Reaction between Magnesias–Chrome Brick/Slag Interface by Electric Furnace Static Slag Corrosion Test

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Reaction of magnesias–chrome (MgO–Cr₂O₃) brick with molten MgO–Al₂O₃–SiO₂–CaO–Fe₂O₃ slag using electric furnace static corrosion test method was investigated by X-ray diffraction (XRD), optical polarized microscopy (OPM), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), scanning transmission electron microscopy (STEM) and electron diffraction (ED). From XRD patterns it is found that the crystalline phases at slag–refractory interface are mostly MgO and MgCr₂O₄ with a minor phase of CaMgSiO₄. The MgO content in MgO–Cr₂O₃ bricks decreases with temperature increasing. The activity coefficient of MgO (γ_{MgO}) in the molten MgO–Al₂O₃–SiO₂–CaO–Fe₂O₃ slag also increases with temperature increasing. The diffusion layer of (Mg,Fe) (Cr,Al)₂O₄ is formed between slag area and MgCr₂O₄ matrix. [doi:10.2320/matertrans.MRA2007079]

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1. Introduction

The conventional ironworks have evolved into a highly efficient operation with high levels of yield and energy efficiency. However, the relatively high capital cost of process plant involved has led to that an increased scale of operation and new blast furnace are typically constructed to produce 2~3 Mpa to achieve economics of scale.¹⁾ A clear trend emerged recently for new process developments in ironmaking to be carried out from virgin ferrous feedstocks with coal as the fuel but without use of the blast furnace are currently the subject of considerable development.²⁾

The direct iron ore smelting reduction (DIOS) process and an environmentally oriented steelmaking process are now the subjects of research. The DIOS process will eliminate the coke oven and sintering plant.³⁾ Although the DIOS process has many advantages, but there are several limiting factors on productivity, including carbonaceous material in slag, slag volume and hot metal temperature, etc. The reduction rate of DIOS process depend on the overall apparent reduction-rate constant and the FeO content of the foamy slag. As far as productivity is concerned, it is necessary to satisfy the reduction rate and thermal state concurrently within controlled hot metal temperature conditions.³⁾ Hence, selected suitable refractories use in smelting reduction furnace environment such as a high temperature of 1823 K, oxidization atmosphere, lower slag basicity (Ca/Si = 1.1), and 5.0 mass% FeO in slag attained are very important.

Magnesias–chrome (MgO–Cr₂O₃) refractories have been widely used in the steel refining process and they are also considered to be strong possible materials for smelting reduction furnaces.⁴⁾ Corrosion of a refractory due to the chemical dissolution is one of the main causes of refractory wear. The relationship between MgO–Cr₂O₃ refractories and slag has been studied by various investigators. The phase

diagram of MgO–Cr₂O₃–SiO₂ has been published by Keith.⁵⁾ Glasser and Osborn⁶⁾ have published the phase diagram of CaO–Cr₂O₃–SiO₂ system. Morita *et al.*^{7,8)} determined the solubilities of MgO and Cr₂O₃ in CaO–SiO₂–Al₂O₃–MgO–Cr₂O₃ system slag. On the other hand, Tao *et al.*^{9,10)} also demonstrated that the reactions of magnesias or magnesias–chrome refractories with molten CaO–SiO₂–Al₂O₃–Fe₂O₃ slags. However, an extensive literature search shows that details of the corrosion reaction of a MgO–Cr₂O₃ refractory with CaO–SiO₂–MgO–Al₂O₃–Fe₂O₃ molten slag have not been clarified.

Many different slag tests have been used in the attempt to simulate the environment as refractory is exposed to in commercial service. In the simplest static test, a cup or pocket is filled with slag and exposed to high temperature to promote slag refractory interaction. More sophisticated slag test such as dynamic slag conditions, introduction of fresh slag and thermal cycling.¹¹⁾ The more sophisticated tests are more difficult to operate reproducibly, but offer more potential for meaningful results because they simulate industrial conditions more realistically. Besides, although the simpler slag tests are suffered by being too remote from the real service environment, they are easier to operate and control.¹¹⁾

In the present study, reaction of magnesias–chrome brick at slag–refractory interface by electric furnace static slag corrosion testing has been studied. The slag examined condition were at 1823~1923 K, oxidization atmosphere, lower slag basicity (Ca/Si = 1.1) and slag containing FeO 5.0 mass%. The purpose of this investigation was to clarify the MgO solubility, microstructure and morphology at the slag–refractory interface for MgO–Cr₂O₃ brick through the electric static slag corrosion test.

2. Experimental Procedure

The starting slag used in oxidization atmosphere at 1823 to

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Table 1 Chemical composition of oxide powders used.

Oxide powders	Composition (mass%)							
	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe	Pb	SO ₄	Others
SiO ₂ ^a	98.92			0	0.01	0.01	0.05	1.01
Al ₂ O ₃ ^b		98.50	0	0	0.02			1.3
CaCO ₃ ^c			55.20		0.01	0.001	0.05	44.739
MgO ^d				>98.00	0.03	0.02	0.1	1.85

a. Nacalai Tesque, INC., Kyoto, Japan

b. J. T. Back, USA

c. Yakuri Chem. Co., Ltd. Osaka, Japan

d. Yakuri Chem. Co., Ltd. Osaka, Japan

Table 2 Source and composition of FeO used.

Source	Composition (mass%)					
	SiO ₂	Al ₂ O ₃	CaO	MgO	FeO	Fe ₂ O ₃
China Steel Corporation	0.21	0.19	0.08	0.02	69.50	30.00

Table 3 Chemical composition of the slag.

Composition (mass%)					C/S ^a
MgO	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃ ^b	
12.0	15.0	32.4	35.6	5.0	1.1

a. C/S = CaO/SiO₂b. Fe₂O₃ contained FeO 69.50 mass% and Fe₂O₃ 30.00 mass%

1923 K was a synthetic MgO-Al₂O₃-SiO₂-CaO-Fe₂O₃ system. Commercial reagents of MgO, Al₂O₃, SiO₂ and CaCO₃ were used. The chemical compositions of these oxide powders are listed in Table 1. The MgO-Al₂O₃-SiO₂-CaO premelt slag was fused in an Al₂O₃ crucible at 1773 K in air for 2 h, then quenched in water, dried and ground in a steel mortar. Subsequently, the ground premelt slag was mixed with FeO to make the described composition for experiments. The composition of FeO used and chemical composition of the experiment slag are listed in Tables 2 and 3, respectively.

The analyzed specimens for the immersion test (60 × 60 × 60 mm) were fabricated out of highly-fired direct-bonded commercial MgO-Cr₂O₃ bricks. The chemical composition and properties of the MgO-Cr₂O₃ bricks are listed in Table 4. The outer crucible for the electric furnace static slag corrosion test 13.2 cm inside diameter, 15.0 cm outside diameter, 12.0 cm depth) was fabricated out of castable refractory. An inner fused-alumina crucible (Al₂O₃ 99.5%), 11.2 cm inside diameter, 13.0 cm outside diameter and 10.0 cm depth, contained the slag (300 g) and alumina crucible was set in the castable crucible.

The schematic diagram of the experimental electric furnace and crucibles used for the static slag corrosion test are shown in Fig. 1. Water-cooled caps sealed the upper and lower ends of the steel chamber. Furnace temperature was controlled by a 20%Rh/Pt-40%Rh/Pt thermocouple connected to the PID program controller.

The castable crucible containing Al₂O₃ crucible, slag and sample was set in the furnace and heated up in air atmosphere. After reaching at the testing temperature, 1823~1923 K, the crucible was held at this temperature for 2 to 8 h. Through corrosion test for a specified time, the MgO-Cr₂O₃

Table 4 Composition and physical properties of the MgO-Cr₂O₃ brick* for slag corrosion test.

Refractory	Composition (mass%)				Physical properties		
	Al ₂ O ₃	MgO	Fe ₂ O ₃	Cr ₂ O ₃	B.D. ^a (g/cm ³)	A.P. ^b (%)	C.C.S. ^c (MPa)
MgO-Cr ₂ O ₃	5.0	53.2	7.3	34.5	3.3	15.3	33

* Provided by supplier (Kuan-Ho DIS-1)

a: B.D.: Bulk density

b: O.P.: Apparent porosity

c: C.C.S.: Cold crush strength

Fig. 1 The schematic diagram of (a) experimental electric furnace and (b) crucible for static slag corrosion test.

brick specimen was removed from the slag by lowering the crucible. After test the specimens were vertically sectioned from the specimen center for corrosion and permeation observation.

The crystalline phase was identified by X-ray diffraction (XRD) which was performed with a Rigaku X-ray diffractometer (Model Rad IIA, Rigaku Co., Tokyo, Japan) with

Fig. 2 The cross section morphology of MgO-Cr₂O₃ brick through electric furnace static corrosion test at 1823 K for 2 h.

CuK α radiation and a Ni filter, at a scanning rate (2θ) of 0.25°/min.

The foils for optical polarized microscope (OPM) (Model Nikon E600 POL, Japan) were prepared via the conventional technique: the sample was sliced to a thickness of about 80 μ m mechanically to optical transparency.

The morphology of the corrosion surface and penetration layer of MgO-Cr₂O₃ brick before and after slag corrosion was examined by scanning electron microscopy (SEM) (Model S-4100, Hitachi Ltd., Tokyo, Japan). The composition was analyzed with energy dispersive spectrometry (EDS) (Model Noran, USA) employing an internal standard method. The mapping and line scanings were attached with the SEM (S-4100).

The foils for transmission electron microscopy (TEM) (Model JEOL 3013, JEOL Ltd., Tokyo, Japan) were prepared via the conventional technique: the sample was taken to the optical thin foils mechanically and ion-beam thinning to electron transparency. Electron diffraction (ED) examinations were made in carefully thinned foils of MgO-Cr₂O₃ bricks after slag corrosion test was operated at an accelerating voltage of 200 kV.

3. Results and Discussion

The cross section morphology of MgO-Cr₂O₃ brick through electric furnace static corrosion test at 1823 K for 2 h is shown in Fig. 2. It indicates that the slag thickness decreases during test, due to the slag penetration into MgO-Cr₂O₃ brick and Al₂O₃ crucible. The obvious corrosion at interface of slag and brick is not found.

X-ray diffraction (XRD) patterns of MgO-Cr₂O₃ brick before test and heated at 1923 K through electric furnace static corrosion test for various times are shown in Fig. 3. In Fig. 3(a), it indicates that the crystallization peaks of MgO-Cr₂O₃ brick surface before test as determined by XRD analysis are periclase MgO and MgCr₂O₄ spinel. XRD patterns of the permeated layer of MgO-Cr₂O₃ brick after corrosion test at 1923 K for various times are illustrated in Fig. 3(b)–(d). It indicates that the reflections of MgO and MgCr₂O₄ successively appear, and a minor crystalline phase, CaMgSiO₄, also shows up. The crystalline phases are found to be mostly MgO and MgCr₂O₄ with a minor phase of CaMgSiO₄ for MgO-Cr₂O₃ at 1823 K and 1923 K, respec-

Fig. 3 XRD patterns of the MgO-Cr₂O₃ brick and at 1923 K through electric furnace static corrosion test for various times: (a) before test, (b) 2 h, (c) 6 h, and (d) 8 h.

tively, after slag corrosion test for various duration time.

The relationship for corrosion test temperature and duration time with the MgO content in the surface region of MgO-Cr₂O₃ brick is shown in Fig. 4. It indicates that for the same duration, the MgO content in the surface region of MgO-Cr₂O₃ bricks decreases with increasing corrosion test temperature. This result is caused by the slag attack MgO-Cr₂O₃ brick and corrosion reaction of brick increasing with test temperature increasing. On the other hand, a higher temperature increases the dissolution rate of MgO, because of the higher diffusivity. For the same test temperature, the MgO content of the surface region of MgO-Cr₂O₃ brick decreases with duration time increasing. When duration time increases from 4 to 8 h, a linear relation for the duration time and the MgO content is obtained.

The relationship of duration time and test temperature with the MgO content in slag for MgO-Cr₂O₃ brick through electric furnace static corrosion test is shown in Fig. 5. The increment of MgO content in slag for MgO-Cr₂O₃ brick test at 1823 K for 8 h only increases about 6.0%. But during test at 1923 K for 8 h, the increment of MgO content suddenly increases to about 16.0%. Figure 5 indicates that the increment rate of MgO content in slag for MgO-Cr₂O₃ brick tested at 1923 K is higher than that at 1823 K and 1873 K for duration time increasing from 4 to 8 h, respectively. This result is due to that as tested at 1923 K, the MgO content in MgO-Cr₂O₃ brick and slag approaches to equilibrium, when duration time attains to 6 h.

Fig. 4 The relationship of the MgO content and corrosion test temperature and duration time in the MgO-Cr₂O₃ bricks.

Fig. 5 The relationship of the MgO content in slag and duration time and test temperature for the MgO-Cr₂O₃ bricks through electric furnace static corrosion test.

The relationship of solubility of MgO with the slag composition was studied with the regular solution model^{9,10)} in which the molten slag consisting of cations of Mg²⁺, Ca²⁺, Fe²⁺, Al³⁺, Si⁴⁺, etc. and anions of O²⁻ relating to these cations in molten slag is assumed. The cations are randomly arranged in the space of O²⁻.¹²⁾

In an $i-j$ binary regular solution system, the activity a_i of component i is obtained from the liquids of the phase diagram and using eq. (1)¹³⁾

$$\ln a_i = \left(\frac{\Delta H_{m,i}}{R} \right) \left(\frac{1}{T_{m,i}} - \frac{1}{T} \right) \quad (1)$$

Fig. 6 The relationship of activity coefficient of MgO (γ_{MgO}) and test temperature and duration time for the MgO-Cr₂O₃ bricks after electric furnace static corrosion test.

where $\Delta H_{m,i}$ is the heat of fusion (J/mol), R is the gas constant (8.314 J/mol), $T_{m,i}$ is melting point (K) of pure component i , and T denotes the test temperature (K).

Activity a_i of component i of a regular solution and activity coefficient γ_i can be obtained from eqs. (2) and (3):¹⁴⁾

$$RT \ln \gamma_i = \alpha_{i,j} \cdot x_j^2 \quad (2)$$

$$a_i = (\gamma_i x_i)^{V_i} \quad (3)$$

where $\alpha_{i,j}$ (J/mol) denotes the interaction energy between (i -ion)-O²⁻(j -ion), x_i and x_j are mole fractions of components i and j , respectively, V_i is the number of cations in molecular formula of i component.

Combining and rearranging equations (1), (2) and (3), then the eq. (4) can be obtained:

$$\alpha_{i,j} = \frac{\Delta H_{m,i}(T - T_{m,i})}{v_i x_j^2 T_{m,i}} - \frac{RT \ln x_i}{x_j^2} \quad (4)$$

Applying this regular solution model to MgO-Al₂O₃-SiO₂-CaO-Fe₂O slag system, the activity coefficient of MgO can be expressed as equation (5):¹⁴⁾

$$RT \ln \gamma_{MgO} = \sum_{i \neq j} \alpha_{i,j} x_i - \sum_{i \neq j} \sum_j \alpha_{i \neq j} x_i x_j \quad (5)$$

In the present study, each concentration (x_i, x_j) in the liquids and their respective temperature are obtained from each $i-j$ binary system phase diagram.¹⁵⁻²¹⁾ The data in JANAF Thermochemical Table are used for heat of fusion and melting point of each component.²²⁾ Hence, temperature on the liquids and $\alpha_{i,j}$ corresponding to x_i and x_j are calculated from eq. (4) and putting the value of $\alpha_{i,j}$ into eq. (5).

The calculated results of γ_{MgO} are obtained and shown in Fig. 6. It indicates that the activity coefficient of MgO in the molten MgO-Al₂O₃-SiO₂-CaO-Fe₂O slag increases with test temperature increasing for the same time. From Fig. 5, it can be found that the slope of each curve, *i.e.* the dissolution rate

Fig. 7 Optical polarized micrographs of the MgO-Cr₂O₃ bricks through electric furnace static slag corrosion test at various conditions of (a) at 1823 K for 2 h and (b) at 1873 K for 4 h.

of MgO from brick to slag = $\frac{\Delta \text{MgO}_{\text{in slag}}}{\Delta t}$ increases with the corrosion test temperature at the same time. According to Figs. 5 and 6, it indicates that the dissolution rate of MgO increases from brick to slag caused by the activity coefficient of MgO in slag increases. This result can be corresponding to the result of Tao *et al.*^{9,10)}

Optical polarized micrographs (OPMs) of the MgO-Cr₂O₃ brick through corrosion test at various conditions are shown in Fig. 7. Figure 7(a) shows the open nicols micrograph of MgO-Cr₂O₃ brick through electric furnace static corrosion test at 1823 K for 2 h. By the extinction and relief of OPM, it can be found the crack, pores, MgO particles and corrosion reaction area. The corrosion reaction occurs around pores and along crack toward the interior, due to the slag in pores or crack penetrating into MgO-Cr₂O₃ brick. Figure 7(b) shows the open nicols micrograph of MgO-Cr₂O₃ brick at 1873 K through electric furnace static corrosion test for 4 h. It indicates that the pore fraction and crack increase due to that the corrosion reaction of MgO-Cr₂O₃ brick increases with the test temperature and duration time increasing. The MgCr₂O₄ phase is around the reaction area such that MgO forms the

Fig. 8 SEM micrographs of the penetration layer of the MgO-Cr₂O₃ brick at 1823 K after electric furnace static slag corrosion test for 4 h: (a) MgO in penetration layer and (b) enlarged view of the pore (by arrow) in Fig. 8(a).

discontinuous phase. Robin *et al.*²³⁾ have pointed out that the discontinuous phase consists of magnesia grains (periclae) which offers the good corrosion resistance against the aggressive environment and mechanical resistance to thermal loading. From Fig. 7(b) it may be found that the grain boundary is another path of corrosion reaction occurring for MgO-Cr₂O₃ brick with molten slag. According to Figs. 7(a) and (b), it is also found that in the MgO-Cr₂O₃ brick interior, the formation of crack increases with test temperature and duration time increased. This result is caused by that the slag more penetrates into MgO and accelerates the dissolution of MgO.

The microstructure of scanning electron microscopy (SEM) for the polished permeated layer of MgO-Cr₂O₃ brick at 1823 K through electric furnace static corrosion test for 4 h is shown in Fig. 8. Figure 8(a) shows the micrograph of MgO in the penetration layer. It indicates the crack and pores in the MgO grains. On the other hand, the corrosion reaction occurs along the grain boundaries of MgO. Figure 8(b) shows the enlarged view of the pore in the Fig. 8(a). Composition of location A (near pore) and location B (in the pore) in Fig. 8(b) are listed in Table 5. It can be found that the MgO content in the pore is lower than that in the MgO grain, due to the corrosion reaction of slag with MgO occurs and forms the sunken hole and creates the eddy

Fig. 9 TEM micrographs and ED patterns of the MgO-Cr₂O₃ brick at 1923 K after electric furnace static slag test for 4 h for (a) BF image, (b) DF image of the MgO-Cr₂O₃ brick matrix, (c) ED pattern corresponding to MgCr₂O₄ phase, (d) DF image of the slag, (e) ED pattern corresponding to CaMgSiO₄ phase, (f) DF image of the diffusion layer between the slag and brick matrix (g) ED pattern corresponding to (Mg, Fe)(Cr, Al)₂O₄ phase.

current such that the stopover time of slag at hole increased, leading to accelerating the dissolution of MgO. Composition of location C in Fig. 8(a) is also listed in Table 5. For the MgO-Cr₂O₃ brick after slag corrosion, the MgO dissolves in slag and forms the phase of CaMgSiO₄. The melting point of CaMgSiO₄ is lower than 1773 K, hence the compound of CaMgSiO₄ in slag may penetrate into the exterior of MgO-Cr₂O₃ brick. From the results in Table 5 and Fig. 8, it is also found that pores and grain boundaries of MgO provide the paths for slag penetration into MgO-Cr₂O₃ brick interior and promote the corrosion reaction.

Micrographs of TEM and ED patterns of MgO-Cr₂O₃ brick at 1923 K after electric furnace static slag corrosion test for 4 h are shown in Fig. 9. Figure 9(a) shows the morphology of bright field (BF) image, it indicates that a diffusion layer forms between slag and MgCr₂O₄ spinel phase in MgO-Cr₂O₃ brick matrix. Figure 9(b) shows the dark field (DF) image of MgCr₂O₄ spinel, it indicates that the micropores disperse in the MgCr₂O₄. The ED pattern (Fig. 9(c)) indexing is corresponding to MgCr₂O₄ spinel phase. Figure 9(d) and (e) also show the development of the microstructure of slag and ED pattern in which CaMgSiO₄ phase in slag is observed. Figure 9(f) shows the development of the microstructure of diffusion layer. The ED pattern (Fig. 9(e)) also provides the criteria for the presence of ferro magnesia-chromite ((Mg, Fe)(Cr, Al)₂O₄) in this system. From Fig. 9, it also indicates that the slag along crack penetrates into

Table 5 EDS analyses of composition at various locations in Fig. 8.

Location	Composition (mass%)			
	MgO	FeO	SiO ₂	CaO
A	87.62	12.38	—	—
B	80.54	19.46	—	—
C	21.3	8.5	32.7	37.5

MgO-Cr₂O₃, interior and with brick occurs corrosion reaction, creates the (Mg, Fe) (Cr, Al)₂O₄ phase. The (Mg, Fe) (Cr, Al)₂O₄ layer can be effective for inhibiting the penetration of slag and increasing the corrosion resistant of MgO-Cr₂O₃ brick.

4. Conclusions

The reaction between MgO-Cr₂O₃ brick and molten MgO-Al₂O₃-SiO₂-CaO-Fe₂O slag using electric furnace static corrosion test method has been investigated. The results obtained in the present study are summarized as follows:

- (1) For the MgO-Cr₂O₃ brick at 1823~1923 K through electric static slag corrosion for various duration time by XRD analysis, the crystalline phases are found to be mostly MgO and MgO-Cr₂O₄ phases with a minor phase of CaMgSiO₄.
- (2) For same duration time, the MgO content in MgO-Cr₂O₃ bricks decreases with the corrosion test temperature increasing.
- (3) The activity coefficient of MgO in the molten MgO-SiO₂-CaO-Fe₂O slag increases with test temperature increasing for the same time.
- (4) Pores and grain boundaries of MgO provide the paths for slag penetrating into MgO-Cr₂O₃ brick interior and promoting the corrosion reaction.
- (5) In the diffusion layer, the phase of (Mg, Fe) (Cr, Al)₂O₄ forms between slag area and MgCr₂O₄ matrix.

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