Corrosion mechanism and kinetic behaviour of refractory materials in contact with CaO-Al2O3-MgO-SiO2 slags

S. JANSSON, V. BRABIE and L. BOHLIN
The Swedish School of Mining and Metallurgy, Filipstad, Sweden

The rate of dissolution of solid MgO-C and doloma into liquid in CaO-Al2O3-SiO2-MgO slag at different temperatures was studied under conditions of forced convection by rotating cylindrical refractory specimens in a stationary crucible containing the molten slag. The corrosion rate was calculated from the change in diameter of the cylindrical specimens.

Refractory specimens were 13 mm in diameter and 70 mm long. The specimens were rotated for 15 to 120 minutes at speeds of 100 to 400 rpm in the molten slag.

The rate of corrosion increased with temperature and with the rotating speed of the rod, and decreased when the slag was nearly saturated with MgO.

The experimental results confirm the assumption that the diffusion of magnesium oxide through the slag phase boundary layer controls the corrosion process.

The corrosion mechanism seems to be the dissolution of the refractory materials into the slag, followed by penetration of pores and grain boundaries and dispersion of the grains in the slag.

Keywords: MgO-C refractory, doloma refractory, molten slag, corrosion rate, corrosion mechanism

Introduction

The dissolution of solid oxides into molten slag is related to ladle life, slag formation and the absorption of non-metallic inclusions by mould flux in continuous casting. Therefore, the clarification of dissolution behaviour of solid oxides into molten slag is an important problem in refining and casting processes. In recent years, the use of materials composed of more than one refractory component tends to increase for improvement of durability of brick. In order to clarify the dissolution behaviour of such composite materials, it may be necessary to understand the dissolution mechanism and kinetics of each component.

At the same time, numerous experiments have shown that there is clear evidence of interaction between liquid steel and refractory materials that are dependent on both the steel composition and the type of refractory material. However, the reactions that transfer elements between the refractories and molten steel are closely related to the product quality.

A group of doloma and magnesia-carbon refractories is an important material for the lining of ladle furnace. The slagging of doloma and magnesia-carbon refractories should be investigated from the viewpoint of ladle furnace practice.

It is shown in the literature that the active motion of the slag film formed by the wetability between the refractory and slag (since the slag film motion accelerates the dissolution rate of the refractory and also induces the abrasion of some refractories) essentially causes the local corrosion of refractories at the slag surface. The active film motion is primarily induced by the Marangoni effect and/or change in the form of the slag film due to the variation of the surface tension and the density of slag film. The local corrosion of refractories at the slag-metal interface is also reasonably explained by a mechanism, which is similar to that of the refractory-slag system.

Corrosion mechanism

Generally speaking, the corrosion process could be defined as any type of interaction between a solid phase and a fluid phase that results in a deleterious effect to either of the phases. The corrosion process is connected with a so-called slag resistance. The resistance of refractories toward slag is determined first of all by equilibrium relations. It is clear that a slag, which is already saturated with a solid phase, cannot further attack a refractory consisting of that solid phase. During the ladle refining of steel the corrosion of the refractory is a very complex process and depends on many factors. Corrosion of the lining material in contact with slag during ladle refining of steel is usually described in three major categories:

• Dissolution, or diffusion, which is a chemical process by which the refractory material is continuously dissolved
• Penetration, by which the slag penetrates into the refractory and causes mechanical effects
• Erosion, which is the abrasion process of the refractory material exposed to gas and slag movement.

Dissolution of the refractory in liquid slag is usually expressed in terms of dissolution rate, which is the rate at which the thickness of the refractory is depleted. It is known that most of the dissolution process of the solid into liquid is controlled by the mass transfer step and its dissolution rate is expressed by following equation:

\[ \frac{dr}{dt} = A_0 U^b, \]  

where \( A_0 \) is a constant.

The dissolution rate can then be expressed by Equation [2]:

\[ v = k(n - n_0), \]  

where \( v \) is the velocity of the slag film, \( n \) is the density of the refractory, and \( n_0 \) is the density of the slag.
where
\( v \) — rate of dissolution
\( k \) — mass transfer coefficient
\( n, a_0 \) — oxide content of slags at the interface and in the bulk, respectively.

Taking into account the dissolution of a magnesia rotating sample into slag, the mass balance of the oxide may be rewritten as follows:

\[
dr \over dt = \frac{k}{100p} \left( \left( \% MgO \right)_s - \left( MgO \right)_b \rho_s \right) \]

Siebring and Franken\(^1\) described penetration of slag in the refractory wall by using the following Laplace equation:

\[
\Delta P = \frac{2\sigma \cos \Theta \eta}{d_{\text{pore}}} \]

where
\( \Delta P \) — capillary pressure difference (Pa)
\( \sigma_{l-g} \) — surface tension liquid—gas (N/m)
\( \Theta_{l-g} \) — wetting angle slag-refractory (\(^o\))
\( d_{\text{pore}} \) — diameter pore /capillary (m).

From the above relation it is clear that a pressure is needed to fill the pores in the refractory, which depends on the wettability of the refractory by the steel or the slag.

In contrast with the steel, the slag wets the refractory wall very well and penetration will occur. The following relation can express the depth of the horizontal penetration of the slag:

\[
L^2 = {\sigma d \cos \Theta \over 2 \eta} t \]

where
\( L \) — penetration depth (m)
\( \sigma \) — surface tension of liquid slag (N/m)
\( \Theta \) — contact angle between refractory and slag (\(^o\))
\( \eta \) — viscosity of slag (Pa\( \cdot \)s)
\( t \) — time (s).

The viscosity is an important factor that affects the penetration. At the boundary layer, where the slag dissolves some refractory oxide, the viscosity of the slag will increases and further attack by the slag is then possible only by diffusion through the viscous slag layer at the interface. As the result, such refractories are fairly resistant even toward slag, which is not completely saturated with the refractory oxides.

At the same time it is seen from the relation that slag resistance is also affected by the refractory porosity. A porous refractory is easily corroded by the slag, which soaks into the pores, whereas a dense single-phase refractory dissolves only slowly. The binding matrix is more rapidly attacked than the solid grains, causing them to become loose and dispersed in the slag without actually dissolving.

It must be observed that two refractory materials with high melting points may form a low melting-point slag at contact.

When the vertical penetration is analysed the following equation is recommended by Wanibe et al.\(^3\).

\[
L = \frac{2\sigma \cos \Theta}{R \rho g} \]

where
\( R \) — pore radius (m)
\( \rho \) — the slag density (kg/m\(^3\))
\( g \) — gravitational constant (ms\(^2\))

The above equations shows that penetration decreases with decreasing surface tension, increasing viscosity and contact angle when \( \Theta > 90^o \).

Slag penetration into the pores can cause deterioration of the refractory wall by the following mechanisms:

- Dissolving the refractory material into the slag and changing the slag properties
- Differential expansion or contraction between refractory and the slag, causing stresses and cracks into the lining
- Considering the statistical scatter in the material properties after slag penetration, the depth of the spalling can be taken to be the same as the depth of slag penetration, \( D_s \).

The depth of the slag penetration depends on many factors and for a given refractory-slag system slag penetration will occur only when the temperature reaches a critical value, \( T_c \), when the slag will not be able to flow.

According to the above criteria the penetration will occur when the temperature is higher or equal to \( T_c \). As the viscosity increases when the solid particles are precipitated, we can expect that slag penetration will cease when the wall temperature falls below the solidification temperature of the slag.

Erosion of the refractory material in contact with the slag depends on the abrasion, which is determined by the high-velocity slag and gases. It is accepted that the erosion effects are not so high when alumina or magnesia linings are used.

In conclusion it can be said that the corrosion rate increases as the temperature increases. The corrosion rate is typically higher for a polycrystalline ceramic than for a single crystal, due to grain boundary effects. The corrosion rate is lower for a natural convection than for a forced one and for cases where either the melt is flowing or the ceramics is moving.

A post-mortem investigation of refractory bricks from a ladle furnace has been done where it is described how the slag basicity affects the slag attack on magnesia refractory material\(^5\). It is shown that if the slag basicity increases the slag attack on magnesia refractory decreases. On the other hand, in the case of chrome-magnesia refractory, the slag attack on the refractory increases when the slag basicity increases. The difference between magnesia and chrome-magnesia refractories can be explained by the fact that a slag with low basicity forms silicates, like merwinit and monticellit, which dissolves MgO in the magnesia refractory. At higher slag basicity the CaO in the slag more quickly attacks spinel- and MgO-chromite bindings in a chrome-magnesia refractory than MgO-MgO bindings in a magnesia refractory.

The investigation shows that it becomes a larger slag attack on the tar-impregnated magnesia refractory than the magnesia refractory alone. The experiment shows that in the tar impregnated magnesia, carbon monoxide is formed at 2–3 mm from the interface. This CO passes (completely or partly) through the slag-infiltrated zone, and practically there a pressure on the periclase grain in such a direction, that these grains can be transported to the slag undisolved. When the gas is in contact with the slag and rises to the surface, a stirring effect occurs and the erosion on the refractory material increases.

Li et al.\(^6\) have investigated the formation of CO bubbles and their effect on MgO-C refractory with consideration on
corrosion mechanisms. As a result of different MgO and graphite wettability by the slag and metal phase, the metal creeping up and formation of slag film is a cyclic process that results in the progress of the local corrosion of MgO-C refractory.

Gas bubbles form mainly according to the reaction between (FeO) in slag film and C(\(_{\text{s}}\)) in the refractory:

\[
(\text{FeO}) + C(\text{s}) = Fe(\text{I}) + CO(\text{g})
\]  

[7]

The local corrosion rate is greatly influenced by the generation position and the number of bubbles generated. Bubbles formed in the tree-phase boundary restrain the local corrosion, while the ones generated at the refractory-metal interface enhance the local corrosion.

Based on the analysis made on the BOF process, Carniglia\(^7\) established that:

• The MgO-C reaction is a minor but significant contributor to the observed brick wear. It probably proceeds at a considerably slower rate and in much narrower zone than might be inferred from laboratory tests on small specimens under isothermal heating.

• Wear rates increase with increasing temperatures of operation, and decreasing \(P_{\text{CO}}\) in the refractory.

• Brick damage by internal oxidation-reduction reactions apparently does not extend greatly behind the carbon boundary, principally because of the large change in equilibrium product gas pressure with \(\Delta T\) and the relatively large temperature gradient presumed to exist behind the hot face during each heat. Impedance to diffusional flow of gases and gradual recession of the hot face also contribute to the pattern of reaction and transport.

Le Coq et al.\(^8\) studied the corrosion of dolomite-carbon refractories. According to their results the main corrosion mechanism seems to consist in the reaction between slag and lime, producing calcium aluminates and calcium silicates, followed by the infiltration of the refractory and the dispersion of periclase grains in the slag.

Riaz et al.\(^9\) describe in their report how a glaze layer forms at the surface on MgO+C refractories and four distinct layers are observed at the interface:

• An outer layer (0–1 mm thick) which is relatively homogeneous

• A two-phase slag infiltrated layer

• A decarburized refractory layer

• A normal refractory brick structure.

The compositions of the infiltrated slag layer were reasonably constant, suggesting that the steel-making process determines them.

Fruehan et al.\(^10\) studied dissolution of magnesia and doloma refractory in EAF slags. They concluded that the rate of dissolution of magnesia appears to be controlled by the liquid mass transfer. The rate of dissolution of doloma refractory seems to be slightly faster than that of magnesia.

**Experimental method**

Figure 1 schematically illustrates the experimental apparatus used to investigate the reaction between the refractory material and molten slag. The crucibles used for the experiments were made of graphite, 50 mm OD x 35 mm ID x 70 mm depth.

The MgO-C test rods were cut from a commercial brick. The test rods of doloma and magnesia/doloma were sintered samples. Table I shows the chemical composition of the test rods.

The synthetic slag was mixed in a tumbler for 24 hours and its chemical composition is shown in Table II.

The graphite crucible containing 60 g of the synthetic slag was placed into the furnace and heated up to the test temperatures (1773 K–1923 K).

When the melt temperature reached the desired level, the test rod was immersed into the slag melt and rotated with 100–400 rpm with a holding time of 15–120 min. The furnace was flushed with 2 l/min. of argon gas during the tests.

The change in the diameter of the refractory rods (\(\Delta d = d_0 - d_t\)), where \(d_0\) is the initial diameter of the refractory rod and \(d_t\), the diameter at time (t), was measured by microscopic analysis, where the error was estimated to be ±0.05 mm.

Roentgen Fluorescence Spectrometry (XRF) was used to analyse the slag, and Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrometer (EDS) for the test rods.

**Results**

The temperature and immersion times of the refractory rods are shown in Table III.

![Figure 1. Experimental apparatus](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO</th>
<th>CaO</th>
<th>SiO(_2)</th>
<th>FeO(_3)</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesia</td>
<td>96.8</td>
<td>1.8</td>
<td>0.6</td>
<td>0.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Doloma</td>
<td>38</td>
<td>59</td>
<td>1.1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Magnesia/doloma</td>
<td>62</td>
<td>36</td>
<td>0.8</td>
<td>0.8</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table II**

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>33</td>
<td>11</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>53.2</td>
<td>31.35</td>
<td>10.45</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>51.52</td>
<td>30.36</td>
<td>10.12</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
In order to verify the consistency of the experimental method some experiments were repeated at 1873 K. The results are in good agreement within the limits of the experimental errors for different experiments.

The change of the rod diameter as a function of time for different refractory materials is shown in Figure 2.

It can be observed that a linear dependency exists for all three refractory materials and that the dolomite is mostly affected compared with the magnesia+carbon, which implies a very low corrosion rate.

The effect of the rotation speed on corrosion rate was examined by using a free MgO slag. The rate of rotation was from 100 to 400 rpm at a temperature of 1873 K. The results obtained are shown in Figure 3.

The increasing of rotation speed from 200 to 400 rpm affects much more doloma compared with doloma/magnesia or magnesia+carbon refractory materials. The magnesia+carbon seems to be very little affected by increasing of the rotation speed and this is in accordance with the results reported by Bygden11, but in contradiction with the earlier studies on the kinetics of refractory materials' corrosion.

The decrease of the dissolution rate with the increasing of MgO content in the slag is shown in Figure 4 and Figure 5. The low corrosion rate into slag with 8% MgO can be attributed to the lower driving force for the dissolution of magnesia and the large slag viscosity.

In order to study how deep the penetrated zone was at the sample, the test rods were moulded in epoxy and later examined in SEM/EDS (Figures 6 and 7). The mapping shows that the slag penetrates the refractory material through pores and cracks. There were also cavities at the surface on the rods, where entire refractory grains had come loose by corrosion. On the test rod surfaces a glazy layer was also observed.

In Figure 6 it can be observed that a thin glazy layer has formed on the surface of the sample when a doloma/magnesia rod is rotated for 30 min at 1873 K with 200 rpm and 8% MgO content in the slag. It can also be observed that the slag has infiltrated the pores of the refractory. The concentration of Al and Si in the infiltrated zone is not as high as it is in the glazy layer at the surface. This indicates that a reaction has occurred between the slag and the refractory material.

Figure 7 shows the same observation when MgO-C rods are used. Here the slag has formed a thin glazy layer at the surface of the sample in the same way as in Figure 6, but the infiltration depth is less than in the case of the doloma/magnesia rods.

**Discussion**

The wear mechanism of different refractory materials by slag is a complex phenomenon. Our experimental results indicate that apart from the chemical attack of the slag on the refractory material, penetration of the slag causes serious direct loss of the refractories.

**The effect of temperature on the dissolution rate**

The effect of temperature on the dissolution rate was investigated on magnesia-carbon rods in contact with free MgO slag at 200 rpm. By using the data from Table IV the mass transfer coefficients shown in the table were calculated by using Equation [3].

Figure 8 shows the effect of temperature on the mass transfer coefficients. The apparent activation energy was calculated from the slope to be 328 kJ/mol, which is in quite good agreement with the values reported in the literature.

It must be observed that the mass transfer coefficients calculated in this paper are lower compared to those reported by Umakoshi *et al*.12 when they used MgO cylinder with 26–36 % porosity. The explanation could be found in the presence of the graphite in the present studies. Mass transfer coefficients calculated for doloma rods are nearly 10 times higher compared to the MgO-C rods.

<table>
<thead>
<tr>
<th>Refractory material</th>
<th>MgO-addition in slag, mass %</th>
<th>Temperature K</th>
<th>Immersion time min</th>
<th>Rotation speed rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dol, Dol/Mag, MgO+C</td>
<td>0–5–8</td>
<td>1773–1823–1873–1923</td>
<td>15–30–60–120</td>
<td>100–200–400</td>
</tr>
</tbody>
</table>

Table III

Test parameters
Effect of the revolution speed on the dissolution rate
It is evident from Figure 3 that the dissolution rates of refractory materials depend upon the rotation rates. This fact shows that the dissolution rate is controlled by the mass transport of solute in the molten slag around the refractory rods. At the same time the results indicate that rotation rates affect much more doloma and doloma/magnesia materials compared to the magnesia-carbon.

Figure 9 shows the linear relationship between log V and log U for the materials used in the present experiments. According to Equation [1] and Figure 9 the lines can be expressed by the following equations:

For doloma - \( \frac{dR}{dt} = A_0 U^{0.69} \)
For magnesia/doloma - \( \frac{dR}{dt} = A_0 U^{0.625} \)
For MgO-C - \( \frac{dR}{dt} = A_0 U^{0.59} \)

where \( A_0 \) is constant.

The above results are in good agreement with the results reported by Matsushima et al.\(^2\) and support the considerations that the dissolution of the refractory materials into the molten slag is a diffusion-controlled process.

The effect of slag composition on the dissolution rate
The effect of MgO content in the slag on the dissolution rate of different refractory materials was investigated by changing the MgO content of molten slag (Table II). It is observed from Figures 4 and 5 that the diameter of the samples decreases with an increase of MgO content of slag. The results show that if the reaction products are soluble or dissociate in the molten slag, the active corrosion may continue to the destruction of the refractory. Increasing of the MgO content into the molten slag determines a decreasing of the solubility of it into the molten slag and as a result it may form an impenetrable barrier so that, after its formation, Figures 6 and 7, further attack is prevented. Now the rate determining steps are the chemical reaction forming the layer, diffusion through the layer, or diffusion through the slag.

Penetration of slag into the refractory material rod
According to Cooper\(^3\) the corrosion of oxides often occurs not by dissolution or evaporation of the oxide, but by the penetration of the solid by some or all the species from the fluid. The liquid phase may be pulled into the open porosity of the solid by capillary forces, and species from the fluid will diffuse both down the grain boundaries and into the bulk of the solid.

This process can cause deterioration of the refractory materials by:
- Completely encasing solid particles by the molten slag
- Causing either an expansion or contraction of solids
- Diffusion of a slag species into the refractory material causing the change in the physical properties.
SEM investigations of some doloma samples confirm the presence of magnesium oxide grains isolated in the slag, Figure 10. This implies the possibility that the mechanical separation of some magnesia particles occurs simultaneously with the dissolution reaction and penetration of the slag. Cooper\cite{13} concluded that for a saturated slag the penetration distance into the refractory material could be greater than in the same system when the solid dissolves in a stagnant fluid. This is in contradiction to our experimental results and to the earlier studies on the corrosion of refractory. Figures 4 and 5 confirm the decreasing of the corrosion rates with the increasing of the MgO content in the slag. At 8% MgO, the slag is assumed to be MgO saturated at 1873 K. The higher wetting angle makes it more difficult for the
slag to penetrate pores and cracks in the refractory. The difference in infiltration on carbon bonded refractory material and non-carbon bonded, is 10 times bigger.

The infiltration of slag on refractory without carbon happens very quickly. It is no doubt that the refractory sucks the slag into the pores with the help of the capillary force. The impact of porosity on the penetration appears to be very important.

This is not the only thing that affects the infiltrating depth. The infiltrating depth is also affected by the temperature gradient in the brick. When the temperature decreases the viscosity increases and the infiltration depth decreases.

The refractory samples used in the present investigation had a homogeneous temperature through the whole rod. The doloma rods were totally infiltrated, while the MgO+C rods show very little infiltration. To explain the above differences, the graphite effect on the infiltration phenomena should be taken into account.

Conclusions
The laboratory experiments and theoretical analysis of the present study show that the corrosion rate of MgO-C and doloma refractory materials increased with rotation speed and temperature and was in linear dependence with time.

The calculation of activation energy of the dissolving process supports the assumption that the mass transfer step through the slag boundary layer is the rate-determining step.

The corrosion rates into free MgO slags were greater than those into slags nearly saturated with MgO.

The corrosion mechanism seems to be the dissolution of the refractory materials into the slag, followed by penetration of the grain boundaries and dispersion of the grains in the slag.

Acknowledgments
The authors wishes to thank the Swedish Ironmaster’s Association (Jernkontoret) and the State Energy Authority (STEM) for financial support of this project.

References

<table>
<thead>
<tr>
<th>Type of refractory</th>
<th>Temp K</th>
<th>Rot. speed rpm</th>
<th>-dr/dt cm/sec</th>
<th>k cm/sec</th>
<th>Δ(% MgO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO+C</td>
<td>1773</td>
<td>200</td>
<td>1.53 x 10^-6</td>
<td>2.12 x 10^-5</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>1823</td>
<td>100</td>
<td>1.23 x 10^-6</td>
<td>1.70 x 10^-5</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>2.01 x 10^-6</td>
<td>3.79 x 10^-5</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>3.10 x 10^-6</td>
<td>4.29 x 10^-5</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>1873</td>
<td>100</td>
<td>3.01 x 10^-6</td>
<td>4.17 x 10^-5</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>5.97 x 10^-6</td>
<td>8.26 x 10^-5</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>8.53 x 10^-6</td>
<td>1.18 x 10^-4</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>1923</td>
<td>200</td>
<td>8.06 x 10^-6</td>
<td>1.12 x 10^-4</td>
<td>8.2</td>
</tr>
<tr>
<td>Doloma</td>
<td>1823</td>
<td>100</td>
<td>2.34 x 10^-6</td>
<td>9.49 x 10^-5</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>4.21 x 10^-6</td>
<td>1.71 x 10^-4</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>6.46 x 10^-6</td>
<td>2.62 x 10^-4</td>
<td>2.8</td>
</tr>
<tr>
<td>Dol/Mag</td>
<td>1873</td>
<td>100</td>
<td>3.06 x 10^-5</td>
<td>1.71 x 10^-4</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>4.55 x 10^-5</td>
<td>2.54 x 10^-4</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>7.57 x 10^-5</td>
<td>4.23 x 10^-4</td>
<td>8.2</td>
</tr>
</tbody>
</table>