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Effect of electromagnetic field on slag corrosion resistance of low carbon MgO–C refractories

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Abstract

Using MgO–C refractories containing 6% carbon and the slag with a basicity (CaO/SiO_2) of around 0.8, the melting slag resistance experiments of low carbon MgO–C refractories were carried out in induction furnace and resistance furnace, respectively. The microstructure of low carbon MgO–C refractories corroded by slag under the different conditions was analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectrometer (EDAX). The results show that in induction furnace having electromagnetic field (EMF), there are $MgFe_2O_4$ spinel with a little of Mn ions generated in the interfacial layer. Part of the solid solution is monticellite [$CaMgSiO_4$] containing a little MnO and FeO. While under the condition of EMF free, there is not $MgFe_2O_4$ spinel in the interfacial layer and the solid solution is monticellite ($CaMgSiO_4$). At a high temperature, EMF increases the diffusion coefficient of $Fe^{2+/3+}$ ions, which displaces Mg^{2+} and forms $MgFe_2O_4$ with a little of Mn ions. There are $MgAl_2O_4$ spinel in the penetration layers under the conditions of both EMF and EMF free. EMF speeds up corrosion of low carbon MgO–C refractories.

Keywords: E. Refractories; Electromagnetic field; Low carbon MgO–C; Slag resistance; $MgFe_2O_4$

1. Introduction

With the development of smelting technology, electromagnetic field (EMF) is widely used in steel metallurgy. For example, EMF is utilized to heat, stir, separate and control flow velocity and shape of molten metal with the uncontact method during the process of long flow rout steelmaking. At the same time, EMF universally exists in the field of arc/induction furnace and secondary refining during the short flow route steelmaking [1–5]. So the interfacial reaction between molten slag and refractories can be inevitably affected by EMF. In theory, the corrosion reaction between molten slag and refractories belongs to the electrochemical reaction, which results in electron transfer and exchange [6–9]. The movement of charged particle in electromagnetic field can be subject to Lorentz force. Potschke [6] reported that double layer would be formed on the interface between liquid slag and refractory materials at a high temperature. The electric potential applied in double layer will change the wettability of liquid slag–refractories. These phenomena have been also described by Lippmann–Young equation [7–9]. Therefore, the existing EMF can change the potential in double layer and affect slag corrosion of refractories. The authors have reported that the electromagnetic field existing at a high temperature could enhance the diffusion and penetration of $Fe^{2+/3+}$ ions to form the $MgFe_2O_4$ phase [4,5]. So the EMF could affect the mechanism of corrosion reaction between the slag and refractories.

At present, more and more researchers have theoretical knowledge that EMF plays a key role on the reaction of slag/refractories. But the detailed study on this problem has not been carried out. For example, how the EMF affects the interfacial reaction? How to prove this influence experimentally? This paper will develop the experiments to research the influence of EMF on the slag resistance of refractories. MgO–C refractories have been chosen in experiments because MgO–C refractories with good thermal shock resistance and slag resistance have been widely used as furnace lining in steelmaking industry and retained an important role in refractories industry. Nowadays the research on MgO–C refractories focuses on carbon content

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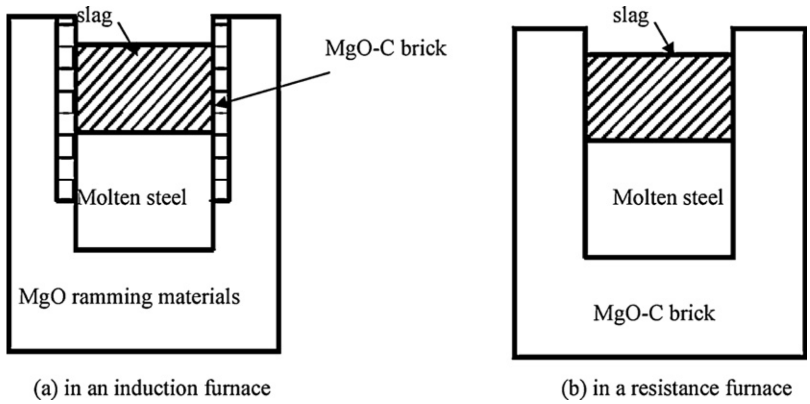

Fig. 1. The schematic diagrams of the experiments. (a) In an induction furnace and (b) in a resistance furnace.

decreasing and the thermal conductivity decreasing. The former could facilitate the decrease of carbon in steel and the later could facilitate the energy saving. In order to avoiding the problem caused by low carbon such as decreasing in oxidant and thermal shock resistance, researchers improved the performance of MgO–C refractories from the aspects of anti-oxidant, matrix, resin bond and so on [10–12]. However in the literature only a few papers have been published about the effect of EMF on slag resistance of low carbon MgO–C refractories.

This paper carried out slag resistance experiments of low carbon MgO–C refractories under the condition of EMF and EMF-free, respectively. The microstructural change of interfacial layer between slag and low carbon MgO–C refractories had been investigated by means of X-ray diffractometer (XRD), scanning electron microscope (SEM) and EDAX. The influence mechanism of EMF on slag resistance of low carbon MgO–C refractories had been revealed.

2. Experimental

Low carbon MgO–C bricks containing 6% carbon and the slag with a basicity (CaO/SiO_2) of around 0.8 were used in the experiments. The chemical composition of the slag was shown in Table 1. Low carbon MgO–C bricks were dried at 200 °C for 24 h and cut into the cuboid-shaped samples with the dimension of 20 mm × 30 mm × 100 mm. The samples were inserted into the lining of vacuum induction furnace (21WGJL0.025-100-2.5P). Then the steel (6 kg) and slag (2 kg) were filled into the lining. The samples were sintered at 1600 °C × 3 h in Ar with the pressure of 0.1 MPa to carry out the slag resistance experiments under the condition of EMF.

The dried low carbon MgO–C bricks were cut into the cube samples with the hole of ∅36 mm × 55 mm. The outer dimension of cube samples was 70 mm × 70 mm × 70 mm. The samples were dried and filled with steel (100 g) and slag (50 g). Then these samples were embedded in carbon and sintered at 1600 °C × 3 h in a resistance furnace. This experiment was the molten slag resistance under the condition of EMF free. The schematic diagrams of the experiments are shown in Fig. 1.

The phase change of slag line for corroded low carbon MgO–C bricks was analyzed by means of X-ray diffractometer (XRD, X'Pert pro). The microstructure change was determined by scanning electron microscope (SEM, XL30TMP) and energy dispersive spectrometer (EDAX, Pheoenix).

Table 1
Chemical composition of slag (mass%).

Fe_2O_3	SiO_2	Al_2O_3	MnO	MgO	CaO	TiO_2	V_2O_5	C/S
22.0	27.5	15.0	3.0	8.0	22.0	2.0	0.5	0.8

3. Results and discussion

3.1. Effect of EMF on the phase change of corroded low carbon MgO–C refractories

Under the condition of EMF and EMF free, the XRD of slag corroded layer for low carbon MgO–C refractories are shown in Fig. 2. It is shown that under two conditions, the major phases

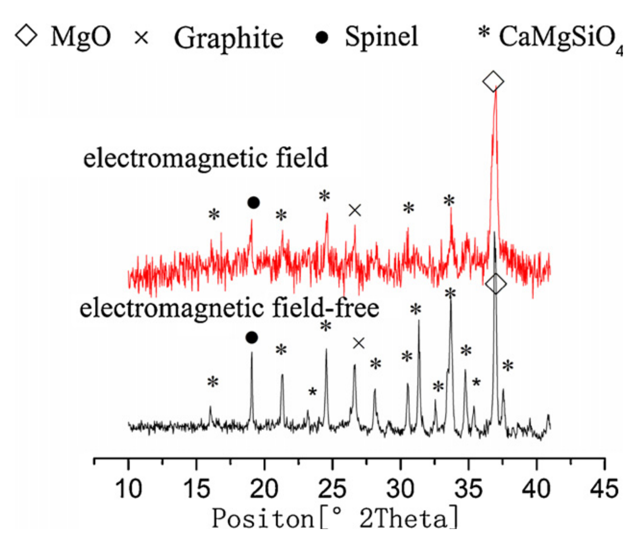

Fig. 2. XRD patterns of the slag corroded low carbon MgO–C refractories under the condition of EMF and EMF-free, respectively.

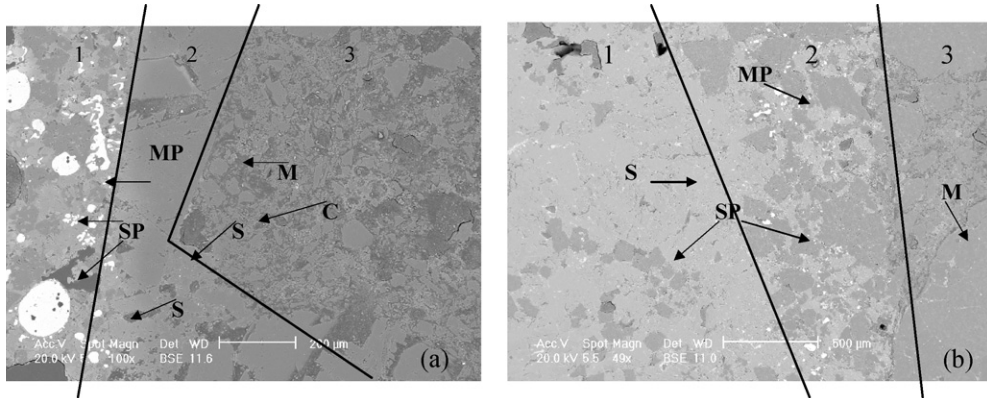

Fig. 3. SEM images of the corroded low carbon MgO–C refractories by slag under the condition of EMF (a) and EMF free (b), respectively. M, magnesia; MP, metal particle; C, graphite; S, solid solution (CMS) and SP, spinel.

are magnesia (MgO) and graphite while the new born phases are spinel and monticellite ($CaMgSiO_4$, CMS).

The SEM of corroded MgO–C refractories in both EMF and EMF free are shown in Fig. 3. Samples A and B indicate the condition of EMF and EMF free, respectively. It is shown in Fig. 3 that samples both A and B have three layers of erosion, penetration and origin. The white region including most of metal and slag is the erosion layer (a1, b1). The grey layer including the white region of some metal/slag and black graphite/MgO is the penetration layer (a2, b2). The black layer including MgO and graphite is the original layer (a3, b3).

In EMF, molten steel and slag are stirring intensively because of the existence of electromagnetic force, which can increase the wear of low carbon MgO–C refractories. As a result, the thickness of erosion layer decreases. The low melting phase becomes less and the particles of magnesia dissolve obviously. The penetration layer of low carbon MgO–C refractories could be studied further because that is the main area corroded by slag. From Fig. 2(a) in EMF, it is shown that the penetration layer comprises of spinel, reduced metal, magnesia and a little solid solution (CMS). It is to be noted that the penetration layer in EMF becomes denser and denser. While in EMF free, the penetration layer comprises of spinel,

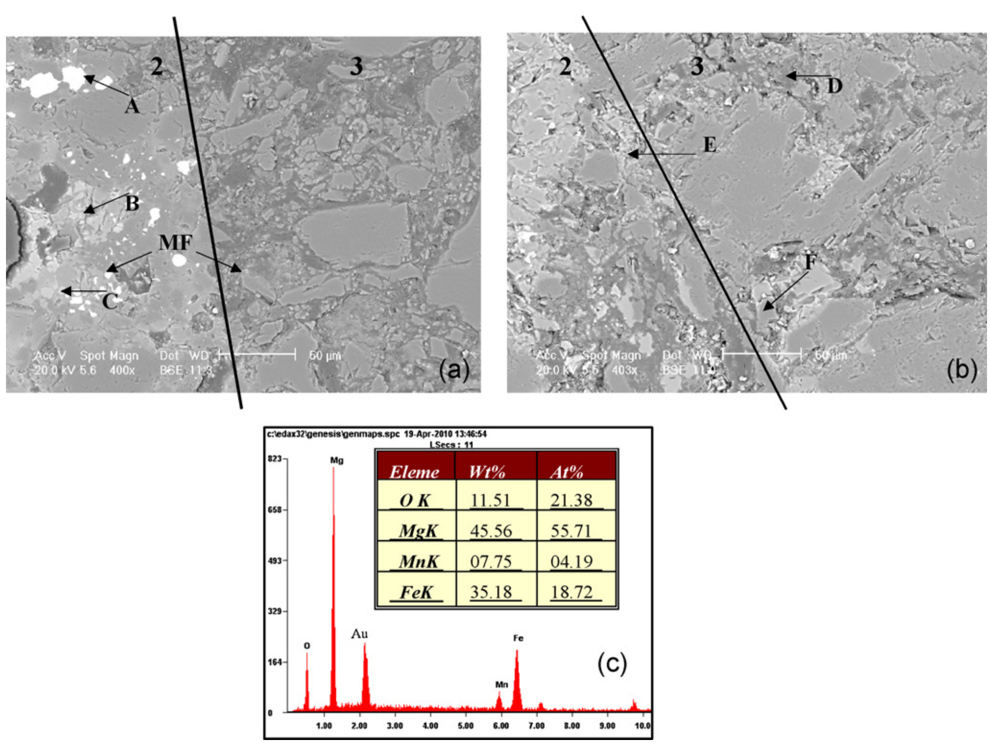

Fig. 4. SEM images of the interface for corroded low carbon MgO–C refractories in electromagnetic field (a) and electromagnetic field-free (b), and the corresponding EDS pattern of point MF (c).

magnesia, metal and solid solution (CMS). And the layer becomes looser and looser, shown in Fig. 2(b).

According to Lippmann–Young equation [8]:

$$\cos\ \theta(U) - \cos\ \theta(0) = \frac{\varepsilon_0 \varepsilon_r U^2}{2d\sigma_{\rm lg}}.$$

where U, θ and ε are the voltage, wetting angle and dielectric constant, respectively. $\sigma_{\rm lg}$ is the interfacial tension between molten slag and refractories. EMF could increase the wettability and penetration of slag into low carbon MgO–C refractories [4,5,7]. So the penetration layer existing in EMF becomes denser than that in EMF free.

The authors [4,5] had researched that EMF can affect the erosion mechanism of MgO–C refractories with carbon content of 14 wt%. It was shown that in EMF the penetration layer exists while in EMF free it does not exist. So in EMF free, the different content of carbon leads to the different corrosion mechanism by slag. With the increase of carbon, the penetration-resistance increases and the densification decreases. That gives rise to the loose structure and easy corrosion. While the graphite is oxidized, the structure becomes looser and looser. So the rate of penetration is slower than that of erosion and leads to the disappearance of penetration layer. As for low carbon MgO–C refractories, the former rate is faster than the latter one and approves the obvious penetration layer. The results agree with the report of Hayashi [12].

3.2. Effect of EMF on corrosion mechanism of low carbon MgO–C refractories

The SEM of corroded slag line for low carbon MgO–C refractories under the condition of both EMF and EMF-free are shown in Fig. 4. The corresponding composition is shown in Table 2.

It is shown from Fig. 4(a) and Table 2 that in EMF there is a reduction reaction of metal oxide in the interface between penetration and origin layer. While in EMF free it is shown in Fig. 4(b) that the reduction reaction does not occur. EMF enhances the penetration of the slag into the refractories and results in the occurrence of reduction reaction between metal oxide in slag and carbon in refractories. This result agrees with the report of Refs. [4,5].

It is also shown in Fig. 4(a) that in EMF, one part of the formed spinel in the interface is $MgAl_2O_4$. The other part is $MgFe_2O_4$ with a little of Mn (denoted as point MF in Fig. 4(a)). The solid solution in EMF is monticellite ($CaMgSiO_4$, CMS)

Table 2
The content of points in the interface for the corroded low carbon MgO–C refractories shown in Fig. 4 (wt%).

	Ca	Si	Al	Mg	Fe	Mn	O
A					100.00		
B	29.95	24.03		13.25	9.17	5.57	18.03
C			52.29	17.4	10.12		20.19
D			54.74	14.34			30.92
E	44.45	22.08		9.21			24.26
F	58.98	19.73		4.23			17.06

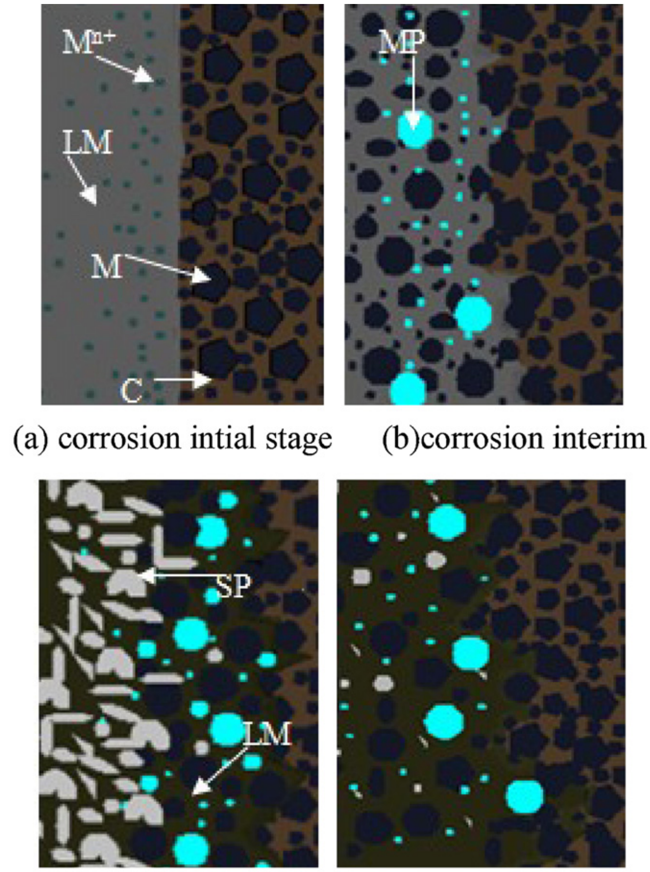

Fig. 5. Model of low carbon MgO–C refractories corroded by slag in electromagnetic field. (a) Corrosion initial stage, (b) corrosion interim, (c) spinel layer forming and (d) spinel layer dissolved.

with a little of Fe/Mn oxide (denoted as point B in Fig. 4(a)). While in EMF free, all the spinel is $MgAl_2O_4$ and there is no Fe/Mn entering into the lattice of monticellite (CMS), denoted as points E and F in Fig. 4(b). EMF enhances the substitution of $Fe^{3+/2+}$ and Mn^{2+} in slag for Mg^{2+} in refractories and forms solid solution [13] consisting of $Fe^{3+/2+}$ and Mn^{2+}. From the phase diagram of CaO–MgO–SiO_2, the liquid phase above 1500 °C is crystallized into solid solution of monticellite (CMS) on cooling [14]. In both EMF and EMF free, there is $MgAl_2O_4$ spinel in penetration. The difference is that spinel phase in EMF contains a little Fe/Mn ions.

According to the above experiments and results, the corrosion mechanism of low carbon MgO–C refractories in EMF can be shown in Fig. 5.

M^{n+} denotes metal ions such as Fe^{3+}, Mn^{2+}, Ti^{4+} and V^{5+}. The symbols of LM and SP, respectively denote the solid solution and spinel. The symbols of MP, M and C, respectively mean metal particles, magnesia and graphite. The corrosion process of low carbon MgO–C refractories in EMF can be described in four stages. Fig. 5(a) is the initial stage that the metal ions in molten slag distribute in the interface between the slag and refractories in EMF. Fig. 5(b) is the interim stage. In this stage, ion of $Fe^{3+/2+}$ and Mn^{2+} could be reduced to metal elements. At the same time, magnesia becomes spalling and dissolved, where the slag begins to erode the refractories. Fig. 5(c) is the stage of spinel ($MgAl_2O_4$ and $MgFe_2O_4$) layer forming. Part of dissolved magnesia in slag reacts with Al (anti-oxidation agent) to form $MgAl_2O_4$ spinel. The other dissolved MgO in slag reacts with FeO and MnO to form $MgFe_2O_4$ spinel consisting of a little Mn ions. The iron content decreases while MgO content increases in solid solution of CMS (as a low melting phase above 1500 °C). Fig. 5(d) is the dissolved stage of the spinels. There is the wear and stirring of EMF, the increasing of FeO content in the solid solution (CMS) and the interfacial reactions. All these factors can cause the spinels to be dissolved into the slag and low carbon MgO–C refractories can be corroded. So magnesia starts spalling and reacts with FeO/MnO, where the corrosion process of stage 2 begins again.

EMF can help formation of $MgFe_2O_4$ spinel consisting of Mn ions. That is a high temperature phase which can increase the anti-oxidation of graphite as well as decrease the penetration of the slag. But the spinel can be dissolved by the slag. At the same time, EMF increases both the wettability and the collision frequency between slag and low carbon MgO–C refractories, which leads to the more serious corrosion of low carbon MgO–C refractories in EMF.

4. Conclusions

1) In EMF, molten steel and slag are stirring intensively because of the existence of electromagnetic force, which can increase the wear of low carbon MgO–C refractories. As a result, the thickness of erosion layer decreases. The low melting phase becomes less and the particles of magnesia dissolve obviously. While in EMF free, the penetration layer comprises of spinel, magnesia, metal and solid solution (CMS). And the layer becomes looser and looser.
2) In EMF there is a reduction reaction of metal oxide in the interfacial layer between penetration and origin layer. While in EMF free that the reduction reaction does not occur. EMF enhances the penetration of the slag into the refractories and results in the occurrence of reduction reaction between metal oxide in slag and carbon in refractories.
3) In EMF, part of the formed spinel in the interfacial layer is $MgFe_2O_4$ with a little of Mn ions and the solid solution is monticellite ($CaMgSiO_4$) with a little of Fe/Mn oxide. While in EMF free, all the spinel is $MgAl_2O_4$ and there is no Fe/Mn ions entering the lattice of monticellite ($CaMgSiO_4$).
4) EMF increases the slag corrosion and oxidation of low carbon MgO–C refractories.

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