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Induced Electro-Deposition of High Melting-Point Phases on MgO–C Refractory in CaO–Al₂O₃–SiO₂ – (MgO) Slag at 1773 K

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Abstract: MgO–C refractory was polarized across the slag-refractory interface at a voltage of 8 V in a synthetic CaO–Al₂O₃–SiO₂ – (MgO) Slag at 1773 K. A deposition layer mainly composed of dicalciumsilicate (2CaO·SiO₂) or spinel (MgO·Al₂O₃) with several hundred microns thick was achieved by cathodic polarization. However, the anodic decay was accelerated in comparison to the cathodic refractories and nonpolarized reference MgO–C refractories. The electrodeposition layer was mainly caused by the reduction of silicate anions, in which a shift of slag composition to the dicalciumsilicate (C₂S) or spinel (MA) primary phase field was induced. Furthermore, the rapid migration of mobile Ca²⁺ and Mg²⁺ ions can also lead to the enrichment of CaO and MgO at the slag/refractory interface. The present voltage level (8 V) is acceptable for the economic considerations and the slag component also need a careful section for the corrosion protection of MgO–C refractories.

Keywords: MgO–C refractory, cathodic polarization, induced electrodeposition, primary phase

Introduction

MgO–C refractories are widely used as furnace and ladle lining due to their high melting point, corrosion resistance and shock resistance [1, 12, 3]. However, a decrease of their service life is often caused by the damage because of chemical corrosion, thermal shock, and mechanical erosion in steelmaking operations. Accelerated corrosion can decrease not only the steel quality through an increase in the number of nonmetallic inclusions but also the service life of

refractories. In order to improve the service life of lining materials and steel quality, some measures must be carried out to reduce the dissolution of MgO–C refractories. In general, the damage of refractory is evaluated based on the penetration depth (defined here as “physical penetration” through the open pore without chemical reaction), and attack of slag (defined here as “chemical penetration” involving interface reactions between the refractories and slag) [4]. Recent studies have shown that the penetration rate of melt into the refractories can be hampered either by using extremely low porosity of refractories, such as density MgO-based ceramic, or by applying a voltage across the slag-refractory interface [5–7]. This finding can be explained using the integrated form of Poiseuille’s law [8], shown in eq. (1)

$$l^2 = \left[\frac{r\gamma \cos \theta}{2\eta} \right] \cdot t \quad (1)$$

where r is the open pore radius of refractory, γ is the interfacial tension, θ is the contact angle between the melt and refractory, η is the slag viscosity, t is corrosion time and l is the penetration depth. The extremely low porosities of refractories can reduce the penetration depth by reducing the parameter r for a given time. An application of an electrode potential across the slag-refractory interface can also reduce the penetration depth by changing γ and θ for a given time. Moreover, the directional shift of cation to the cathode can also lead to an increase of slag viscosity (η) surrounding the cathode. All operations can reduce the penetration depth (l) of slag into the refractories as explained in formula (1). Recent studies of MgO refractories immersed in slag have found that a spinel (MgO·Al₂O₃) layer is formed on the MgO surface, significantly slowing the further dissolution of MgO [6, 9, 10]. As is known, liquid oxides are ionic in nature at high temperature and the formation of spinel involves the counter-diffuse of ions, which can be controlled by using applied voltage. Unfortunately, no further studies involving the slag component and the amplitude of applied voltage are investigated aiming at the formation process of deposition layer.

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In the present work, a deposition layer formed on the MgO–C refractory surface in contact with a CaO–Al₂O₃–SiO₂–(MgO) slag under an applied voltage has been studied and reported. Dicalciumsilicate (C₂S) was prone to be deposited on the cathode surface in the CaO–Al₂O₃–SiO₂ slag and spinel (MA) was achieved easily in the CaO–Al₂O₃–SiO₂–10% MgO slag

Experimental

A piece of MgO–C refractory was drilled a $\varnothing 3 \times 5$ mm² blind-hole in one of the electrode faces. The electrode was fastened to a $\varnothing 3 \times 1000$ mm² molybdenum rod by applying a drop of high temperature cement into the blind-hole and hardening at 100 °C for 24 h. Similarly to standard practice, MgO–C refractories were used as the cathode and anode in the experiment, respectively. The electrodes were all dipped into the slag for 60 min at 1773 K, and the distance between anode and cathode as well as the immersion depth was 10 mm. A RLD-3020 potentiostat was used as a power source.

After removal and air-cooling, all samples were prepared for SEM/EDS analysis by sectioning, grinding and polishing using standard procedures. All the experiments were carried out under Ar atmosphere at 1773 K in a self-constructed test furnace (Figure 1).

The phase first depositing from a slag is termed primary phase and the composition range in which the primary phase remains stable is known as the primary phase field. In this work, a synthetic slag with the composition (Table 1) close to the primary phase field of dicalciumsilicate (2CaO.SiO₂) or spinel (MgO.Al₂O₃) was chosen. Slag preparation commenced with a homogenization step by mixing the appropriate amounts of high-purity CaO, SiO₂, Al₂O₃ and MgO in a ball mill for 8 h, followed by melting the mixture in a clay-bound graphite crucible at 1773 K in a muffle furnace. The slag was then ground and remelted several times to produce a homogeneous slag. After that, the homogenized slag was placed in a graphite crucible with $\varnothing 80 \times 70$ mm² for the following experiments.

The phase composition of cross-section for polarized MgO–C refractories was analyzed by means of X-ray

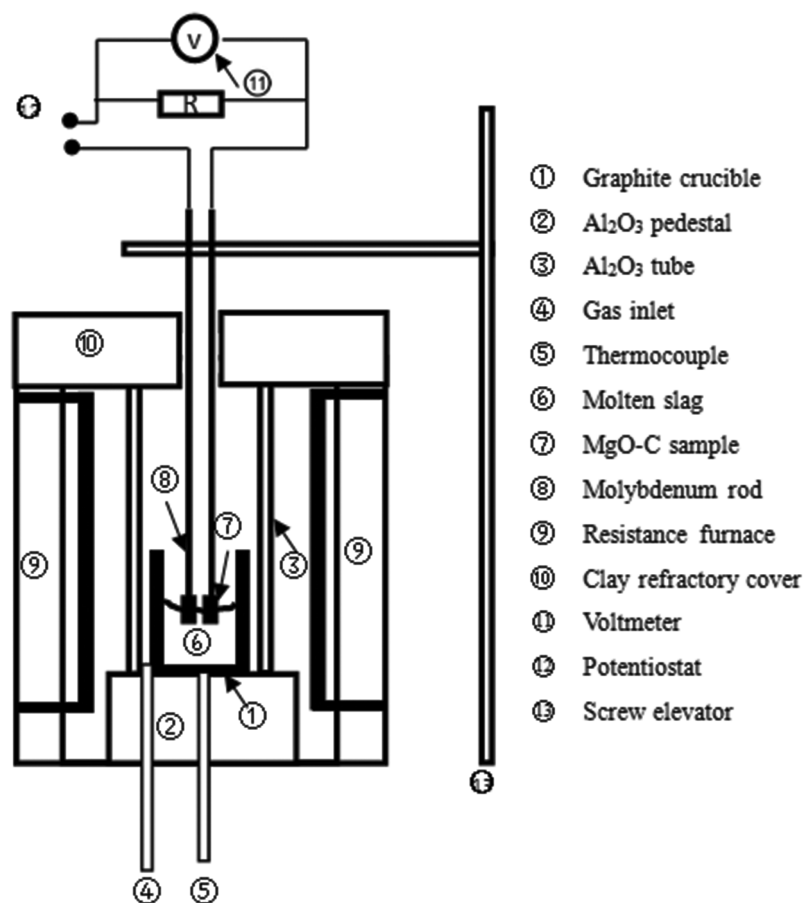


Figure 1: Scheme of the test furnace.

Table 1: Composition of synthetic slags.

Samples No.	Mass fraction %				$R = (\text{CaO} + \text{MgO})/\text{SiO}_2$
	CaO	SiO ₂	Al ₂ O ₃	MgO	
1	40	48.5	11.5	–	0.8
2	35	43.5	11.5	10	1.0

diffractometer (XRD, PANalytical X'Pert PRO, Dutch PANalytical Corporation). The microstructure was determined by scanning electron microscope (SEM, SU-5000, Hitachi High-Technologies Corporation) equipped with Energy Dispersive Analysis System of X-ray (EDS, Pheoenix, EDAX Limited Corporation).

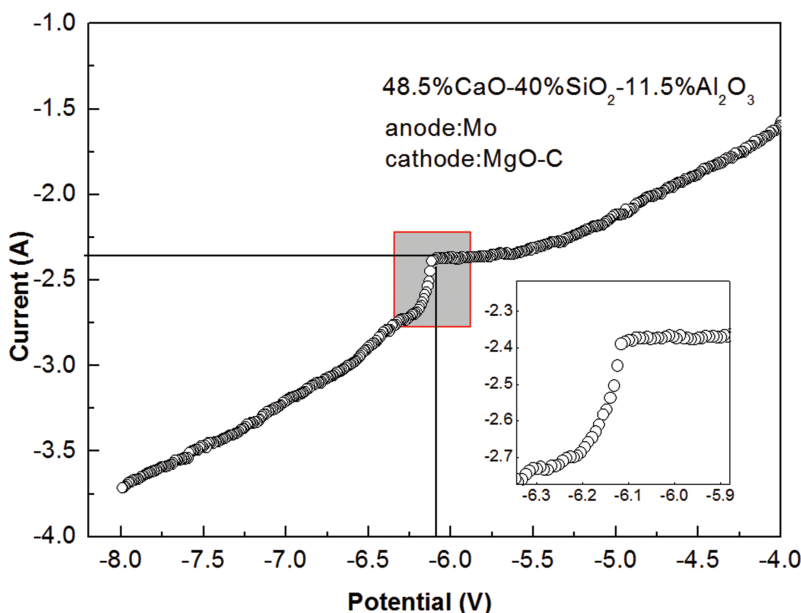
Results and discussion

Reduction potential of silicate and physical properties of synthetic slag

As mentioned above, the reduction of silicate anions can be the drive force for the formation of desired primary phase, explained as the known back rule in the ternary diagram. In order to determine the reduction potential of silicate anions in the present synthetic slag, a linear sweep voltammetric curve (LSV) was performed in a double-electrode electrochemical cell using a Princeton Versa STAT 4 workstation (Princeton Instruments, American). A molybdenum rod and

the prepared MgO–C electrode were used as the counter electrode and working electrode, respectively. The LSV curve of No.1 slag is shown in Figure 2. As displayed in Figure 2, a pronounced current increase was observed around the voltage of -6.1 V, corresponding to the reduction reaction of silicate anions. The finding was in agreement with the result of Allanore's report [11]. No other recognizable current increase was observed, suggesting that the reduction of Ca^{2+} or Al^{3+} was very difficult in the present casting range. Notably, the reduction potential of silicate anions measured here is more negative than that of silicon dioxide calculated from the thermodynamic data and Nernst formula (-1.2 V) due to the electrode over-potential, IR drop and the conductor drop and etc. Comparing to those of Ca^{2+} and Al^{3+} , the reduction potential of Mg^{2+} in No.2 slag is more negative, and thus the No.2 slag presumably shows the similar electrochemical phenomenon displayed in Figure 2 between 0 and -8 V. Therefore, all the experiments were conducted at voltages of 8 V across the anode and cathode interface, which could ensure the reduction of silicate anions.

As known, the viscosity of synthetic slag is also an important index for the penetration depth. The viscosity curves of synthetic slag are shown in Figure 3. The viscosities of synthetic slags decreased with an increasing temperature, and the values of No.1 and No.2 slags were about 0.64 and 0.21 Pa.s at 1773 K, respectively. The results showed that the No.2 slag involving 10% MgO could be more aggressive than that of No.1 slag into the refractories due to its low viscosity. According

**Figure 2:** LSV curve in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag.

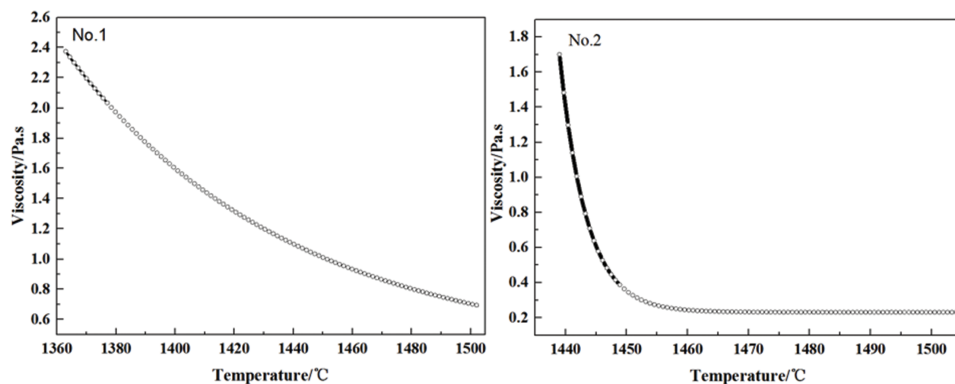


Figure 3: Viscosity curves of the synthetic slags.

to the reference [12], the conductivity of synthetic slag is around $0.12 \Omega^{-1} \text{cm}^{-1}$ at 1773 K, and thus the IR drop between the electrodes was negligible.

Appearance, micrograph and phase component of polarized MgO–C refractory

Figure 4 exhibits the appearances of polarized electrodes and reference electrodes. As shown in Figure 4(a₀), the reference sample covered with a viscous slag exhibited a decreasing cross-section, indicating the slag penetration into the MgO–C refractory was inevitable, and then a

portion of refractory were peeled off from the body surface due to the temperature-dependent thermal expansion coefficient between the slag and refractory. However, a remarkable difference was detected for the polarized electrodes. The anode polarized at 8 V was attacked significantly after 60 min and exhibited a recognizable and discrete appearance (Figure 4(a₁)), deriving from a complete slag penetration, interfacial chemical and electrochemical reactions. On the other hand, the cathode polarized at –8 V showed a negligible damage due to the formation of solid deposition layer (Figure 4(a₂)). The deposition layer was attached tightly on the surface of cathode, leading to a smooth and regular surface. Also, the reference sample corroded in

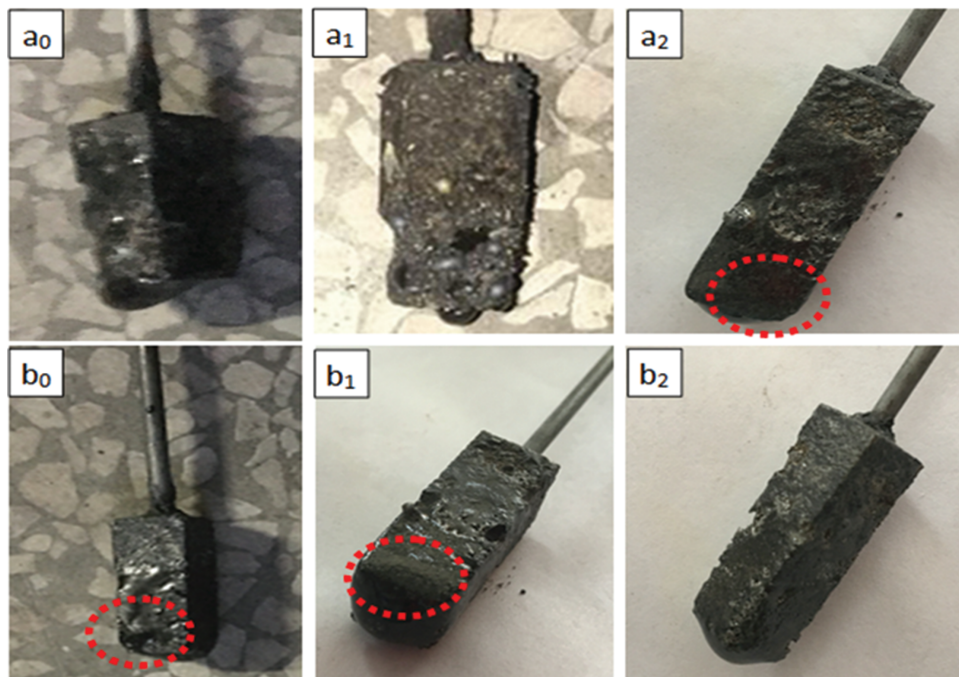


Figure 4: Appearance of MgO–C refractory corroded in different slag components (a–No.1 and b–No.2) (the subscript 0, 1 and 2 represent reference sample, anode and cathode, respectively).

CaO–SiO₂–Al₂O₃–10% MgO slag displayed no obvious appearance damage but an exfoliated edge marked in red circle at the sample bottom (Figure 4(b₀)). Although, the viscosity of slag containing MgO was low, the dissolution of MgO–C refractory was hampered due to the relatively low concentration gradient of MgO between the slag and refractory. Comparing to that corroded in CaO–SiO₂–Al₂O₃ slag, the anode corroded in the slag involving 10% MgO also displayed a less corrosion, indicating that the addition of MgO into the slag was favorite for the corrosion protection of MgO–C refractory, even at an extreme condition (Figure 4(b₁)). Furthermore, the cathode corroded in the slag containing 10% MgO exhibited a complete and regular appearance, suggesting no corrosion happened at the surface (Figure 4(b₂)). Notably, both the reference sample and polarized samples exhibited a good corrosion resistance in the slag involving 10% MgO, indicating that the addition of MgO in molten slag was very beneficial to the corrosion protection of basic refractory materials, such as MgO-base refractories.

SEM-micrographs of the slag/MgO–C interfacial regions in Figure 5 confirmed this impression shown in Figure 4 for the reference and polarized samples. In order to obtain the penetration depth of slag into the refractory, a small amount of ZrO₂ was used as a tracer. An obvious penetration layer approximately 150 to 200 μ m in depth was detected close to the boundary according to the trace of tracer element Zr, indicating that the reference sample was corroded through diffusion dissolution among the boundary layer (Figure 5(a₀)). A recognizable and clean boundary was observed near the sample-slag interface due to the active dissolution of MgO–C refractory in a CaO–SiO₂–Al₂O₃ ternary system

(Figure 5(a₁)). The anode dissolution is accelerated presumably by the change of interfacial tension at the slag-refractory boundary under applied voltage [13]. However, no visible penetration was related to the reference sample immersed in CaO–SiO₂–Al₂O₃–MgO quaternary system (Figure 5(b₀)), in agreement with the relative complete appearance observed in Figure 4(b₀). According to the trace of Zr, the penetration depth of reference sample was about 60 to 100 μ m, which is less than that immersed in CaO–SiO₂–Al₂O₃ system. The appearance of anode immersed in slag containing 10% MgO also exhibited the same phenomenon as that immersed in CaO–SiO₂–Al₂O₃ system (Figure 5(b₁)). A several hundred micron thick deposition layer was observed on the surface of MgO–C cathodes obtained both in CaO–SiO₂–Al₂O₃ ternary system and CaO–SiO₂–Al₂O₃–MgO quaternary system (Figures 5(a₂) and 5(b₂)). Further investigation was performed to identify the solid layer deposited on the MgO–C cathode surface according to the mapping scanning and EDS phase analysis. EDS analysis of the light yellow area shown in Figure 6(a₁) confirmed that the deposition layer consisted of dicalciumsilicate (2CaO.SiO₂, C₂S) (Table 2). The observed layer disintegration during the cooling process is a well-known behavior of dicalciumsilicate (C₂S) caused by temperature-dependent thermal expansion coefficient changed with an associated volume expansion of 12% (Figure 5(a₂)). Additionally, small amounts of silicon metals were also visually identified in the C₂S. A spinel-matrix involving a rather low CaO and SiO₂ content was observed adherent to the cathode surface in CaO–SiO₂–Al₂O₃–MgO quaternary system (Figure 6(b₂)). The spinel has a nominal composition of MgO.Al₂O₃ (Table 2). Still farther out obviously higher amounts of silicon metals were visually determined close to

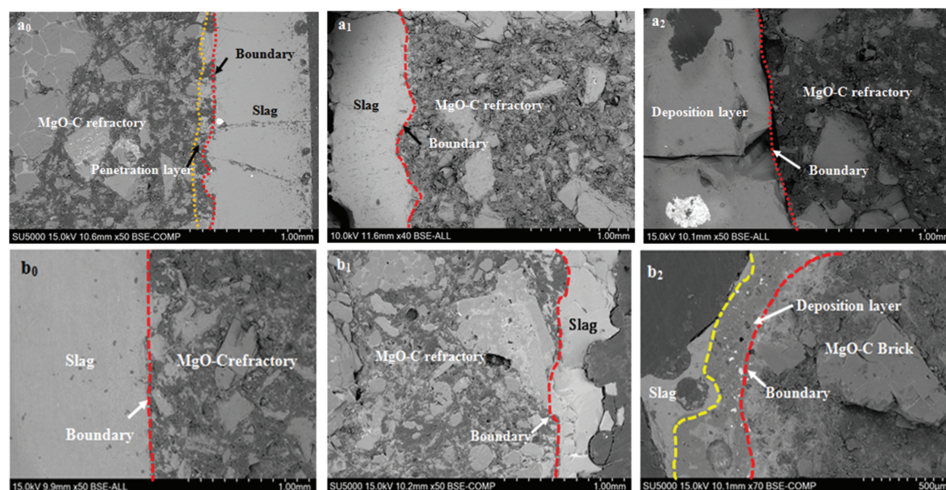


Figure 5: Interfacial structure of MgO–C refractory corroded in different slag components (a–No.1 and b–No.2) (the subscript 0, 1 and 2 represent reference sample, anode and cathode, respectively).

Table 2: Cathodic sediment phase composition of different slag.

Sample No.	Phase	Mass fraction %						Main component
		C	Mg	O	Ca	Si	Al	
1	①	0.8	67.3	37.1	0.5	0.3	—	MgO
	②	—	7.6	25.8	47.3	14.0	5.3	2CaO.SiO ₂
	③	0.5	0.6	12.2	—	84.5	2.1	Si
	④	1.2	12	31.2	27.8	14.6	13.2	Slag
	⑤	1.8	67.4	30.1	—	—	—	MgO
2	⑥	2.7	0.1	4.1	0.3	91.7	0.6	Si
	⑦	5.3	17.0	37.5	1.2	2.3	36.7	MgO.Al ₂ O ₃
	⑧	1.2	6.5	38.0	11.2	22.9	20.2	Slag

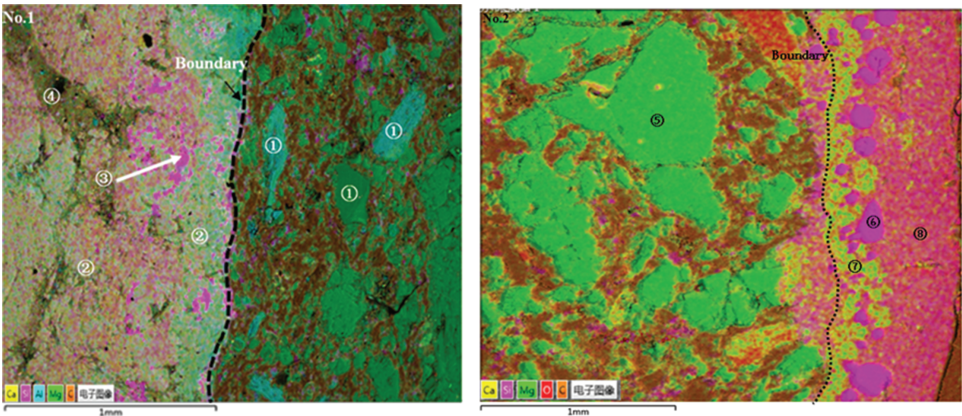


Figure 6: EDS analysis of MgO-C cathode interface produced in different slag for a: CaO-SiO₂-Al₂O₃ slag and b: CaO-SiO₂-Al₂O₃-10% MgO slag.

the sample-slag interface (Figure 6(b₂)). Table 2 exemplarily showed that the gross slag composition in the interfacial region was a bit different from that of the bulk composition, further confirming that the accumulation of Ca²⁺ and Al³⁺ was produced under applied voltage. Because of the uncertainties of EDS-measurements, more evidences should be pursued to confirm the results.

XRD analysis of the reference sample, anode and cathode is displayed in Figure 7. As shown in Figure 7(a), the reference sample was mainly composed of uncorroded MgO, C crystals and some negligible spinel grain, indicating the active dissolution of MgO–C refractory and the inevitable interface reaction between the molten slag and MgO–C refractory. However, a different phenomenon was related to the reference sample corroded

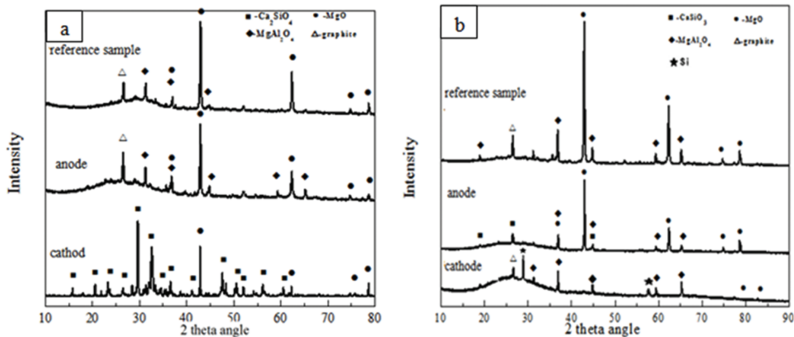
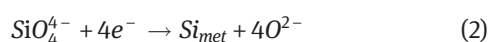


Figure 7: XRD analysis of corroded MgO-C samples in a: CaO-SiO₂-Al₂O₃ slag and b: CaO-SiO₂-Al₂O₃-10%MgO slag.

in the slag containing 10% MgO. In addition to uncorroded MgO-grains, more diffraction peaks of spinel are observed (Figure 7(b)), suggesting that the addition of MgO into slag facilitated the formation of spinel crystals. Compared to the spinel formed under applied voltage (Figure 6(b₂)), the spinel crystals formed here were discrete and were peeled off easily from the surface. Similar phase components were obtained on the anode surface both in CaO–SiO₂–Al₂O₃ slag and CaO–SiO₂–Al₂O₃–MgO slag. Complete C₂S diffraction peaks were detected on the cathode surface immersed in CaO–SiO₂–Al₂O₃ slag, in agreement with the results observed in Figure 5(a₂). Spinel was the main phase close to the cathode interface, along with some Si metals displayed in the brighter part in Figure 5(b₂). These findings further confirmed the positive effect of applied voltage on the cathode by forming a deposition layer, which contributed to the corrosion resistance of MgO–C refractory.

Electrochemical deposition mechanism

As mentioned above, Si metal existed around the cathode range, which was confirmed by the SEM/EDS analysis. The shift of silicate complex-anions under applied voltage was hampered because of their big ions radius, and then they were reduced into Si metal near the cathodes. This could be depicted as eq. (2)



Oxygen ions were also obtained due to the ionic nature at high temperature, and were promoted to shift in the anode direction. Therefore, the supposed anodic reaction was the oxidation of oxygen ions to oxygen and then was consumed by carbon oxidation involved in the MgO–C refractory, which accelerated the damage of anode. The supposed anodic reactions could be expressed as following:



During the reduction of silicate anions to silicon metals, the slag near the cathode was partly deprived of the oxide composition, as displayed in Figure 8. Electrochemical reduction of silicate anions led to a shift of local slag composition towards the dicalciumsilicate (C₂S) or spinel (MA) primary phase field, marked from the dot “a” to dot “b” or from dot “c” to dot “d” through a known back rule

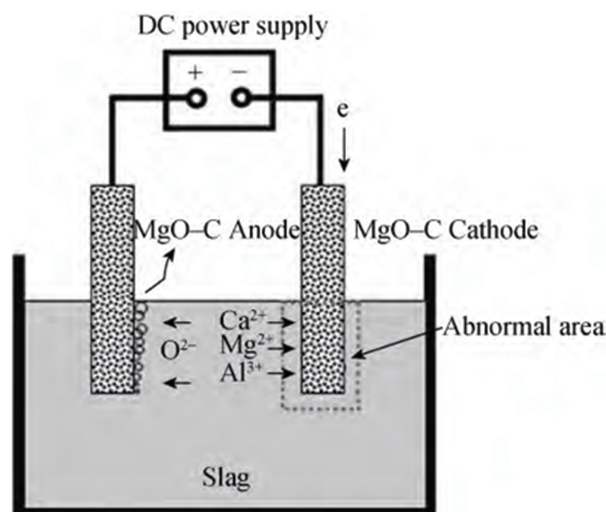


Figure 8: Principle of induced electro-deposition.

in the CaO–SiO₂–Al₂O₃ ternary diagram or CaO–SiO₂–Al₂O₃–10% MgO quaternary diagram conducted using Factsage software at the present experiment temperature (Figures 9(a) and 9(b)). The increasing thickness of deposition layer was related to the on-going reduction of silicate anions. The induced deposition layer on the cathode surface effectively cut off the connection between the slag and MgO–C refractory. It should be noted that the deposition layer attached tightly on the surface of MgO–C refractory and had a higher melting-point than that of slag, which contributed to the corrosion protection of MgO–C refractory. However, the continuous oxidization of C involved in MgO–C refractory could result in a porous nature in the anode, which led to an active dissolution in the anode, in agreement with the discrete appearance exhibited in Figure 4(a₁). On the other hand, because of the electrostatic alteration of the slag/refractory interface, the rapid migration of mobile Ca²⁺ ions and their accumulation at the cathode range could result in a locally increased CaO-content. This action was also beneficial to the formation of dicalciumsilicate (C₂S). Additional, the hampered diffusion of Mg²⁺ ions produced through electrode dissolution into the slag was also to be expected under the applied voltage. Given the natural convection of ions, a voltage of 8 V was required for the immobilization of Mg²⁺ ions at the cathode's edges, quickly resulting in a local MgO-saturation. As the thermodynamic calculations can accurately mirror the experimental findings in Figure 6, Factsage calculations were also carried out in the MgO-saturated slag at 1773 K. First deposition was predicted for a CaO concentration of app. 51 %, gradually increasing the amount of C₂S, along with the reduction of silicate

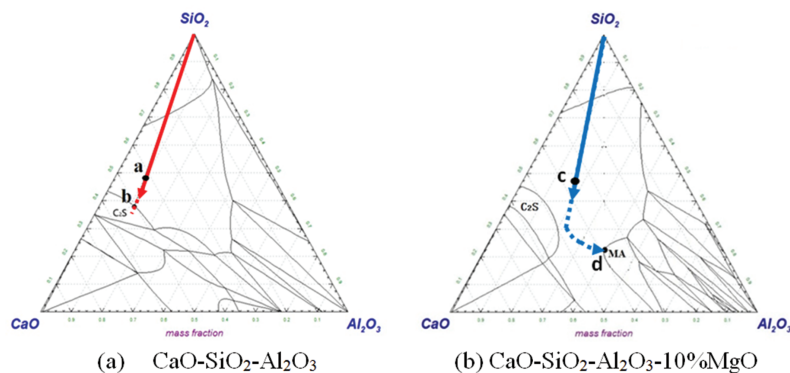


Figure 9: CaO-Al₂O₃-SiO₂-(10% MgO) isothermal phase diagram at 1773K.

anions and accumulation of Ca²⁺ ions around the cathode. Therefore, the phase composition of deposition layer was mainly dependent on the slag composition. If the slag composition deviated the C₂S primary phase field, even the CaO content exceeding up 51%, no expecting deposition layer (C₂S) was observed on the cathode surface. However, a different fact was detected in the slag consisting of 10% MgO, and the deposition layer was composed of spinel even at a low CaO content. The electrochemical process was unclear and further investigation must be proceeded.

Conclusions

In the present work, the induced electro-deposition layer (C₂S or MA) was achieved by cathodic polarization at an applied voltage of 8 V in different slags. The corrosion resistance of cathode was improved because of the deposition layer, whereas the anode degradation was substantially accelerated because of the damaged electrochemical reaction. The applied voltage exerted on not only the reduction of silicate anions, but also the accumulation of Ca²⁺ and Mg²⁺ ions. The reduction of silicate anions could result in a shift of slag composition to the dicalciumsilicate (C₂S) or spinel (MA) primary phase field. Basic cations, such as Ca²⁺ and Mg²⁺, were most susceptible to the applied voltage, and shifted to the cathode, which led to enrichment of CaO or MgO around the cathode range. The saturated MgO and CaO content around the cathode could protect the cathode involved in basic oxides, such as MgO-matrix refractories. Conversely, the anode decay was accelerated due to the oxidation of carbon involved in refractory and the decreased interfacial tension. Therefore, the cathodic

polarization was beneficial to the basic oxide refractory. It also should be noted that the present voltage level (8 V) is acceptable for the economic considerations and the slag composition also needs a careful section for the corrosion protection of MgO-C refractories.

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