A Study on Molten Steel/Slag/Refractory Reactions during Ladle Steel Refining

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ABSTRACT

During the production of steel the degree of oxide inclusions partly depends on the reaction of the melt with the furnace lining, the ladle lining and the pouring system. The refractory material may be eroded by the molten steel and slag as well as corroded through chemical reactions with the slag and molten steel and the deoxidation products.

In this report the effects of revolution speed, temperature and steel composition on the rate of dissolution of MgO-C refractory samples into Al-deoxidised molten steel and CaO-Al2O3-SiO2-MgO slag were examined by the rotating cylinder method. The steel was deoxidised by adding metallic aluminium. Cylinders of MgO-C refractory material were immersed in Al-deoxidised molten steel in the range of 1600 to 1700°C and were rotated at 100 to 800 rpm during different times.

The experimental results show that the rate of dissolution of MgO-C refractory materials increased with the temperature, rotating speed of the cylinder and immersion time. This supports the assumption that the diffusion of magnesium through the slag boundary layer formed around the refractory samples would be the rate-determining step. Mass transfer coefficients calculated on the basis of experimental results are in good agreement with earlier published results.

The formation of a thin oxide layer at the interface is due the reaction between magnesium vapour and the CO generated by the reaction MgO and C in the refractory walls. The oxide inclusions formed in the steel have been shown mainly to consist of MgO, Al2O3 and a mixture of them.

The rate of dissolution of solid MgO-C into liquid 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. The specimens were rotated for 15 to 120 minutes at speed of 100 to 400 rpm in the molten slag.

The rate of corrosion increased with temperature and with 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 elements in the refractory materials into the slag, followed by penetration into the pores and grain boundaries. Finally, grains are loosened from the refractory into the slag.

Key words: reoxidation, aluminium killed steel, inclusions, refractory, molten slag, corrosion rate, corrosion mechanism.
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Arvika, May 2005

Sune Jansson
SUPPLEMENTS

The present thesis is based on the following papers:

**Supplement 1:** “A laboratory study of dissolution of magnesia refractory in Al-killed low-carbon steel melts”
*S. Jansson, V. Brabie and P. Jönsson.*

*Submitted for publication: Iron. & Steelmaking, May 2005.*

**Supplement 2:** “Corrosion mechanism and kinetic behaviour of MgO-C refractory material in contact with CaO-Al2O3-SiO2-MgO slag”
* S. Jansson, V. Brabie and P. Jönsson.*

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1. 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 the 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 the 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 [1-5] have shown that there is a clear evidence of interaction between liquid steel and refractory materials which is dependent on both the steel composition and the type of refractory material. Therefore, the reactions that transfer elements between the refractories and molten steel are closely related to the product quality.

It is well known that non-metallic inclusions could form inside the steel or is descended from external sources like refractory bricks, slag or alloying materials. Theirs composition and size are directly depended of steel, slag or ceramic materials compositions. When the molten steel is treated in a ladle, the reaction between steel and the refractory lining have a great influence on the steel purity.

Many steel plants use MgO-C refractories with a content of C between 5 and 20 wt-% as ladle refractory lining nearest the molten steel. The function of the carbon is to fill out the porous structure and to avoid the slag to penetrate. One explanation to this is that the wetting angle between slag and graphite is big and that a dense layer of MgO and CO is formed which works against the slag penetration.

The research of the reaction between molten steel and refractory material is presented in supplement 1, and the research of reaction between molten slag and refractory material is presented in supplement 2.

2. THEORETICAL BACKGROUND

2.1. Thermodynamics and thermo physical phenomena

Thermodynamic assumptions and the experimental results show that magnesium gas should be formed when the steel is treated in the ladle where the refractory material consists of MgO+C bricks [1]. This magnesium is a potential source of MgO containing inclusions.

Earlier investigations [1-4] that are done on MgO-C refractory materials describe the reduction of MgO by carbon according to the following reaction:
\[
\text{MgO}(s) + C(s) = \text{Mg}(g) + \text{CO}(g) \tag{1}
\]

\[
\Delta G^0 = 624032 - 295.95 \ T \tag{2}
\]

where \(T\) is the temperature in K.

The reduction of MgO with C appears at higher temperature than the temperature that is used for steel making, but if the partial pressure for magnesium gas and carbon monoxide decreases it can occur at lower temperature. Thus, reaction [1] may occur during the vacuum degassing in the ladle.

**Figure 1** shows the free energy for formation of MgO and CO\(_{(g)}\) as a function of temperature and partial pressure. The abrupt change in the line \(2 \text{Mg} + \text{O}_2 = 2 \text{MgO}\) occurs at the boiling point of magnesium metal. The recorded free energy of formation above this temperature is calculated on the basis of metal vapour at 0.1013 MPa. The other three lines in the magnesia group show the stability of MgO as a function of temperature when the partial pressure of magnesium metal is reduced. The corresponding series of CO\(_{(g)}\) stability relates to various partial pressures of CO\(_{(g)}\) as indicated. By using the data from figure 1, it is easy to predict various partial pressures and temperatures at which the reduction of MgO by carbon will be thermodynamically feasible.

**Figure 1.** Equilibrium relations for carbon monoxide and magnesium \(^[2]\).

Watanabe, Takahashi and Nakatani \(^[3]\) suggest that a dense layer of MgO\(_{(s)}\) forms on the surface of the brick, which has contact with the molten steel. This comes from the magnesium gas that diffuses through pores and reacts with the oxygen in the steel and forms the MgO-layer. The MgO-layer on the surface prevents the molten slag and steel to react with the refractory through pores and cracks. Dissolving of MgO\(_{(s)}\) to the steel can result in formation of inclusions, which is not desirable in production of very clean steel.
Carbon monoxide gas that is formed when the magnesia is reduced to Mg, reacts with dissolved aluminium in the steel and forms aluminium oxide. Together with MgO they can form spinel according to the following reactions:

\[ 2 \text{[Al]} + 3 \text{CO}(g) = \text{Al}_2\text{O}_3(s) + 3 \text{[C]} \]  
\[ \text{[Mg]} + \text{CO}(g) = \text{MgO}(s) + \text{[C]} \]  
\[ \text{Al}_2\text{O}_3(s) + \text{MgO}(s) = \text{MgO} \cdot \text{Al}_2\text{O}_3(s) \]

The overall reaction involves the following steps:

- Diffusion of CO\(_{(g)}\) to the boundary layer
- Chemical reaction of CO\(_{(g)}\) at the interface
- Diffusion of dissolved C and O to the bulk and the growth of the oxide at the interface

According to Lee and Zhang \[^{[5]}\] the motion of the slag film caused by surface tension phenomena (wettability) between the refractory and slag essentially causes the local corrosion of refractories at the slag surface, see figure 2. This is because the slag film motion accelerates the dissolution rate of the refractory and also induces the abrasion of some refractories.

![Figure 2. Illustration of the motion of the slag film caused by the surface tension phenomena between the refractory and slag \[^{[5]}\].](image)

The active film motion is dominantly induced by the Marangoni effect \[^{[6-7]}\] 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 explained reasonably by a mechanism, which is similar to that of the refractory/slag system, see figure 3.
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, can not 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, which is dependent on many factors. Some of the factors are depended on reaction kinetics.

2.2. Kinetic reactions

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

These three types of corrosion will be discussed with consideration to the research.

**Dissolution** of the refractory in liquid slag is usually expressed in terms of a dissolution rate, which is the rate at which the thickness of the refractory is depleted. It is known that mass transfer is the dominant rate controlling step in the dissolution processes of solids into liquids, and that the dissolution rate could be expressed by the following type of equation \[^{[8]}\] performing to the experiments in this work:

\[
-\frac{dr}{dt} = A_s U^b, \tag{6}
\]
where \( r \) is the radius of the rotating cylinder, \( t \) is the time, \( A_o \) is a specific constant for different conditions, \( U \) is the periphery velocity of the rotating cylinder and \( b \) is a constant. The dissolution rate can then be expressed by equation [7]:

\[
v = k(n_s - n_b) \tag{7}
\]

where \( v \) is the rate of dissolution, \( k \) is the mass transfer coefficient, \( n_s, n_b \) is concentration content in steel/slag at the interface and in the bulk, respectively.

A common way to simulate the dissolution of solid material into liquid when the liquid is stirred is to rotate the solid sample in the liquid. Taking into account the dissolution of a magnesia rotating sample into steel or slag, the mass balance of the oxide may be rewritten as follows, equation [8] and [9]:

\[
-\frac{dr}{dt} = \frac{k}{100 \rho} \langle (%Mg)_s \rho_s - (Mg)_b \rho_b \rangle \tag{8}
\]

\[
-\frac{dr}{dt} = \frac{k}{100 \rho} \langle (%MgO)_s \rho_s - (MgO)_b \rho_b \rangle \tag{9}
\]

Generally speaking the dissolution of the refractory into the slag at the interface is governed by the following mechanism, see also figure 4:

- Chemical reaction at the interface
- Transport of reacting species through the liquid slag

In figure 4 you can see that the slag has attacked the refractory and penetrated into the refractory, and at the same time the dissolution of refractory material into the slag has continued. After a while, \( t = t_2 \), the penetration of the slag has reach deeper into the refractory material and the boundary layer has diffused/eroded into the slag.
Figure 4. Illustration of dissolution of refractory into slag at the interface \([5]\).

Siebring and Franken \([9]\) described penetration of slag in the refractory wall by using the following equation:

\[
\Delta P = \frac{4\gamma_{l-g} \cos \theta}{d_{\text{pore}}} \tag{10}
\]

where \(\Delta P\) is the capillary pressure difference (Pa), \(\gamma_{l-g}\) is the surface tension liquid–gas (N/m), \(\theta\) is the wetting angle slag-refractory (°) and \(d_{\text{pore}}\) is the diameter of pore/capillary (m).

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

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

\[
L = \sqrt{\frac{\gamma d_{\text{pore}} \cos \theta}{2\eta t}} \tag{11}
\]

where \(L\) is the penetration depth (m), \(\gamma\) is the surface tension of liquid slag (N/m), \(d_{\text{pore}}\) is the pore diameter (m), \(\theta\) is the contact angle between refractory and slag (°), \(\eta\) is the viscosity of slag (Pa.s) and \(t\) is the 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 increase and the further attack by the slag is then only possible by diffusion through a viscous slag layer at the interface.

At the same time, it is seen from the equation [11] that slag resistance is also affected by the refractory porosity. A porous refractory is more easily corroded by the slag, which soaks into the pores, whereas a dense single phase refractory is only slowly dissolving. The binding matrix is more rapidly attacked than the solid grains causing them to become loose and dispersed in the slag without actually dissolving, see figure 5.

![Figure 5. Illustration of binding matrix, solid grains and porosity](image)

It should be noted that two refractory materials with high melting points may form a low melting-point slag on contact. For example, Al₂O₃ has a melting point at 2326 K and CaO has a melting point at 3172 K, and a specific mix of them (~50/50) has a melting point at 1686 K [10].

When the vertical penetration is analysed the following equation is recommended by Riaz et al. [11].

\[
L = \frac{2\gamma \cos \theta}{R \rho g}
\]

where \( R \) is the pore radius (m), \( \rho \) is the slag density (kg/m³) and \( g \) is the gravitational constant (m/s²).

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

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

- Dissolving of the refractory material into the slag which changing the slag properties
- Differential expansion or contraction between refractory and the slag causing stresses and cracks in the lining
- Spalling, which can be taken to be the same as the depth of slag penetration, \( D_p \) [12]
Erosion of the refractory material in contact with the slag is dependent on the abrasion, which is determined by the high-velocity slag and gases. It is common opinion that the erosion effects are not so high when alumina or magnesia linings are used. As a conclusion, 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 convection where either the melt is flowing or the ceramics is moving.

3. EXPERIMENTAL WORK

In order to experimentally study the corrosion mechanism and kinetic behaviour of refractory materials in contact with molten steel or molten slag, laboratory trials were conducted.

3.1. Materials

The chemical composition of the refractory material that was used in the experiment is shown in table 1.

Table 1. Chemical composition of the refractory test rod, wt-%.

<table>
<thead>
<tr>
<th>MgO</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.8</td>
<td>1.8</td>
<td>0.6</td>
<td>0.3</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The test rods were cut from a commercial brick and had a diameter of 13 mm and a length of 70 mm. The density of the refractory material was 3.1 g/cm³ and the porosity was 5%.

The steel has the chemical composition that is shown in table 2.

Table 2. Chemical composition of the steel, wt-%.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>0.01</td>
<td>0.08</td>
<td>0.004</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

The steel was deoxidised by 0.1 or 0.01 wt-% aluminium.

The chemical compositions of the slags are shown in table 3.

Table 3. Chemical composition of the slags, wt-%.

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>CaO/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>56</td>
<td>11</td>
<td>33</td>
<td>0</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>53</td>
<td>11</td>
<td>31</td>
<td>5</td>
<td>4.8</td>
</tr>
<tr>
<td>3</td>
<td>52</td>
<td>10</td>
<td>30</td>
<td>8</td>
<td>5.2</td>
</tr>
</tbody>
</table>
The synthetic slags were mixed in a tumbler for 24 hours before the experiments, to making it homogenous. In the steel experiments alumina crucibles were used (50 mm OD x 44 mm ID x 75 mm depth), and in the slag experiments graphite crucibles were used (50 mm OD x 35 mm ID x 70 mm depth).

### 3.2. Experimental set-up

The experimental furnace used in this study is schematically illustrated in figure 6.

![Figure 6. Schematic drawing of the experimental furnace.](image)

The furnace is a high temperature furnace with a graphite resistance-heating element, supplied by Thermal Technology Inc. The crucible containing pure iron (300 g) or synthetic slag (60 g) was placed into the furnace and heated to the test temperatures. When the melt temperature reached the desirable level, the test rod was immersed into the melt and rotated with different rotation speeds at different holding times. Note, that the rod was rotated in order to simulate the effect of stirring in the ladle. More specifically, the stirring will lead to velocities along the refractory which will affect the refractory wear. Before the test rods were immersed
into the steel, the steel was killed with an addition of 0.1 or 0.01 wt-% metallic aluminium. The furnace was flushed with 2 l/min of argon gas during all the tests. Traces of moisture, CO₂ and oxygen in the commercial Ar gas (supplied by Air Liquid, 99.9997 % pure) were removed by passing the gas through a gas cleaning system. A schematic diagram of the system is presented in figure 7.

![Schematic diagram of the gas cleaning system](image)

**Figure 7. Schematic picture of gas cleaning system used in the experiments.**

The moisture in the gas was removed by passing the gas through columns of silica gel as well as Mg(ClO₄)₂. The CO₂ was absorbed by ascarite and traces of oxygen were removed by passing the gas through magnesium chips at 773 K.

After the experimental runs, the change in the diameter of the refractory rods, \( \Delta d = d_0 - d_t \), where \( d_0 \) is the initial diameter of the rod and \( d_t \) the diameter at time (t), was measured. The error was estimated to be ± 0.02 mm. The chemical composition of steel was determined using an Optical Emission Spectrometer (OES), and X-ray Roentgen Fluorescence Spectrometry (XRF) was used for the slag. In addition, the test rods were analysed in a Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrometer (EDS). The inclusions found in the steel samples were also examined by SEM/EDS. Diameters of the rod samples were measured, than the samples were moulded in epoxy and the cross section examined in microscope.
4. RESULTS

4.1. Experiments with molten steel

The temperature, immersion time, rotation speed and Al-addition in the steel are shown in table 4.

<table>
<thead>
<tr>
<th>Al-addition in steel, wt-%</th>
<th>Temperature K</th>
<th>Immersion time min</th>
<th>Rotation speed rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1; 0.01</td>
<td>1873; 1923; 1973</td>
<td>60; 120; 180; 240</td>
<td>0; 100; 400; 800</td>
</tr>
</tbody>
</table>

There was a thin oxide layer formed at the surface of the rods when the refractory rods were immersed into molten steel. The growth of the oxide layer seems to be increasing exponential with the holding time and the rotation speed at 1873 K, see figure 8.

The thin oxide layer was examined in SEM/EDS and the layer was found to consist of Mg, Al, and Ca oxides and also CaS, see figure 9. There were also small particles of Fe in the layer.

Figure 8. Growth of oxide layer at different holding times and rotation speeds, 1873 K, 0.1 % Al-addition.
The oxide layer was easily removed from the test rods so measurements of the radius of the MgO-C rods could be done. This results shows that the decrease of the radius is linear to the holding time and the rotation speed. In figure 10 the decrease of the rod diameter at different holding times and different rotation speeds is shown.

![Figure 9. X-ray images for C, O, Mg, Al, S, Ca and Fe and SEM micrograph of the oxide layer at the MgO-C/steel interface.](image)

![Figure 10. Decreasing of the test rods diameter in different times and different rotations speed, 1873 K, 0.1% Al.](image)

### 4.2. Experiments with molten slags

The temperature, immersion time, rotation speed and MgO-addition in slag are shown in table 5.

<table>
<thead>
<tr>
<th>MgO-addition in slag, wt-%</th>
<th>Temperature K</th>
<th>Immersion time min</th>
<th>Rotation speed rpm</th>
</tr>
</thead>
<tbody>
<tr>
<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 5. Test parameters for the slag experiments.*
The change of the rod diameter as a function of time is shown in figure 11 and 12. It can be observed that a linear dependency exists for the magnesia-carbon refractory material and that it is very little affected, which implies a very low corrosion rate. The effect of the rotation speed on the corrosion was examined. The speed of rotation was varied from 100 to 400 rpm at a temperature of 1823 K and 1873 K. The magnesia-carbon sample seems to be very little affected by increasing of the rotation speed in MgO-free slag and this is in accordance with the results reported by Bygden [13], but in contradiction with some other studies [8, 14] on the kinetics of refractory materials corrosion.

Figure 11. Decrease of MgO-C rod diameter as a function of time and rotation speed in MgO-free slag with basicity 5.1 at 1823 K.

Figure 12. Decrease of MgO-C rod diameter as a function of time and rotation speed in MgO-free slag with basicity 5.1 at 1873 K.

The decrease of the dissolution rate with the increasing of MgO content in the slag is shown in figure 13. The low corrosion rate into slag with 8% MgO can be attributed to the lower driving force (concentration gradient) 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, see Figure 14. The mapping shows that the slag penetrates the refractory material through pores and cracks. The penetration depths were approximately 1 mm for all the samples. 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.

It can also be noted 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 13.** Corrosion of MgO-C rods pertaining to different slag compositions (1873 K, 200 rpm).

**Figure 14.** X-ray images of MgO-C refractory/slag interface after immersion in slag containing 8 wt-% MgO at 1873 K rotated at 200 rpm during 15 min.
5. DISCUSSION

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

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

The effect of temperature on the dissolution rate was investigated on magnesia-carbon rods in contact with 0.1 wt-% aluminium-killed steel and in contact with free MgO slag. The decrease of the radius was linear to the change of the temperature. In Figure 15 the decrease of the rod diameter at different holding times and different temperatures is shown at 400 rpm for steel and 200 rpm for slag.

![Figure 15. Effect of temperature on the dissolution. Steel at 400 rpm with 0.1 wt-% Al-addition and slag at 200 rpm in free MgO slag.](image)

5.2. *The effect of the revolution speed on the dissolution rate*

It is evident from Figures 10, 11 and 12 that the dissolution rates of refractory materials depend upon the rotation speeds. This fact shows that the dissolution rate is controlled by the mass transport of solute in the molten slag around the refractory rods. Figure 16 shows the linear relationship between log V and log U for the MgO-C material used in the present experiments. V is the corrosion rate and U is the rotation speed.
According to equation [6] and figure 16 the line can be expressed by the following equation:

For steel  \[-\frac{dr}{dt} = A_1 U^{0.24}\]  \[\text{[13]}\]

For slag  \[-\frac{dr}{dt} = A_2 U^{0.59}\]  \[\text{[14]}\]

where $A_1$ and $A_2$ are a constants. Constant 0.24 and 0.59 were calculated from the slope of the lines in figure 16.

### 5.3. Formation of inclusions in steel

The investigation of the aluminium-deoxidised steel shows, after the refractory rod has been rotated during the tests, that there has been a formation of inclusions in the steel. When the holding time was increased, there were less numerous inclusions than it was at the shorter times. This is due to that at longer times the inclusions have the possibility to separate from the metal bath and rise to the surface. The inclusions were less numerous when the rotation speed was increased compared to the slower rotation speed. This depends on the stirring effect that gives the possibility for the inclusions to reach the surface. The inclusions found in the steel were examined using SEM/EDS. The results showed that the inclusions contained MgO and Al₂O₃. Furthermore, the sizes of the inclusions were 2 - 6 μm, see figure 17.
The formation of spinel is practically a very significant aspect of the reaction between MgO-C refractory and aluminium deoxidised molten steel. As the magnesium gas diffuses into the molten steel the following reaction is taking place:

\[
\text{MgO} \cdot \text{Al}_2\text{O}_3 = [\text{Mg}] + 2[\text{Al}] + 4[\text{O}]
\]  

For which the equilibrium constant can be written as:

\[
K_{\text{spinel}} = \frac{a_{\text{Mg}} \cdot a_{\text{Al}}^2 \cdot a_{\text{O}}^4}{a_{\text{MgO} \cdot \text{Al}_2\text{O}_3}}
\]

As the initial alloys did not contain any magnesium, the presence of MgO in the inclusions should indicate a result from the contamination by the refractories/steel reaction. This was supported by the findings that no MgO was found in inclusions analysed in steel samples taken before melting.

### 5.4. Formation of an oxide layer at the steel/refractory interface

According to Pickering and Batchelor [1] and Watanabe at al. [3] the reaction \( \text{MgO} + \text{C} = \text{Mg} + \text{CO} \) proceeds to the right at higher temperatures and Mg\(_{\text{(g)}}\) diffuses towards the free surface of the sample where it encounters a higher \( P_{\text{O}_2} \). Thereafter, magnesium is oxidised to MgO, were it condenses and forms a MgO layer. At the same time, according to Schwerdtfeger [15], Brabie [16] and Poirier at al. [17] the CO\(_{\text{(g)}}\) formed during MgO\(_{\text{(s)}}\) reduction by carbon will diffuse to the interface where it will react with the molten steel forming MgO or Al\(_2\)O\(_3\) according to the following reactions:

\[
2[\text{Al}] + 3\text{CO}_{\text{(g)}} = \text{Al}_2\text{O}_3(\text{s}) + 3[\text{C}]
\]

\[
[\text{Mg}] + \text{CO}_{\text{(g)}} + \text{MgO}_{\text{(s)}} + [\text{C}]
\]

Reactions occur in two stages. The first stage occurs immediately after the reactive CO gas comes into contact with the surface of the steel. As a result, a thin oxide film of Al\(_2\)O\(_3\) and/or MgO is formed at the end of the first stage.

As an oxide layer is formed at the interface, the rate-controlling step for the second stage of oxidation has been shown to be the growth of the oxide layer by dissociative adsorption of CO molecules at the gas/oxide interface. Now the diffusion through the
oxide layer will be the rate-controlling step. The formation of a surface layer will inhibit any further oxidation by CO, by retarding the diffusion of carbon and oxygen across the layer.

5.5. Penetration of slag into the refractory material

The dissolution process in the refractory material is supported by SEM investigations of the samples. The slag has penetrated the refractory material in pores and cracks. It is possible to observe that the slag phase has a concentration gradient at the boundary layer between slag/refractory, see figure 18.

According to Cooper [18] 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 elements from the fluid slag. 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 solid
- Diffusion of a slag species into the refractory material causing a change in the physical properties

![Figure 18. X-ray images of MgO-C refractory/slag interface after immersion in free MgO slag at 1873 K on 200 rpm during 60 min.](image)

The higher wetting angle makes it more difficult for the slag to penetrate pores and cracks in the refractory. This is not the only thing that affects the infiltrating depth. The infiltrating depth is also affected by the temperature gradient in the brick. The temperature gradients will cause the viscosity to increase and then the infiltration depth will decrease.

Figure 19 illustrates penetration in the refractory by slag at different conditions, hot face, high temperature and low viscosity. If the surface of the refractory has a hot face the
penetration will increase and if the slag has a high temperature the penetration is increased.

![Diagram of penetration conditions]

*Figure 19. Illustration of different penetration conditions* [5].

The penetration and dissolution of the refractory by slag can schematically be described as a cycle where the slag consumes the refractory gradually as the wear continues, see *Figure 20*. The figure describes what happens when the slag is in contact with the refractory and the reactions that are involved in the different steps in the cyclic corrosion.

![Diagram of dissolution cycle]

*Figure 20. Penetration and dissolution cycle of the refractory.*

### 5.6. The effect of slag composition on the dissolution rate

The effect of MgO content in the slag on the dissolution rate of magnesia-carbon refractory material was investigated by changing the MgO content of molten slag (*Table 3*). It is observed from *figure 13* that the diameter of the samples, decreases with increasing of the MgO content in the slag.
The results show that if the reaction products are soluble or dissociate in the molten slag, the corrosion may continue to wear of the refractory. An increase of the MgO content in the molten slag may result in a decrease of the solubility of MgO into the molten slag, and as a result it may form an impenetrable barrier. After its formation, figure 14, further attack is prevented. Now the rate determining step should be the chemical reaction forming the layer, diffusion through the layer, or diffusion through the slag.

6. SUMMARY AND CONCLUSION

Laboratory experiments were conducted for the investigation of the reaction between aluminium deoxidised molten steel, molten slag and MgO-C refractory. The theoretical results show that the MgO of the MgO-C refractories can react at the steel/ladle refining temperature with carbon. As a result, Mg\(_{(\text{g})}\), SiO\(_{(\text{g})}\) and CO\(_{(\text{g})}\) are formed which can react with molten steel and slag.

The experimental results show that a MgO layer is formed at the refractory/steel interface. The formation of the thin oxide layer at the interface is due to the reaction between magnesium vapour and the CO\(_{(\text{g})}\) generated by the reaction between MgO and C in the refractory rods.

The oxide inclusions in the steel have been shown to mainly consist of MgO, Al\(_2\)O\(_3\) or a mixture of these. The composition range, origin and mechanism of formation of the oxide inclusions were discussed and it is concluded that MgO and spinel could be formed. Some of the finest inclusions are considered to be formed as secondary inclusions during cooling and solidification of the steel and they are connected only with the diffusion of magnesium from the refractory rods to the molten steel.

Increasing of temperature, rotation speed and holding time increase the dissolution of the refractory material in to the molten steel and slag. Mass transport coefficients calculated based on the experimental results correspond well with published results for other refractory/steel systems. The calculation of the activation energy of the dissolution process supports the assumption that the mass transfer step through the slag boundary layer is the rate-determining step.

The corrosion rates using free MgO slags were greater than that using 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.

7. FUTURE WORK

The following specific subjects are suggested:

1. Experimental investigations have shown that spinel inclusions are formed during ladle refining of steel. Since there is some discrepancy between different research groups and steel plants opinions about the presence of spinel inclusions in steel
samples, there is a need of more studies on the potential reactions for reduction of MgO by aluminium.

2. Owing to a complex combination of different reactions and phenomena, the corrosion of MgO-C lining during ladle refining of steel seems to be very important in the slag line. During preheating of the ladle and stirring and degassing of molten steel the reaction between the MgO-C and furnace atmosphere gives rise to a decarburized zone, which can be infiltrated by molten slag. Further studies are needed in order to understand the refractory lining behaviour in contact with air, Ar and CO atmospheres.

3. The experimental results suggest that the slag-refractory reaction inside the refractory pores may play an important role in suppressing the slag penetration. Effects of slag chemistry (saturation level) and temperature on wetting and penetration of refractories by slags should be studied in order to understand the possibilities to decrease corrosion.

8. REFERENCES