of the horizontal cross-section of reacted specimens

Fig. 5. Appearance of MgO-C refractory specimens immersed in CaO-SiO₂-Al₂O₃-MnO slag at 1 600°C for (a) 0 min (b) 60 min (c) 120 min and (d) 360 min.

Fig. 6. A plot of reaction area as a function of rotation speed in CaO-SiO₂ slag composition at 1 600°C for 120 min.

Fig. 7. A plot of reaction area as a function of immersion time in CaO-SiO₂ slag composition at 1 600°C.

did not clearly show the reaction area. Therefore, the decrease in the average radius of the MgO-C refractory specimen was calculated by measuring the decrease of weight, and used as a corrosion index. The corrosion index can be expressed by:

$$L = x - \left(\frac{w}{\rho h \pi} \right)^{\frac{1}{2}} \quad \text{..... (2)}$$

where L is the decrease of the average radius (cm), x is the radius (cm) of the specimen before immersed in slag, w is the weight (g) of the specimen after immersed in slag, h is the height (cm) of the specimen before immersed in slag, and ρ is the bulk density of the specimen before immersed in slag.

It is assumed that the bulk density and height were fixed as can be seen in Figs. 5(b), 5(c) and 5(d). Eventually, the top and basal plane of the specimen did not decrease during immersed in slag as can be seen in Figs. 5(b), 5(c) and 5(d).

The chemical composition of the reaction area of the MgO-C refractory reacted to CaO-SiO₂ slag was analyzed using wave dispersive spectroscopy (WDS). The spinel phase formed at the interface area of the MgO-C refractory reacted to CaO-SiO₂-Al₂O₃ slag was identified by X-ray diffraction (XRD) analysis. The reaction product at the surface of the MgO-C refractory reacted to CaO-SiO₂-Al₂O₃-MnO slag was analyzed using energy dispersive spectroscopy (EDS).

3. Results and Discussion

3.1. Corrosion Behavior with CaO-SiO₂ Slag Composition

First, the dependence of the corrosion behavior of MgO-C refractory on rotation speed, immersion time, and slag basicity was investigated in the case of the simplest slag composition: CaO-SiO₂.

The reaction area as a function of rotation speed is plotted in Fig. 6. The reaction area of MgO-C refractory increases with increasing rotation speed. This implies that the mass transport of solute in the molten slag around MgO-C refractory increases with increasing rotation speed.¹⁰⁾

The reaction area as a function of immersion time is shown in Fig. 7. The reaction area of MgO-C refractory rapidly increases at the beginning and it slowly increases after 100 minutes. This appears that the interface grain is rapidly reacted around the circumference at the beginning and the reacted area is slowly increased through solid diffusion.

Figure 8 shows the reaction area as a function of basicity in CaO-SiO₂ slag composition. The reaction area of 21.1% was obtained at the basicity of 0.5. The reaction area was remained to be 18% and 17.6% at the basicity of 0.8 and 1.1. Considering error of reaction area measurement about 3%, the MgO-C refractory is affected little by increasing basicity in CaO-SiO₂ slag composition.

Fig. 8. A plot of reaction area as a function of basicity in CaO–SiO₂ slag composition at 1600°C for 120 min.

Table 4. Chemical composition of reaction area (wt%).

Composition (wt%)		
CaO	SiO ₂	MgO
38.8	50.9	10.3
31.3	52.8	15.9

The chemical composition of the reaction area of the specimen in Fig. 3(a) was determined by EPMA /WDS measurement and by referring to the Slag Atlas¹¹⁾ (Table 4). The reaction area was composed of ternary oxides consisting of CaO, SiO₂ and MgO. “Akermanite (2CaO·MgO·2SiO₂)” or “Diopside ((Ca,Mg)O·MgO·2SiO₂)” phase is mostly expected due to the penetration of slag or diffusion of ions at high temperature.

3.2. Corrosion Behavior with CaO–SiO₂–Al₂O₃ Slag Composition

The decrease in the radius of the MgO–C refractory after the reaction as a function of Al₂O₃ content in CaO–SiO₂–Al₂O₃ slag composition is plotted in Fig. 9. The concentration of Al₂O₃ was determined by considering the saturation based on the Slag Atlas.¹²⁾ Figure 9 shows that the decrease in the radius occurred with 0 wt.% and 10 wt.% Al₂O₃ content but not with 20 wt.% and over.

The XRD analysis of the surface of the MgO–C refractory reacted to CaO–SiO₂–Al₂O₃ slag with different Al₂O₃ content is presented in Fig. 10. According to this XRD analysis, there is formation of a spinel phase on the surface of the MgO–C refractory when Al₂O₃ content in the slag is 20 wt.% and over, but the spinel phase does not form when Al₂O₃ content in the slag is less than 20 wt.%. This implies that the formed spinel phase prevents the corrosion of the MgO–C refractory. In addition, the Al₂O₃ content in CaO–SiO₂–Al₂O₃ slag causes the increase of viscosity¹²⁾ resulting in low mass transfer coefficient of MgO in the slag, which also reduces the corrosion of the refractory.

3.3. Corrosion Behavior with CaO–SiO₂–Al₂O₃–MnO Slag Composition

Next, the corrosion behavior of the refractory was inves-

Fig. 9. A plot of the decrease in radius as a function of concentration of Al₂O₃ in CaO–SiO₂–Al₂O₃ slag at 1600°C for 360 min.

tigated for CaO–SiO₂–Al₂O₃–MnO slag composition, which is important because it is the slag composition for actual ferromanganese manufacturing operation condition.

3.3.1. The Effect of Slag Composition in the Corrosion Behavior

The appearance of the MgO–C refractory immersed in CaO–SiO₂–Al₂O₃–MnO slag is shown in Fig. 4(b). The degradation of MgO–C refractory was very intense compared with the MgO–C refractory immersed in CaO–SiO₂ slag or CaO–SiO₂–Al₂O₃ slag (shown in Figs. 2(b) and 4(a) respectively). The reaction product at the surface of the reacted MgO–C refractory was observed by EPMA/EDS. Table 5 shows the chemical composition of reaction product at the MgO–C refractory surface.

The result shows high content of Mn at the surface of the reacted MgO–C refractory. This observation indicates that the carbon of the MgO–C refractory was oxidized by the reaction with easily reducible MnO in the slag according to the following reaction.

And, when MnO is added, the melting temperature of the slag is decreased¹²⁾ resulting in the increase of corrosion. Both reasons significantly affect the corrosion rate of MgO–C refractory.

Figure 11 shows a plot of decrease in the radius as a function of immersion time for different slag compositions. The decrease rates of the radius are calculated for the three slag compositions in Eqs. (4), (5) and (6).

$$\frac{dr}{dt}(\text{CaO-SiO}_2) = 1.08 \times 10^{-7} \text{ m/min} \dots\dots\dots (4)$$

$$\frac{dr}{dt}(\text{CaO-SiO}_2\text{-Al}_2\text{O}_3) = 2.98 \times 10^{-8} \text{ m/min.} \dots\dots (5)$$

$$\frac{dr}{dt}(\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MnO}) = 7.30 \times 10^{-6} \text{ m/min} \dots\dots (6)$$

The highest corrosion rate of the MgO–C refractory occurred in CaO–SiO₂–Al₂O₃–MnO slag composition (7.30 × 10⁻⁴ cm/min), the actual ferromanganese manufacturing operation condition.

Fig. 10. X-ray patterns of MgO-C refractory in various Al_2O_3 content of CaO-SiO₂-Al₂O₃ slag composition at 1600°C during 360 min: (a) 0 wt.% Al_2O_3 content, (b) 10 wt.% Al_2O_3 content, (c) 20 wt.% Al_2O_3 content, (d) 40 wt.% Al_2O_3 content.

Table 5. Chemical composition of reaction product at MgO-C refractory surface (wt.%).

Composition (wt%)			
Mn	C	Si	O
69.96	6.91	0.49	22.64

Fig. 11. A plot of decrease in the radius as a function of immersion time for different slag compositions at 1600°C showing the effect of slag composition on corrosion behavior.

3.3.2. Kinetic Analysis of Temperature Effect on the Corrosion Behavior

In order to show the effect of temperature on the corrosion behavior the decrease in the radius as a function of immersion time is presented in **Fig. 12** for the case of CaO-

Fig. 12. Effect of temperature as function of immersion time in CaO-SiO₂-Al₂O₃-MnO slag composition.

SiO₂-Al₂O₃-MnO slag composition. The decrease rate of the MgO-C refractory radius increases with increasing temperature.

The mass transport coefficients k can be calculated from the slope of **Fig. 12** using Eq. (7).

$$-\frac{dr}{dt} = \frac{k}{100\rho} \left((\% \text{MgO})_s \rho_s - (\% \text{MgO})_b \rho_b \right) \dots\dots (7)$$

where ρ is the bulk density of the MgO-C refractory, and ρ_s and ρ_b the slag density at the interface and the bulk, respectively. The density values (ρ_b) of the slag and the saturation value of MgO ($\% \text{MgO})_s$ in the slag for the calculation were determined from the Slag atlas.¹²⁾

Fig. 13. Effect of temperature on mass transfer coefficient with CaO-SiO₂-Al₂O₃-MnO slag.

An Arrhenius equation¹³⁾ relating the mass transport coefficient k and the temperature T , Eq. (8) and its logarithmic form, Eq. (9) are used to calculate the activation energy:

$$k = A \cdot \exp(-E_a / RT) \quad (8)$$

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (9)$$

where k is the mass transport coefficient, A is pre-exponential term, T is the absolute temperature (K), R is the ideal gas constant (J/mol K), and E is the activation energy (J/mol).

Figure 13 shows a plot of the mass transport coefficient in log scale versus $1/T$ at 1450–1600°C. The activation energy calculated from the slope was 123 kJ/mol.

3.3.3. Kinetic Analysis of Dissolution Rate Effect on the Corrosion Behavior

Under forced convection where the molten slag is agitated, the dissolution rate for a rotating MgO-C refractory can be expressed by the following equation:¹⁴⁾

$$J = D(C_s - C_m)/3.09(U/\nu x)^{1/2}(\nu/D)^{1/3} \quad (10)$$

where U is the bulk velocity of the fluid (cm/s), ν is the kinematic viscosity (cm²/s), and x is the thickness of the interface (cm). Using the values of D and ν determined from the Slag atlas¹²⁾ and FACTSAGE, Eq. (10) gives $J = 1.16 \times 10^{-3}$ g/cm²s for the CaO-SiO₂-Al₂O₃-MnO slag composition in Fig. 11. On the other hand, J can also be calculated by:

$$J = -\rho \frac{dr}{dt} \quad (11)$$

where ρ is the bulk density of the MgO-C refractory, and r is the radius of the refractory specimen. Using the experimental value of decrease rate in radius, the J value of 1.97×10^{-3} g/cm²s was obtained, which appeared in a agreement with the value calculated by Eq. (10). The difference between the calculated J and the measured J seems to be caused by the calculation assumption of Eq. (2), which may no longer validate at the severe corrosion condition as shown in Fig. 5(d).

The mass transport coefficient k could be calculated using Eisenberg's equation.¹⁵⁾

$$k = 0.0791 Re^{-0.33} Sc^{-0.66} U \quad (12)$$

where Re is the Reynolds number ($= Ud/\nu$), Sc is the Schmidt number ($= \nu/D$), U is the periphery velocity of the cylinder and D is the diffusivity of MgO in the slag. Substituting the values for the CaO-SiO₂-Al₂O₃-MnO slag composition in Eq. (12), the k value of 2.52×10^{-3} cm/s was obtained, which agrees with the experimental value 3.09×10^{-3} cm/s derived by Eq. (7).

4. Conclusions

(1) The corrosion of MgO-C refractory in CaO-SiO₂ slag increases with increasing rotation speed and increasing immersion time for composition. The corrosion of MgO-C refractory decreases with increasing basicity.

(2) As Al₂O₃ content in CaO-SiO₂-Al₂O₃ slag increases, the corrosion of the MgO-C refractory decreases. When Al₂O₃ content is 20 wt.% and over, a spinel phase forms on the surface of the refractory, which prevents the corrosion of the refractory. The addition of Al₂O₃ also reduces the corrosion of the refractory due to the increase of viscosity of the slag.

(3) The degradation of MgO-C refractory immersed in CaO-SiO₂-Al₂O₃-MnO slag is very intense due to the oxidation of the carbon in MgO-C refractory in the reaction with MnO in slag composition. The addition of MnO also enhances the corrosion of the refractory due to the decrease of the melting temperature of the slag.

(4) The agreement between the theoretical and experimental values implies that the corrosion rate is determined by mass transport.

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