A STUDY OF SLAG CORROSION OF OXIDES AND OXIDE-CARBON REFRACTORIES DURING STEEL REFINING

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Ismail Kasimagwa: A Study of Slag Corrosion of Oxides and Oxide-carbon Refractories during Steel Refining

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ABSTRACT

The use of ceramic material as refractories in the manufacturing industry is a common practice worldwide. During usage, for example in the production of steel, these materials do experience severe working conditions including high temperatures, low pressures and corrosive environments. This results in lowered service lives and high consumptions of these materials. This, in turn, affects the productivity of the whole steel plant and thereby the cost. In order to investigate how the service life can be improved, studies have been carried out for refractories used in the inner lining of the steel ladles. More specifically, from the slag zone, where the corrosion is most severe. By combining thermodynamic simulations, plant trails and post-mortem studies of the refractories after service, vital information about the behaviour of the slagline refractories during steel refining and the causes of the accelerated wear in this ladle area has been achieved.

The results from these studies show that the wear of the slagline refractories of the ladle is initiated at the preheating station, through reduction-oxidation reactions. The degree of the decarburization process is mostly dependent on the preheating fuel or the environment. For refractories without antioxidants, refractory decarburization is slower when coal gas is used in ladle preheating than when a mixture of oil and air is used. In addition, ladle preheating of the refractories without antioxidants leads to direct wear of the slagline refractories. This is due to the total loss of the matrix strength, which results in a sand-like product.

Thermal chemical changes that take place in the slagline refractories are due to the MgO-C reaction as well as the formation of liquid phases from impurity oxides. In addition, the decrease in the system pressure during steel refining makes the MgO-C reaction take place at the steel refining temperatures. This reduces the refractory’s resistance to corrosion. This is a serious problem for both the magnesia-carbon and dolomite-carbon refractories.

The studies of the reactions between the slagline refractories and the different slag compositions showed that slags rich in iron oxide lead mostly to the oxidation of carbon/graphite in the carbon-containing refractories. This leads to an increased porosity and wettability and therefore an enhanced penetration of slag into the refractory structure. If the slag contains high contents of alumina and or silica (such as the steel refining slag), reactions between the slag components and the dolomite-carbon refractory are promoted. This leads to the formation of low-temperature melting phases such as calcium-aluminates and silicates. The state of these reaction products during steel refining leads to an
accelerated wear of the dolomite-carbon refractory.

The main products of the reactions between the magnesia-carbon refractory and the steel refining slag are MgAl$_2$O$_4$ spinels, and calcium-aluminates, and silicates. Due to the good refractory properties of MgAl$_2$O$_4$ spinels, the slag corrosion resistance of the magnesia-carbon refractory is promoted.
ACKNOWLEDGEMENTS

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Ismail Kasimagwa

Borlänge, August 2010
SUPPLEMENTS

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Supplement II: “The use of thermodynamic computations to predict the phase transformation in MgO-C refractories during steel refining”; I. Kasimagwa and V. Brabie
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Supplement III: “Thermo-Calc and SEM analysis of the dolomite lining during steel refining”; I. Kasimagwa and V. Brabie
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**Supplement I:** Literature survey, refractory analyses and major part of writing

**Supplement II:** Literature survey, thermodynamic calculations and all writing

**Supplement III:** Literature survey, thermodynamic calculations, post-mortem analyses and major part of writing

**Supplement IV:** Literature survey, thermodynamic calculations, post-mortem studies and major part of writing

Parts of the work were presented in the following conferences:

I. “The use of thermodynamic computations to predict the phase transformation in MgO-C refractories during steel refining”; I. Kasimagwa and V. Brabie, 2nd International Congress on Ceramic (ICC), June 29-July 4, 2008, Verona, Italy:


III. “Thermo-Calc and SEM analysis of the dolomite lining during steel refining”; I. Kasimagwa and V. Brabie, Third Nordic Symposium for Young Scientists in Metallurgy; May 14-15, 2008, TKK, Espoo, Finland

IV. “Predictions and Simulations of the Slag-Refractory Reactions During Steel Refining”; I. Kasimagwa, 11th annual Brinell Centre Conference & SFMT Spring Meeting 1 2008; Bergby Gårg, Hallstavik, Sweden; 9-10 April, 2008
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1. INTRODUCTION

Refractories are very important materials used in the manufacturing industry. More specifically, they are used in the production of steel, cement, glass etc. The service life of these types of materials is determined by how good they can resist the working conditions of a given process e.g. the steel making process. In the steel industry, these materials are used as furnace lining in vessels for holding and transporting liquid steel and slag.

1.1. Overview of the steel production process

Figure 1 shows an example of the general route to the production of steel. In this case, liquid steel is tapped from the Electric Arc furnace (EAF) to the ladle. After the removal of the oxidizing slag, the ladle full of liquid steel is transported to the ladle furnace to be refined.

Figure 1. The schematic of the steel production process at Ovako Steel plant in Hofors.

Steel refining is one of the most important process steps in the production of clean steel. Here, the composition, temperature and inclusions contents of liquid steel are adjusted
before casting. The higher temperatures and low pressures at this stage of steel refining have a big impact on the stability of the ladle refractories during service. Due to the severe working conditions, the steel ladle is lined with refractories of different quality. The refractories with the best quality are used in contact with liquid slag during steel refining.

1.2. Aim of the work

The wear of the slagline refractories of the ladle during service in the steel industry is investigated. The areas of interest in steel production are the steel refining process and ladle preheating, which all have a big effect on the corrosion/wear of the refractories. The methods used in this investigation include thermodynamic simulations, plant trials and post-mortem studies of the refractories after service. The three methods complement each other such that vital information of the mechanisms causing degradation of the slagline refractories is determined and understood.

The main aim of the thesis is to clarify the mechanisms of interfacial reactions between molten slag, gas phase and refractory materials during steel refining. Part of the work is to predict the corrosion behaviour and qualitatively compare the corrosion resistance of refractory materials in different slags.

Generally, the work in this thesis is divided into 3 main parts. In the first part, the effect of ladle preheating on the wear of the slagline refractories is analysed, supplement 1. This investigation is followed by the study of the thermal chemical changes taking place in the slagline refractories during steel refining without any slag encounter, supplement 2. Finally, the reactions between the slagline refractories and different slag compositions are studied in supplements 3 and 4.

Figure 2 shows the framework of this thesis and stages in the ladle recycling in the steel plant, in which the different supplements are focused. As shown, the work in the thesis initiated with the study of the reactions between the slagline refractories and the gas phase, by analysing the effect of ladle preheating on the wear of the refractories. During the tapping of liquid steel from the EAF to the ladle, there is a drastic increase in temperature from that used at ladle preheating to the temperature used during steel refining. This leads to thermal chemical changes taking place in the slagline refractories. These changes are similar to those taking place inside the refractories during steel refining as the temperature gradient decreases in the ladle lining. In order to study the reactions between the slagline refractories and slag, two main types of slag compositions were considered. One of the slag
compositions comes from the primary furnace and the others from the steel refining process as shown in Figure 2. The results from the study of the reactions between the slag and the slagline refractories were successfully completed by the post-mortem analyses of the refractories after service in order to get some information of the history of the refractories. As explained above, the work in the different supplements interacts providing a thorough analysis of the degradation mechanisms of the slagline refractories.

Figure 2. The structure of the work in this thesis and the stations in the ladle recycling in the steel plant where the different supplements are focused.
The results will help the companies to obtain a better understanding of the behaviour of the refractory materials in the steel refining condition and the causes of the accelerated wear in the slag zone. This will be discussed more in detail later in the thesis.
2. THEORETICAL CONSIDERATIONS

2.1. Refractory-gas interactions

The use of oxides and oxide carbon refractories in the steel refining ladle is a common practice in the steel industry. These materials have good refractory properties such as high melting temperatures, which enables their use in ladles and steel refining vessels. Generally, the carbon-containing refractories are usually made up of binders, oxides, graphite and oxidation inhibitors in the form of metallic or metal-carbides powder. Carbon in the refractory exists in the form of fine and reactive pyrolytic carbon from binders such as pitch or resin in the refractory matrix and as graphite flakes.

The use of carbon/graphite as a component in the refractories leads to an improved slag corrosion resistance, due to the non-wetting characteristics of graphite by the steel refining slags. This property leads to a reduced slag penetration and dissolution. Graphite also improves the refractory’s resistance to thermal mechanical spalling, due to an improved thermal conductivity and a decreased thermal expansion [1-2].

Apart from the advantages mentioned above, the main drawback of the carbon-containing refractories is oxidation. This is due to the fact that carbon/graphite is easily oxidized by air in the ambient atmosphere, which results in refractory de-bonding and an increased porosity (figure 3). This is the main reason why supplement 1 mainly focused on the effect of ladle preheating on the wear of the slagline refractories.

In order to improve the oxidation resistance of the carbon/graphite-containing refractory, different types of additives such as metallic powder (most commonly; aluminium and/or silicon) have been introduced into the refractory microstructure to delay the de-bonding effect and the oxidation of graphite [1-2].

Apart from slowing down the carbon oxidation, antioxidants also lead to the densification of the refractory. Therefore, also a decrease of its porosity as well as the formation of a protective oxide layer at the refractory surface, which reduces slag infiltration as shown in figure 3 (only when the affinity of oxygen in the process is high; for example in, AOD processes), formation of ceramic bonds which improve the refractory’s strength at high temperature etc [1-2].

5
Another very serious problem of having graphite in the refractory during steel refining (high temperature and low pressure) is connected with the thermodynamic stability of this component in contact with the oxide part of the refractory. For example, this type of instability is known as the MgO-C reaction (reaction 1) in the magnesia-carbon refractories:

\[
\text{MgO (refractory) + C (refractory) = Mg (g) + CO (g)} \quad (1)
\]

\[
\Delta G^0 = 646923 - 403.214T + 13.39T \ln T, [J] \quad 1380-2500 \; \text{K} \quad (2)
\]

During service reaction (1) takes place, which results in the consumption of carbon/graphite, an increased porosity content and therefore a decrease in the corrosion resistance of the refractory. Both the temperature and the pressure in the refining process have a big effect on the reaction kinetic of the type of instability shown by reaction (1). As the changes taking place in the refractories can play an important role on the refractory’s stability, supplement 2 has been dedicated to studying the thermal changes taking place in the slagline refractories such as magnesia-carbon and dolomite-carbon. Also, explaining the effects they have on the corrosion resistance of the refractories.

### 2.2. Refractory-slag interactions

Even though the refractories used in the slag zone closest to liquid slag and steel are of highest quality as mentioned earlier, analyses of the wear profile of the ladle lining after
steel refining indicates a higher wear occurs in this ladle area than in any other part of the ladle as shown in **Figure 4**. This is mainly due to slag corrosion, as is explained in **supplements 3** and **4**.

**Figure 4** Schematic of the wear in the slag zone of the ladle lining during steel refining [3-4].

The corrosion of oxide-carbon refractories by slag during steel refining is a complex process involving numerous mechanisms and factors. The most important corrosion mechanisms leading to a severe wear of the slagline are:

I. *Oxidation-reduction* processes, caused by the reactions between the easily reducible oxides such as FeO and the main components of the refractory.

II. *Dissolution/diffusion*, a chemical process by which the refractory material is dissolved into slag.

III. *Penetration*, whereby the slag infiltrates the refractory structure leading to structural/chemical changes (or structural spalling).

IV. *Erosion*, which is the abrasive wear of the refractory caused by the movement in liquid steel and slag.
What complicates the corrosion of industrial refractories is that the different corrosion mechanisms interact, which contributes to the total wear of the refractory material. As an example, the oxidation/reduction damage of the refractory leads to the increase in the content, size and size distribution of the open pores. These in turn, enhances slag penetration/structural spalling and the refractory erosion (due to decreased refractory strength) as shown in figure 5.
The physical and chemical properties of the slag and refractory are very important for the stability and wear resistance of the refractory lining during service. There are many parameters influencing the slag-refractory reactions as shown in Figure 6. Both the extrinsic (e.g. temperature, lining design etc.) and the intrinsic (e.g. composition) properties of the slag and the refractory have a big influence on the refractories’ resistance to corrosion. For example, the corrosion process of the refractories used in steel production is highly influenced by the composition of both the slag and the refractory (as mentioned earlier). When designing a slag to be used during steel production, one has to make sure that the components of the slag system, similar to those of the refractory lining being used, are over their saturation limit. If not, the refractory lining will be dissolved by the slag until saturation is attained [2, 4].

Figure 6  A schematic showing the interaction between the physical and chemical properties of the slag and the refractory [2, 5].
Apart from the slag and the refractory composition, other properties that have a big influence on the slag corrosion of the refractory are slag viscosity, surface tension, basicity, temperature, porosity content etc.

Besides the carbons non-wettability, which suppresses slag penetration as mentioned above, other ways to improve the slag corrosion resistance of carbon-bonded refractories are: i) using large crystallite size therefore providing less surface area for slag attack e.g. using fused grains instead of sintered grains; ii) upgrading the refractory via chemical purity (e.g. eliminating/lowering impurities such as \( \text{Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \), which may react with the refractory leading to low-temperature melting phases during service, decreasing the refractory’s resistance to dissolution); iii) introducing matrix additives to raise the matrix melting temperature; iv) reducing or eliminating low-temperature melting additives; v) decrease the porosity content and pore sizing of the refractory by using glazings or coatings and having a high density, which reduces infiltration and dissociation by slag etc [2, 5-6].

**2.3. Temperature profile**

Heat can be transferred in three different ways, namely by:

- Conduction, which is the transfer of thermal energy from a higher to a lower temperature zone in the material
- Convection, the transfer of thermal energy from one part of the system to another as a result of the bulk motion of a fluid or a gas
- Radiation, whereby the heat is transferred between two surfaces by transmission of photo electrons or electromagnetic waves through space

The thermal profile of the different linings that make up the ladle wall was achieved by application of transport and rate phenomenon equations.

*Figure 7* shows a schematic of the linings of the ladle wall during steel production, in two dimensions. Two equations were used to describe the flow of heat energy from liquid steel through the ladle linings to the surrounding atmosphere. Fourier’s law of conduction [7-9], *equation 3*, was used to describe the heat transfer through the different linings of the ladle wall, with the assumption that stead state is valid and that there is no heat generation within the refractory lining:
\[
\dot{Q} = -kA \frac{dT}{dx} = kA \frac{T_0 - T_x}{X} \quad (3)
\]

\[
\frac{dQ}{dt} = \dot{Q}, \text{ heat transfer per unit time, [J/s]}
\]

Q = thermal energy in joules, [J]

k = thermal conductivity coefficient [W m\(^{-1}\) K\(^{-1}\)]

A = surface area of the lining from which the heat is transferred, [m\(^2\)]

T\(_0\) = temperature at inner surface of the lining, [K]

T\(_x\) = temperature at the outer surface of the lining of thickness X, [K]

(T\(_0\) > T\(_x\))

X = thickness of the lining, [m]

From equation 3, the heat flux through the refractory lining can be derived as shown by equation 4 below.

\[
q_x = \frac{\dot{Q}}{A} = -k \frac{dT}{dx} = k \frac{T_0 - T_x}{X} \quad (4)
\]

where \(q_x\) is the heat flux [J/m\(^2\)s], i.e. the amount of energy that flows through a particular surface per unit area per unit time, in the x direction.

The rate of heat transfer by convection from the outer surface (steel plate (4)) of the ladle wall to the surrounding atmosphere and from liquid steel to the hot face of the ladle wall on the other hand is described by Newton's law of cooling [7-9]. This relationship states that the rate of heat loss of a body is proportional to the difference in temperatures between the body and its surroundings, equation 5. This equation can be transformed to equation 6, which describes the heat flux (i.e. the heat flux is the amount of energy that flows through a particular surface per unit area per unit time) from the surface of the ladle to the surrounding atmosphere.

\[
\dot{Q} = hA(T_{\text{atm}} - T_{\text{surface}}) \quad (5)
\]

h = heat transfer coefficient, [W/(m\(^2\)K)]

\(T_{\text{atm}}\) = temperature of the surrounding atmosphere, [K]

\(T_{\text{surface}}\) = temperature on the surface of the ladle lining, [K]
The heat flux from liquid steel to the hot face of the ladle lining is described by equation 7.

\[ q_x = \frac{\dot{Q}}{A} = h(T_0 - T_m) \]  

\[ T_0 = \text{temperature at the hot face of the ladle wall, [K]} \]
\[ T_m = \text{temperature for liquid steel, [K]} \]

---

**Figure 7** The schematic of linings of the ladle wall in two dimensions.

By combining Fourier’s law of conduction for the different layers and Newton’s law of cooling, the total heat flux through the multilayer of the ladle wall, as shown by equation 8, was achieved. The total heat flux through the multilayer, equation 8 was then combined with the Fourier’s law of conduction (equation 4) and Newton's law of cooling (equation 7), leading to the final expression for the temperature profile of the MgO-C lining, equation 9.
\[ q_x = \frac{T_m - T_{atm}}{\left( \frac{1}{h_0} + \frac{\Delta x_1}{k_1} + \frac{\Delta x_2}{k_2} + \frac{\Delta x_3}{k_3} + \ldots + \frac{1}{h_1} \right)} \]  \hspace{2cm} (8)

\[ T(x_i) = T_m \left[ \frac{1}{h_0} + \frac{x_i}{k_1} \right] q_x = T_m \left[ \frac{1}{h_0} + \frac{x_i}{k_1} \right] \left( \frac{T_m - T_{atm}}{\left( \frac{1}{h_0} + \frac{\Delta x_1}{k_1} + \frac{\Delta x_2}{k_2} + \frac{\Delta x_3}{k_3} + \frac{\Delta x_4}{k_4} + \frac{1}{h_1} \right)} \right) \]  \hspace{2cm} (9)

\[ 0 \leq x_i \leq \Delta x_i \]

In the above equations, \( q_x \) \((\text{W/(m}^2))\) is the heat flux in the \( x \) direction i.e. the rate of heat transfer per unit cross section area of the refractory, \( k_1 \) is the thermal conductivity of the MgO-C refractory lining, marked 1 in figure 7. Furthermore, \( \Delta x_1 \) is the thickness. Behind the MgO-C lining lays the magnesite layer with the thickness \( \Delta x_2 \) and the conductivity \( k_2 \). This is followed by an isolation layer (\( k_3 \) and \( \Delta x_3 \)) and the steel plate (\( k_4 \) and \( \Delta x_4 \)). The heat transfer coefficient (\( h_1 \)) from the steel plate to the surrounding atmosphere with the temperature \( T_{atm} \) (295 K) is around 14 \( \text{W/m}^2\text{K} \) and \( h_0=2000 \text{ W/(m}^2\text{K])[7] \) for molten metal in contact with the refractory wall. The thermal conductivity (\( k_4 \)) for the steel plate is around 42 \( \text{W/m*K} \) [8]. The parameter \( T_m \) is the liquid steel temperature.

More details of the calculation discussed above, as well as the values of the thickness of the different linings and the conductivity are shown in supplement 2.
3. EXPERIMENTAL

The experimental work can be divided into two main areas, namely:

1) Plant trials (supplement I)
2) Post-mortem studies (supplement III and IV)

3.1. Materials

3.1.1 Preheating experiments/Plant trials
The refractory materials used in this work were of a MgO-C type used in the slag zone of steel refining ladles. Some of the refractories used in this work contained anti-oxidants. The compositions of the refractories used in the preheating experiments at the different steel plants are shown in table 1.

Five samples were used in the pre-heating experiment at steel plant A. Four of the refractories were made of high-quality fused magnesia, resin bonded and belonging to the same type, Ankarbon AC 82. These refractories contained aluminium and silicon powder as antioxidants. Two of the four refractories contained larger grains of anti-oxidants (<3000 µm), whereas the remaining contained finer grains (<100 µm). All four refractories contained a carbon content of 10 wt%. The fifth refractory type was exactly the same as that used at steel plant B, with a chemical composition shown in table 1.

The refractory used at steel plant B contained no anti-oxidants and had a carbon content of around 12 wt%. This refractory was made of fused magnesia, which was resin bonded. The refractory used in the preheating experiments at steel plant C also contained anti-oxidants (Al) and had a carbon content of 5 wt%.

The porosity content of the refractories used in the preheating experiments at the different steel plants varied between 4 and 6 vol. %, as shown in table 1. In addition, all refractories had a bulk density of around 3 g/cm³.
Table 1  Chemical compositions and other data of the refractories used in the preheating experiments at the different steel plants.

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<tr>
<th>COMPONENTS</th>
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<td></td>
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<td>Bulk density, g/ cm³</td>
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</table>

3.1.2  Post-mortem
Due to the fact that magnesia-carbon and dolomite-carbon refractories are used in the slag zone of the steel refining ladles, both types of refractories were included in the post-mortem studies. The initial chemical compositions of the refractories are shown in Table 2.

3.2.  Experimental procedure

3.2.1  Preheating experiments/ Plant trials
Experiments were carried out under production conditions at three steel plants called steel plant A, B and C respectively. These experiments were intended to examine the influence of the ladle preheating conditions on the wear/corrosion of the slagline refractories during industrial conditions (or the gas-refractory reactions).
3.2.1.1 Experimental set-up

At steel plant A, the refractories were preheated for 48 hr using coal gas. During the preheating period, the test refractories were placed on an iron support positioned 800 mm below the top of the ladle. The experimental set-up of the refractories in the vertical direction is shown in figure 8.

Figure 8.  The schematic experimental set-up (left) showing the placement of the test refractory in the ladle during preheating at steel plants A and B. On the right is a photograph of the refractories in the iron support.

The experimental set-up at steel plant B was similar to that at steel plant A as shown in figure 8. Also, the preheating process took around 16 hours. The pre-heating fuel was a mixture of oil and air.

At steel plant C, two types of slagline refractories of different quality were placed at the ladle bottom during preheating as shown in figure 9. The refractories were electrically heated and the preheating time was estimated to 144 hours (6 days).

The maximum preheating temperature was $1000^\circ$C in all the preheating experiments. After the preheating process, the test refractories were removed from the ladles and examined.
3.2.2 Post-mortem analyses

With the aim of getting more information about the slag corrosion behaviour of the slagline refractories, the refractories were collected from the slag zone of the steel refining ladles after service. Then, post-mortem analyses were carried out on the refractories microstructure using a Scanning Electron Microscope equipped with an Energy Dispersive Spectrometry (SEM-EDS). The microscope was operated in the backscatter mode. Samples were cut from the spent refractories, mounted in epoxy, grinded, polished and gold coated before the microscopy examination.
4. THERMODYNAMIC SIMULATIONS

The thermodynamic simulations are part of the work presented in supplements II, III and IV. In order to study the effect of temperature on the thermal chemical changes of the refractories, the thermodynamic based software (Thermo-Calc) was used. The software was used to study the reactions taking place between the refractories and the different slag compositions during steel refining. The oxide database SLAG2 was used in the calculations. The thermodynamic calculations were carried out at 1873 K and 101325 Pa (1 atmosphere). The total mass of the system was always maintained at 100 g.

The total amount of slag that penetrated the refractory systems was estimated from the point of view of the porosity content. For the dolomite-carbon refractory (A), the penetrated slag was 6 wt-% of the total refractory mass whereas 4 wt-% for the magnesia-carbon refractory (B).

The chemical compositions of the refractories used in the calculations are shown in table 2. During steel refining, the ladle refractories (dolomite-carbon (A) or magnesia-carbon (B)) came into contact with two different slag compositions shown in table 2. Slag compositions 2 and 3 represent the slag compositions used during steel refining whereas slag composition 1 represents the slag carryover from the primary furnace. During service, the dolomite-carbon refractory comes into contact with both slag compositions 1 and 2 whereas the magnesia-carbon refractory interacts with compositions 1 and 3.
Table 2  Properties of the refractory and novel refractory and slag compositions used in the thermodynamic calculations, wt-%.

<table>
<thead>
<tr>
<th>COMPONENTS</th>
<th>REFRACTORIES</th>
<th>SLAG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>CaO</td>
<td>56.16</td>
<td>1.518</td>
</tr>
<tr>
<td>MgO</td>
<td>37.92</td>
<td>86.60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.48</td>
<td>0.18</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.96</td>
<td>0.54</td>
</tr>
<tr>
<td>FeO</td>
<td>0.48</td>
<td>0.446</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>10.71</td>
</tr>
<tr>
<td>Apparent porosity [Vol-%]</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Bulk density [g/cm³]</td>
<td>2.90</td>
<td></td>
</tr>
</tbody>
</table>
5. RESULTS AND DISCUSSION

This section is divided into three main parts. The first part presents the results from the experiments about the effect of ladle preheating on the wear of the slagline refractories (supplement I). The second part of this section discusses the thermal chemical changes taking place in the slagline refractories before coming into contact with slag (supplement II). Final the last part of this section presents the result from the study of the reactions between the slagline refractories and different slag compositions (supplements III & IV).

It should be mentioned that the thermodynamic data for the reactions presented in this section were collected from references [10-12].

5.1. Effect of ladle preheating on refractory wear

The values shown below (and in table 2) of the thickness of the decarburized layers are averages of at least six measured values. A slide calliper was used to measure the thickness, after completion of the pre-heating.

![Figure 10. The pre-heating schedules of the test refractories at the different steel plants.](image)

```latex
\begin{figure}
\centering
\includegraphics[width=\textwidth]{pre_heating_schedules.png}
\caption{The pre-heating schedules of the test refractories at the different steel plants.}
\end{figure}
```
The preheating schedules of the test refractories at the different steel plants are shown in figure 10. This figure shows that steel plant C had the lowest preheating rate in comparison to steel plant A and B. Steel plant A had a preheating rate of 20.8 degrees/hr whereas the rate for plants B and plant C were 62.5 degrees/hr and 6.9 degrees/hr, respectively. The variation of the preheating rate with time is shown in figure 11.

![Preheating rate graph](image)

**Figure 11.** The rate of preheating of the refractories at the different steel plants.

### 5.1.1 Refractories without anti-oxidants

According to the observations made on the test refractories from steel plants A and B after the preheating experiment, a 4.0 mm and 5.0 mm thick layer respectively, were decarburized on the surfaces. The colour difference between the decarburized layer (a) and the non-decarburized (b) one was evident. The decarburized layer was light brown in colour. Furthermore, the remaining part of the refractory was dark gray with brown particles, as shown in figure 12. In addition, the decarburised layer had no strength at all as it broke
down to a sand-like product (c) consisting of fine and coarse particles, as shown in the photo-image in figure 12.

Figure 12. The results from the tests at Steel plant A and B (refractories without antioxidants) after 16 and 48 hours respectively, of ladle pre-heating:

a) Decarburized layer,
b) A cross section of the test refractory showing the colour of the non-decarburized layer,
c) Sand-like product due to the total loss of matrix strength,
d) The surface where the decarburized layer has fallen off.

Another observation was that when the decarburized layer had fallen off, open pores of different sizes were formed. The bigger pores, with a size of 1- 4 mm in diameter, were situated in the areas that originally contained the bigger MgO particles as shown on surface d) in figure 12.

If the decarburization rate is defined as the decarburized thickness divided by the preheating time, the decarburization rate was 0.31 mm/hr at steel plant B and 0.08 mm/hr at steel plant A as shown in table 3. Thus, the refractory decarburization is 3.8 times slower when coal gas is used during ladle pre-heating compared to when a mixture of oil and air is used. These
results show the effect of the pre-heating fuel/environment on the refractory decarburization. Similarities can be seen between the present results and those reported by Jansson et al [2] in their laboratory experiments. Both results indicate that an air atmosphere contributes more to the refractory decarburization.

<table>
<thead>
<tr>
<th>Steel plant</th>
<th>Refractory Type</th>
<th>Anti-oxidants</th>
<th>Pre-heating Method</th>
<th>Pre-heating Time t, hr</th>
<th>Thickness x, mm</th>
<th>Decarburization Rate r, [mm/hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MgO-C</td>
<td>Yes</td>
<td>Coal gas</td>
<td>48±2</td>
<td>3.4±0.2</td>
<td>0.071±0.008</td>
</tr>
<tr>
<td>A</td>
<td>MgO-C</td>
<td>No</td>
<td>Coal gas</td>
<td>48±2</td>
<td>4.0±0.3</td>
<td>0.08±0.01</td>
</tr>
<tr>
<td>B</td>
<td>MgO-C</td>
<td>No</td>
<td>Oil/air</td>
<td>16±1</td>
<td>5.0±0.3</td>
<td>0.31±0.04</td>
</tr>
<tr>
<td>C</td>
<td>MgO-C</td>
<td>Yes</td>
<td>Electrical</td>
<td>144±6</td>
<td>16.0±0.5</td>
<td>0.111±0.008</td>
</tr>
</tbody>
</table>

As shown above, the wear of the ladle slagline refractories does not only take place during steel refining, but also at the pre-heating station through the redoxidation reactions. The degree of decarburization of the redoxidation reactions is dependent on the refractory composition as well as the preheating conditions (time and fuel).

The reaction products from the burning fuel contribute to the redoxidation corrosion of the refractory as shown by reactions (10) and (12). This corrosion process results in increased porosity, de-bonding of the refractory, swelling and weakening. Furthermore, finally breakdown, for example to a sand-like product as shown in figure 12.

\[
\text{CO}_2 (g) + \text{C}(s) = 2\text{CO} (g) \quad \text{(10)}
\]
\[
\Delta G_{10}^0 = 169008 - 172.192T, [J] \quad \text{(11)}
\]
\[
\text{H}_2\text{O} (g) + \text{C} (s) = \text{CO} (g) + \text{H}_2 (g) \quad \text{(12)}
\]
\[
\Delta G_{12}^0 = 134515 - 142.363T, [J] \quad \text{(13)}
\]

Carbon in the refractory will also be directly oxidised by the oxygen in the atmosphere, according to reactions (14) and (16). This worsens the oxidation damage of the refractory.

\[
2\text{C} (s) + \text{O}_2 (g) = 2\text{CO} (g) \quad \text{(14)}
\]
\[
\Delta G_{14}^0 = -225754 - 173.028T, [J] \quad \text{(15)}
\]
\[
C (s) + O_2 (g) = CO_2 (g) \quad \text{(16)}
\]

\[
\Delta G_{16}^0 = -394762 - 0.836T, [J] \quad \text{(17)}
\]

5.1.2 Refractories with anti-oxidants

After preheating at steel plant C, the decarburized layer (burnt layer) was measured to be 16 mm as shown in figure 13. This corresponds to a decarburization rate of 0.11 mm/hr. The decarburized layer is light brown in colour, whereas the non-decarburized one is dark brown.

![Decarburized and Non-Decarburized Layers](image)

Figure 13. The decarburized layer of a refractory sample (containing antioxidants) from steel plant C, after 144 hours of ladle pre-heating.

According to the above observations, the decarburized layer had lost some of its strength in comparison to the non-decarburized one. However, the decarburized layer remained attached to the rest of the sample. The boundary region between the decarburized and non-decarburized zones was the weakest point. Therefore, a loosening of the decarburized layer occurred during sample preparation. Thus, there was a low tendency of formation of a sand-like product from the decarburized layer. The high strength of the decarburized layer could be explained by the presence of antioxidants in the refractory, which delay the de-bonding effect of the refractory.

Observations made on all samples from steel plant A indicated the presence of a smaller decarburized layer on the surface. The decarburized layer was estimated to have a depth of
3.4 mm for both the refractories with finer and coarser grains of antioxidants. This corresponds to a decarburization rate of around 0.071 mm/hr. The decarburized layer for all samples was light brown in colour, but dark gray with brown MgO particles for the non-decarburized one as shown in figure 14. The decarburized layer for the refractory with coarser grains of antioxidants was slightly lighter in colour and weaker in strength in comparison to the refractory containing the finer grains of antioxidants.

For the refractories containing anti-oxidants, the oxidation process is slowed down, as shown by equations (18) to (28). These reactions show that the refractory is protected against the reduction-oxidation corrosion if aluminium is used as the anti-oxidant. This is the main reason for the remaining high strength in the decarburized layer as shown in figures 13 and 14.

![Figure 14](image.png)

**Figure 14.** The decarburized layer of a refractory with anti-oxidants from steel plant A.

After some weeks in storage, cracks started to propagate on the surface of the two samples. The cracks propagated earlier for the refractory samples containing coarser grains (<3000 µm) of anti-oxidants than those with finer ones (<100 µm), as shown in figure 15. More specifically, the crack thickness was 0.8 mm after 4 weeks of storage for the coarse-grain refractory. After 6 weeks of storage, the crack size was up to 1.5 mm. Finally, after 9 weeks of storage it was 8 mm.
For the finer-grain refractory, no cracks at all could be found after 4 weeks in storage. After 6 and 9 weeks of storage, the crack size was found to be up to 0.3 mm and 1.5 mm, respectively.

Figure 15. Cracking of the refractories with antioxidants after the pre-heating experiments:
   a) Contains coarser grains of antioxidant (<3000 µm)
   b) Finer grains of anti-oxidants (<100 µm)

During ladle pre-heating, alumina is formed by the reaction between aluminium and oxygen in the atmosphere as shown by reactions (18) and (20). This product may have a big influence on the stability of the refractories. The oxidation of aluminium in the refractory
according to reactions (18) and (20) leads to a 26 % relative volume expansions [13] in the host material causing it to crack as shown in figure 15.

\[
2\text{Al (s)} + \left(\frac{3}{2}\right)\text{O}_2 (g) = \text{Al}_2\text{O}_3 (s), \quad (18)
\]
\[
\Delta G_{18}^0 = -1675100 + 313.195T \cdot [J] \quad (19)
\]
298< T< 933 K

\[
2\text{Al (l)} + \left(\frac{3}{2}\right)\text{O}_2 (g) = \text{Al}_2\text{O}_3 (s) \quad (20)
\]
\[
\Delta G_{20}^0 = -1682927 + 323.239T \cdot [J] \quad (21)
\]
933 < T< 2315K,

Apart from the reaction between aluminium and oxygen in the pre-heating environment, alumina can also be formed by the reaction between aluminium anti-oxidants and carbon monoxide (reaction product), equation (22). According to Zhang et al [14], this oxidation reaction is accompanied by a 142 % volume expansion. This in turn will result in crack propagation in the material as shown in figure 15.

\[
2\text{Al (l)} + 3\text{CO (g)} = \text{Al}_2\text{O}_3 (s) + 3\text{C (s)} \quad (22)
\]
\[
\Delta G_{22}^0 = -1344296 + 582.781T \cdot [J] \quad (23)
\]

Aluminium, which is used as an anti-oxidant in the refractory may, also react directly with carbon. This will lead to the formation of aluminium carbide (\(\text{Al}_4\text{C}_3\) (s)) as shown by reactions (24) and (26):

\[
4\text{Al (l)} + 3\text{C (s)} = \text{Al}_4\text{C}_3 (s) \quad (24)
\]
\[
\Delta G_{24}^0 = -264973 + 95.061T \cdot [J] \quad (25)
\]
T>933 K

\[
4\text{Al(s)} + 3\text{C(s)} = \text{Al}_4\text{C}_3 (s) \quad (26)
\]
\[
\Delta G_{26}^0 = -215894 + 41.481T \cdot [J] \quad (27)
\]
T<933 K,

The formation of this product is another possible explanation for the cracking tendency of the refractories containing aluminium as anti-oxidant. For example, earlier studies by Etter et al [15] and Gokce et al [16] suggested that the fatigue crack growth in the refractories, as shown in figure 15, was a result of the hydration of \(\text{Al}_4\text{C}_3\). This was believed to form during ladle pre-heating due to reactions (24) and (26).
Table 4. EDS analysis of the precipitates on the surface of the refractory containing coarser grains of anti-oxidants.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical analysis [%]</td>
<td>0.77</td>
<td>4.17</td>
<td>52.43</td>
<td>14.89</td>
<td>27.75</td>
</tr>
</tbody>
</table>

The EDS analysis results indicated the presence of a MgO·Al₂O₃ spinel phase on the surface of the refractory containing anti-oxidants after ladle pre-heating, as shown in table 4. However, no Al₄C₃ could be found. The presence of MgO·Al₂O₃ spinel in the refractory after the pre-heating process indicates that a transformation of aluminium to MgO·Al₂O₃ spinel had taken place. Theoretically, this may occur due to the following reaction:

\[
\text{MgO} (s) + \text{Al}_2\text{O}_3 (s) = \text{MgAl}_2\text{O}_4 (s) \quad (28)
\]

\[
\Delta G_{28}^0 = -22175.2 - 10.832T, [J] \quad (29)
\]

Spinel formation in the refractory is also another explanation for the cracking observed after ladle pre-heating, as shown in the pre-heating results in figure 15. As the cracking tendency appears between 3 and 6 weeks after the pre-heating process, the limited time of the refractory usage, which ranges from 1-2 weeks, might not be enough for this phenomenon to appear. Apart from the cracking of the refractory, the in-situ spinel formation in the refractory, according to reaction (28), may have some positive effect on the corrosion resistance of the refractory. This is due to the higher volumetric stability and the blockage of the pores in the refractory. This, in turn, inhibits the penetration of the corrosive gases and slag into the refractory, which results in an increased corrosion resistance.

As mentioned earlier, the cracking tendency appeared earlier in the refractories containing larger grains (<3000 µm) of anti-oxidants than those containing finer grains (<100 µm). The possible explanation for the faster cracking tendency of the refractories with larger grains is the fact that the larger grains of antioxidants lead to bigger phase transformations from aluminium to alumina. Thereafter, to magnesia-alumina spinel during pre-heating. This, in turn, results in more stress build-up in the refractory and therefore a higher cracking tendency, as shown in figure 15.
Reflecting back to the results summarised in table 3, it was shown that the decarburization rate for the refractories from steel plant A was almost the same independent of the refractory composition (with antioxidants or without antioxidants). This indicates that antioxidants only play a vital role in refractory decarburization when the preheating fuel is more oxidising than reducing, as is the case when coal gas is used. This conclusion is based on the fact that coal gas contains mainly methane (CH$_4$), carbon monoxide (CO) and hydrogen (H$_2$), which are all reducing gases.

5.2. Thermal chemical changes in the slagline refractories

The results from the investigation of the effect of refining temperature on the stability of the magnesia-carbon and dolomite-carbon refractories are shown in figures 16 and 17, respectively. Firstly, reactions do take place between the impurity oxides such as CaO (only for the MgO-C refractory), SiO$_2$ and Al$_2$O$_3$, leading to the formation of a liquid slag phase in the refractory during steel refining. The main products of these reactions are calcium silicates and calcium aluminates.

The formation of the liquid slag phase initiates at around 1600 K for the magnesia-carbon refractory, whereas at 1700 K for the dolomite-carbon refractory. These temperatures are below the steel refining temperatures.

Figure 16  Transformations in the magnesia-carbon refractory during steel refining.
As shown in figures 16 and 17, reactions do also take place between the impurities such as CaO (only for the MgO-C refractory), SiO$_2$ and Al$_2$O$_3$, and the refractory oxide resulting in the formation of magnesia-alumina spinel for the magnesia refractory or calcium aluminates and silicates for the dolomite refractory. Due to the fact that a magnesia-alumina spinel has a high melting point, it is possibly dissolved by the impurity slag. Even though the dolomite refractory contained lower levels of impurities in the initial refractory composition than the magnesia refractory as shown in table 2, it contains a higher content of liquid during steel refining. Therefore, it has a higher effect on the physical and mechanical properties of the refractory.

As shown in these results, the refractory composition is of great importance for the performance of the refractories at high temperatures. Formation of impurity liquids in the refractory at steel refining temperatures will also have negative effects on the refractories resistance to dissolution and therefore corrosion.

In addition to the above mentioned, it has been reported that refractories in service tolerate the formation of small amounts (1-5%) of melts without losing their structural characteristics [17].

According to Rigaud [2], if the formation of low-melting temperature eutectics and large amounts of liquids can be avoided, the corrosion resistance of the refractory would be high.

Figure 17 Transformations in the dolomite-carbon refractory during steel refining.
Another transformation taking place in the two refractories, with a significant effect on their stability and corrosion resistance, is the MgO-C reaction, reaction 1. This reaction is due to the fact that magnesia and graphite are not stable in contact with each other at higher temperatures. More specifically, slightly above the steel refining temperatures. One of the consequences of this reaction is an increased porosity content in the refractory structure and therefore a decrease in the refractories’ corrosion resistance. According to the calculation results in supplement 2, this reaction occurs until all carbon (graphite) in the refractory is consumed. This takes place at around 2040 K in both the dolomite-carbon and magnesia-carbon refractories as shown in figures 16 and 17.

As pressure is an important factor when it comes to steel refining, it is of great interest to examine its effect on the stability of the slagline refractories. Figure 18 shows the influence of the pressure on the MgO-C reaction. This figure demonstrates that a decrease in the system pressure below 1 atmosphere means that the self-destruction of the refractories takes place during steel refining. In the part of the refractory where this scenario is a possibility (e.g. the hot-face), the refractory will lose its non-wetting characteristic to the steel refining slags. This will lead to increased slag penetration and dissolution.

![Figure 18](image)

**Figure 18** The influence of pressure and temperature on the MgO-C reaction.
With these results in mind, it is also of great importance to estimate the amount of refractory affected by the instability problems mentioned in the section of the thermal chemical changes taking place in the slagline refractories during steel refining.

**Figure 19** shows the temperature profile of the ladle linings during steel refining combined with the results in **figures 18 and 16**. Here, it can be seen that if the temperature is maintained at 1873 K, the MgO-C reaction will be expected to take place in the magnesia-carbon refractory only if the pressure in the system drops below 20000 Pa. More specifically, below 20000 Pa around 40 mm of the refractory from the hot-face will be affected by this problem.

According to the temperature profile in **figure 19**, the whole magnesia-carbon lining will be affected by the low temperature melting impurities. More details regarding the calculations can be found in **supplement 2**.
Figure 19  The temperature profile of the ladle linings showing the refractory thickness affected by the instability problems discussed above and the effect of pressure on the MgO-C reaction.

5.3.  Refractory-Slag reactions

5.3.1  Dolomite-carbon refractory-slag reactions

Figures 20 to 21 show the reactions between the dolomite-carbon refractory and the slag compositions 1 and 2 (table 2), used before and during steel refining respectively. As mentioned in the previous section, the content of slag penetrating into the dolomite-carbon refractory is 6 wt-% of the total mass of the refractory system.

When the refractory is penetrated by a slag composition containing a high content of alumina and silica, such as the steel refining slag (slag composition 2), the main reaction products are tri-calcium aluminates and silicates as shown in figures 20 and 21. Calcium aluminates and silicates result from the reactions between CaO in the refractory and Al₂O₃ and silica in the slag, as shown by reactions 30 and 32:

\[
3\text{CaO (refractory)} + \text{SiO}_2 (\text{slag}) = \text{Ca}_3\text{SiO}_5 (s) \quad (30)
\]
\[
\Delta G^0_{30} = -118826 - 6.6947T, [J] \quad (298-1773 \text{ K}) \quad (31)
\]

\[
2\text{CaO (refractory)} + \text{CaAl}_2\text{O}_4 (\text{slag}) = \text{Ca}_3\text{Al}_2\text{O}_6 (s) \quad (32)
\]
\[
\Delta G^0_{32} = 234.3 - 11.3977T, [J] \quad (T>1000 \text{ K}) \quad (33)
\]

The formation of higher contents of tri-calcium silicates and aluminates lead to higher quantities of liquid slag (phase 3) in the refractory during steel refining, as shown in figure 20. If the liquid slag from the impurities (Al₂O₃ and SiO₂), which was estimated to 4 wt-% at 2000 K (figure 17), is added to the penetrated slag (6 wt-%), the total amount of liquid slag that should be in the refractory is 10 wt-%. According to figure 20, the total liquid slag found in the refractory is 11 wt-%, which is higher than the expected value of 10 wt-%. This difference indicates that the refractory and slag have reacted with each other.
Figure 20. The results of the interaction between the dolomite carbon refractory and the steel refining slag (slag composition 2; 6 wt-% slag mass), with a) the main figure and b) the lower part of the main figure.

When the dolomite-carbon refractory is penetrated by a slag rich in iron oxide, the liquid slag is only 5.6 wt-% as shown in figure 21. As iron, a reaction product of the oxidation process of graphite by iron oxide according to reaction 34, melts below the steel refining temperature, it will also contribute to an increase in the liquid phase in the refractory system with 1.5 wt-%.

\[
\text{FeO (slag) + C (refractory) = Fe (l) + CO (g)} \quad \text{(34)}
\]

\[
\Delta G_{34}^0 = 151125 - 151.105T, [J] \quad \text{(35)}
\]

This means that the total mass of the liquid phases in the refractory system after an iron-rich slag penetrates the refractory is around 7 wt-%. When comparing these results to the results in figure 20, it indicates that a slag containing a high content of iron oxide contributes less to the increase in the liquid phases in the refractory system than that containing higher silica and alumina contents.

The results in figures 20 and 21 also indicate that a high content of iron oxide in the slag results in more oxidation of graphite in the refractory at lower temperatures (1140 K),
according to reaction 34. This leads to an increased porosity content and wetting. Therefore, promotion of the slag corrosion of the dolomite-carbon refractories.

As shown in the simulation results presented above in figure 20, gas is generated by reactions (1) and (34). According to Sunayama et al [18], the gases generated in the refractory cause a convention flow in the vicinity of the pore exit. Furthermore, turbulence layers causing a rapid dissolution of the refractory into slag. Apart from the negative effects discussed above, the generated gases may suppress slag penetration into the refractory. This is due to that they diffuse towards the slag-refractory interface.

Figure 21. The results from the interaction between the dolomite refractory and the primary furnace slag (slag composition 1) of 6 wt%.

As shown above, the steel refining slag, rich in alumina and silica, attacks the dolomite refractory mainly through reactions with CaO in the refractory. This leads to the formation of low-temperature melting phases such as calcium silicates and aluminates (figure 20). These can easily be eroded by slag due to forced convection during ladle treatment. This is the possible explanation for the accelerated wear of the dolomite-carbon refractory during steel refining. These results of the thermodynamic simulations are in good agreement with those reported by Le Coq et al [19].
5.3.2 Magnesia-carbon (MgO-C) refractory-slag reactions

The reactions between the magnesia-carbon refractory and the steel refining slag (slag composition 3), containing a high alumina content, results mainly in the formation of MgAl_2O_4 spinel, calcium aluminates and calcium silicates as shown in figure 22. These reaction products lead to the formation of the liquid slag phase in the refractory during steel refining. In addition, as the MgAl_2O_4 spinel has a high melting point, it is possibly dissolved by the silicate-rich liquid slag in the refractory during steel refining.

If the MgAl_2O_4 spinel is not dissolved by the silicate-rich slag, its formation in the refractory may have a big influence on the properties of the refractory during service. Ganesh et al [20] investigated the effect of the spinel phase on the magnesia-carbon refractory. They found the spinel to have a positive effect on the slag erosion and penetration resistance of the refractory. The possible explanation for the improved corrosion resistance is the higher volumetric stability and the blockage of the pores in the refractory by the spinel phase. This, in turn, inhibits the penetration of the corrosive slag into the refractory structure.
If the slag originating from the impurities (1.5 wt-%, figure 16) is added to the penetrated slag of 4 wt-%, the expected liquid slag in the refractory after slag penetration should be 5.5 wt-%. According to the results in figure 22, the content of liquid phases in the magnesia-carbon refractory during steel refining is 6.5 wt-%, which is higher than the expected value. The difference between the expected value and the actual value is a result of the reactions between the steel refining slag and the magnesia-carbon refractory. This difference represents the contribution of the MgAl$_2$O$_4$ spinel, as shown in figure 22.

Closer analyses of figures 22 and 23 indicate that having higher contents of alumina in the slag enhances the formation of MgAl$_2$O$_4$ spinel and calcium-aluminates at the slag-refractory interface. However, higher iron oxide contents promote the oxidation of carbon/graphite in the refractory.

![Figure 23](image_url). The results from the interaction between the MgO-C refractory and the primary furnace slag (slag composition 1).

- a) the main figure and
- b) the lower part of the main figure.

### 5.3.3 Post-mortem studies of the dolomite-carbon refractory

The following section consists of the results from the post-mortem studies of both the magnesia-carbon and the dolomite-carbon refractories after service in the steel refining conditions.
Figure 24 shows the EDS mapping images of the elements distributed at the slag-refractory interface of the dolomite-carbon refractory after service in the steel refining conditions. Apart from calcium and magnesium, which are elements present both in the slag and the refractory, other elements that were found at the hot-face were aluminium, silicon and iron. Silicon and aluminium, which are all elements in the slag, had penetrated much deeper into the refractory structure than iron. More specifically, the iron elements are situated closer to the slag–refractory interface. There is a lack of a clear boundary between the refractory particles and the slag elements such as Fe, Si and Al in figure 24. This indicates that these are products of the reactions between the slag and the refractory. The possible reaction products are calcium-silicates (CaO·SiO$_2$), calcium-aluminates (CaO·Al$_2$O$_3$) and or calcium-ferrites (CaO·Fe$_2$O$_3$). As these reaction products are in liquid form during steel refining, the refractory wear by erosion will be enhanced. EDS area analysis of the surface shown in figure 24 indicated a composition of 28 wt% calcium, 42 wt% oxygen, 10 wt% magnesium and 7 wt% iron. Furthermore, the presence of low contents of aluminum and silicon. This indicates that the refractory was attacked by a slag rich in iron oxide such as the primary furnace slag. The typical FeO content in this type of slag at this particular steel plant lies between 5 and 30 wt-% FeO.

Figure 24. EDS elemental maps of the hot-face microstructure of the slag penetrated dolomite carbon refractory (wd25_X170_20kv).
The post-mortem studies also showed that the penetration of slag into the refractory structure happened mainly in the bonding regions of the dolomite particles, as shown in EDS elemental maps in figure 25. Iron signals are picked up along the slag penetration route, with higher quantities (signals) towards the hot-face. If the penetrated refractory shown in figure 25 is compared to the refractory unaffected by the penetrating slag shown in figure 26, it is clear that there is no bonding phase or carbon-containing material in the refractory microstructure closer to the slag-refractory interface. This indicates that it had been oxidized by iron oxide in the penetrating slag, which enhances attack by the steel refining slag.

Figure 25. EDS elemental maps of the microstructure closer to the interface between slag and the dolomite carbon refractory. (X100_20kv_wd25).
The wear mechanism of this refractory is possibly initiated by the oxidation of carbon in the refractory by the easily reducible oxides in the slag such as iron oxide, which results in an increased porosity. Therefore, the dolomite-carbon refractory is easily penetrated by the steel refining slag. During slag penetrating into the refractory structure, reactions do take place between the refractory and the slag components, leading to the formation of low temperature melting phases such as calcium-silicates and aluminates. As the formed phases are in liquid form during steel refining, they are easily eroded by the moving slag and liquid steel. This leads to an accelerated wear in the slagline. The loss of carbon at the slag-refractory interface also enhances the dissolution of the refractory, due to increased wettability by the steel refining slags.

Figure 26. EDS elemental maps of the microstructure of the dolomite carbon refractory unaffected by slag penetration. (X100_20Kv_wd25).
5.3.4 Post-mortem studies of the magnesia-carbon refractories

Microscopic analyses of the microstructures of the highly corroded refractories showed that the slag had penetrated as deep as the cold-face during service, as shown in figure 27. At the cold-face, the penetrated slag (white or light gray phase) was distributed mainly in-between the bigger MgO-particles. Slag distribution inside the bigger particles was in a net-like structure and composed generally of calcium silicates. The slag phase at the cold-face contained a high content of iron oxide in some areas. As an example, EDS point analyses showed that the slag phase in figure 27(B) was composed of 36 wt-% Ca, 34 wt-% O and 17 wt-% Fe, with low amounts of Si, Mg and Al. This indicates that the slag at the cold-face originated from the primary furnace. Most likely, it had penetrated through openings/cracks in the ladle lining to the cold-face, with limited reactions with the magnesia-carbon refractory.

Figure 27. SEM back scatter electron images of the microstructure at the hot-face (A) in comparison to that of the cold-face (B), in a highly corroded MgO-C refractory.

In the hot-face microstructure (figure 27A), metallic iron droplets (white) were observed. The position of the droplets in the hot-face microstructure indicated that the refractory was first penetrated by a slag containing a high content of iron oxide such as the primary furnace slag. The metallic iron droplets in the hot-face microstructure possibly indicate a reaction between carbon in the refractory and iron oxide in the penetrating slag. In addition, a closer analysis of the hot-face microstructure indicated that phase transformations had taken place in the refractory during steel refining.
**Figure 28** shows the typical microstructures found at the hot-face marked a), b), c) and d). Microstructure (a) contains MgAl$_2$O$_4$ spinels embedded in a phase similar to that of the ladle slag (CaO-Al$_2$O$_3$-SiO$_2$) situated closest to the slag-refractory interface. **Figure 28b** shows MgAl$_2$O$_4$ spinels (dark gray) surrounded by a calcium-silicate slag. Behind the above microstructures comes c) composed of MgAl$_2$O$_4$ spinels (dark gray), a calcium silicate slag (light gray), iron-rich phases (white) and pores (black).

The microstructure containing magnesia-alumina spinel, calcium-silicate slag and metallic iron droplets, and pores (c), shown in **figure 28**, was found behind the slag-refractory interface but closer to the non-penetrated zone. In addition to that, the size of the MgAl$_2$O$_4$ spinels and its aluminium content decreased towards the cold-face, for example **figures 28 b) to c)**.

Microstructure d) contains MgO particles imbedded in a calcium-silicate slag.

As is well known, the new phases in the refractory structure after slag penetration do present physical and thermal properties that are slightly different from the host material. This will lead to mismatches between the new phases and the host refractory. Therefore, a decrease of the refractory’s mechanical strength and resistance to erosion during steel refining.

![Figure 28](image_url)  
**Figure 28.** SEM images of the different microstructures at the interface between slag and the MgO-C refractory;  
- a) A mixture of MgO-Al$_2$O$_3$ spinel (MA; dark gray) and slag (light gray),  
- b) MA spinel surrounded by calcium silicate slag,  
- c) MA spinel (dark gray), calcium silicate slag, iron droplets (white) and pores (black),  
- d) MgO particle imbedded in Ca-Si slag.
As shown in **figure 29**, another common feature observed in the hot-face microstructure of the highly corroded refractories is the increased porosity content. The increased porosity is possibly a result of the consumption of carbon in the refractory by the oxidation reaction with iron oxide in the slag and or the MgO-C reaction at the hot-face. The consequence of the increased porosity content of the refractory, as mentioned earlier, is an increased penetration of slag into the refractory structure. Therefore, a decrease in its corrosion resistance.

![SEM image of the typical microstructure at the hot-face of the highly corroded refractory containing an increased porosity compared to the original refractory.](image)

**Figure 29.** SEM image of the typical microstructure at the hot-face of the highly corroded refractory containing an increased porosity compared to the original refractory.
Degradation/corrosion of the slagline refractories during usage is the main focus of the investigations presented in this thesis. This is an important topic for many steel plants around the world and its complexity provides challenges to the solved.

In order to clarify the mechanisms of interfacial reactions between the gas phase and refractory materials, the effect of ladle preheating on the wear of the slagline refractories was analysed, supplement 1. As has been shown, ladle preheating has a big influence on the wear of the refractories. The main mechanism of refractory degradation at this stage is decarburization. This results in an increased porosity, de-bonding and total loss of matrix strength for the refractory in use. In addition, this is more severe for the refractories without antioxidants. The preheating fuel plays an important role regarding the extent of the refractory wear. For example, it has been shown that using a coal-gas fuel is less detrimental to the refractory’s resistance to degradation than a mixture of oil and air.

After preheating, the warm ladle is transported to the melting furnace (e.g. EAF) for tapping of liquid steel. To this moment, the maximum temperature of the slagline refractories is around 1000 °C. At tapping, there is a drastic increase in the temperature of the refractories from below 1000 °C to temperatures above 1600 °C. This leads to thermal chemical changes taking place in the refractory material such as the MgO-C reaction and the formation of liquids from the impurities oxides, as shown in supplement 2.

As well known, the pressure is a very important property when it comes to steel refining. The decrease of the system pressure to very low levels (for example below 20000 pa according to the simulation results in figure 19), during steel refining destabilizes the refractory by promoting the MgO-C reaction, reaction 1.

Whereas the MgO-C reaction takes place closest to the hot-face of the working lining (e.g. the magnesia-carbon refractory), the formation of impurity liquid affects the whole refractory from the hot-face to the cold-face. These changes contribute to a decreased corrosion resistance and changes in the physical and mechanical properties of the refractories. At tapping of liquid steel from the melting/primary furnace to the ladle, liquid steel is accompanied by an oxidizing slag (primary furnace slag). Reactions do take place between the slagline refractories and this type of slag composition as explained in supplements 3 and more in the results section of the thesis.
The decreased corrosion resistance of the refractory enhances attacks by the primary furnace slag. Due to the fact that this type of slag contains easily reducible oxides such as iron oxide, this leads to more consumption of carbon/graphite in the refractory. In addition, an increased porosity and wettability. The increase in these two properties enhances the attack of the slagline refractory by the steel refining slag. The refractory degradation at this stage is caused mainly by the reactions between the refractory and slag components. The reactions between these two phases may lead to the formation of low temperature melting phases such as calcium aluminates and silicates, and merwinite as shown in supplements 3 and 4. The state of the reaction products during steel refining leads to accelerated wear in the slag zone, more especially for the dolomite refractories.

As has been shown, the work in the different supplements interacts providing thorough analyses of the degradation mechanisms of the slagline refractories in use. Also, a better understanding of the behaviour of the refractory materials in the steel refining condition and the causes of the accelerated wear in the slag zone was obtained.
7. CONCLUSIONS

The work in this thesis has been focused on the wear mechanisms of the slagline refractories such as magnesia-carbon and dolomite-carbon refractory materials during service in the steel plant. The main findings of this study are presented below:

- The results show that the wear of the slagline refractories of the ladle is initiated at the preheating station, through the redioxidation reactions.

- The degree of the decarburization process is mostly dependent on the preheating fuel. Other factors like the refractory composition and preheating time are also of great importance.

- For the refractories without antioxidants, the refractory decarburization is slower when coal gas is used during ladle preheating than when a mixture of oil and air is used.

- Ladle preheating of the refractories without antioxidants leads to a direct wear of the slagline refractories. This is due to the total loss of the matrix strength, which results in a sand-like product. This finding was found to be independent of the preheating method.

- The reaction between the main components of the refractories, MgO-C reaction, affects magnesia-carbon as well as dolomite-carbon refractories. The MgO-C reaction takes place at 2040 K if the system pressure is 1 atmosphere, according to the calculations results. The decrease in system pressure below 0.2 atmospheres (20000 Pa.) during steel refining makes the MgO-C reaction take place at steel refining temperatures.

- The formation of liquid phases by the impurity oxides during service has a big effect on the high-temperature strength of the refractory and their wear resistance.
• The slags rich in iron oxide lead mostly to the oxidation of carbon in the carbon-containing refractories leading to an increased porosity and wettability, and therefore a reduced corrosion resistance.

• The high contents of alumina and/or silica in the slag promote reactions between the slag components and the dolomite-carbon refractory. This leads to the formation of low-temperature melting phases such as calcium aluminates and silicates.
8. FUTURE WORK

The present work has studied the corrosion/wear of the magnesia-carbon and dolomite-carbon refractories during service. The results presented were based on thermodynamic simulations, post-mortem studies and plant trails. This shows that there is a need to complement the thermodynamic results with some laboratory experiment. Some suggestions are:

- Laboratory experiments to investigate the effect of the different slag compositions used in this work on the wear of the slagline refractories.

- Laboratory experiment to correlate the wear/corrosion of the slagline refractories to their composition with respect to the impurities, at steel refining conditions.

- More thermodynamic simulations of the reaction between the slag compositions and other refractory types used in the slagline, but not included in present work.

- A correlation of the thermodynamic simulations to the mechanical properties of the slagline refractories.
9. REFERENCES

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[18] H. Sunayama and M. Kawahara; “Effect of Dense Layer Formation on Dissolution Rate of MgO-C Refractory in Molten Slag”; Advances in Science and Technology Vol. 45 (2006); pp. 162-166
