Interaction of molten secondary metallurgical ladle slag with MgO-C refractories

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ABSTRACT

The present work experimentally studied the corrosion behavior of MgO-C ladle refractory exposed to molten slag during steel refining. The corrosion of ladle refractories, especially at the slag line, causes issues that require maintenance and repair and can even lead to melt outages.

INTRODUCTION

Carbon bonded ceramics are in high demand in iron and steelmaking industries as the refractory material [1,2]. The addition of carbon into the oxides is considered as the beneficial approach to enhance its thermal properties such as thermal shock resistance, thermal conductivity, minimize the corrosion, and erosion process of the liquid slags, i.e. due to the low wettability of graphite to the liquid slags [3–5]. Magnesia-carbon refractory materials (MgO-C) is the most widespread carbon bonded ceramic for steelmaking industry. They are applied as a lining material in steel ladles, basic oxygen furnaces (BOF), electric arc (EAF) furnaces, and casting furnaces [6–8]. The service life of refractory material can vary from type steelmaking. This is strongly correlated the factors such as: temperature, pressure, atmosphere, and chemical reactivity of the melt. Changing these production conditions could enhance the carbon oxidation, the increasing of open porosity, and the dissolution of MgO grains into slag [9–11]. All of this phenomena lead to a decrease of life time of the refractory [12].

Normally, when the steel ladle is preheated above 500 °C, carbon from the MgO-C refractory material reacts with oxygen in the pores and form CO₂ gas on the surface of the refractory [13]. Subsequently, as the CO₂ temperature rises, the CO₂ gas reacts further with carbon to form CO gas. This type of reaction is called direct carbon oxidation. However, above 1400 °C an indirect carbon oxidation takes place in the MgO-C refractory. This reaction involves the reaction between MgO and carbon, found in resin and graphite, resulting in the formation of Mg and CO gases [14–17].

The oxidation process not only increases the weight loss of the refractory material, but also enhances the open porosity. Open porosity represents the effective volume of pores within the refractory that can be penetrated by melt. An increase in the open porosity of the refractory has a negative effect on the corrosion resistance of the refractory in contact with molten slags and metals. Corrosion in MgO-C can be divided into three stages [14]:

1 - The penetration of the melt into the hot surface of the refractory material. If the temperature of the refractory falls below the solidus temperature of the melt, the melt freezes and penetration stops.

2 - If the melt does not freeze, it penetrates the capillaries of the refractory. The melt penetrates the refractory material through the capillary infiltration, which affects the refractory matrix. Infiltration usually occurs when there are large temperature gradients from the hot surface to the cold surface of the refractory material.

3 - Refractory material is impregnated with melt to such an extent that the core is held together by the melt as the matrix corrodes.

According to the increased requirements, a change in the chemical composition of the steel or process leads to a change in the chemical composition of the slag. These changes directly affect the ability of the slag to dissolve the refractory, and the thermophysical properties of the slag. The penetration and infiltration of refractory material by the melt is influenced by the open porosity, wetting angle of the refractory, viscosity, surface tension, and contact time, Equation 1 [18–21].

\[ r^2 = \frac{r \cdot \sigma \cdot \cos \theta}{2h} \]  

Equation 1

where \( r \) (m) is the open pore radius of refractory, \( \sigma \) (N/m) is the surface tension of the slag, \( \theta \) is the contact angle between the slag and refractory, \( \eta \) (Pa s) is the slag viscosity, \( t \) (s) is the contact time and \( l \) (m) is the infiltration depth.

Hence, a combination of high viscosity, low surface tension, open porosity, and appropriate contact angle serves to minimize the infiltration of slag into the refractory and subsequent dissolution [18]. Besides, temperature also has a great influence on MgO-C refractory wear, with increasing temperature, the viscosity values decrease and the maximum dissolution of MgO in the slag increases. This allows the slag to penetrate deeper into the refractory and actively dissolve its grains, weakening the entire structure.

Borges et al. studied the addition of sodium to desulphurisation slags and showed the sodium addition to calcium-aluminium silicates increases the dissolution of MgO grains and reduces the life of the steel ladle [22]. Guo et al. investigated the effect of VOD (Vacuum Oxygen Decarburization) slag with 15 wt% Al₂O₃ content on the refractory material MgO-C at 1650 °C and low oxygen partial pressure [23,24]. Later on, a porous MgO layer was formed on the sample surface instead of a dense MgO layer. This indicates that under these experimental conditions, Mg gas oxidation from molten oxides is not complete. Such porous MgO layer in industrial and turbulent conditions is not effective for slowing down the slag infiltration into the refractory material. The authors also argued that at temperatures above 1650 °C, the oxidation of MgO-C by atmospheric oxygen or metal oxides in the slag is limited and the main reaction of decarburization of refractory is indirect carbon oxidation in MgO + C. Liu et al. observed direct and indirect dissolution of MgO particles in a low basicity CaO-Al₂O₃-SiO₂ slag. He demonstrated that the dissolution rate of MgO increases with increasing slag temperature and decreases strongly with increasing MgO concentration in the slag [25]. Wang et al. investigated the dissolution rate of MgO solids in synthetic ladle slag. According to their experimental results, the increase of Al₂O₃ and MgO in slag decreases the dissolution rate of MgO due to the formation of magnesia spinel layer at the interface, and the increase of CaO/SiO₂ basicity also increases the dissolution rate of solid MgO in slag [26]. Several studies have demonstrated that when slags containing Al₂O₃ come into contact with MgO-C refractories, the surface of the refractory forms a protective layer of magnesian spinel. This magnesian spinel layer acts as a barrier, inhibiting the infiltration of slag [27–29].

The present study is a logical continuation of two previous studies, where the effect of SiO₂ addition on changes of thermo-physical properties of slag and the interaction between refining slag with CaO/Al₂O₃ ratio 1:1 on refractory MgO-C material [7,30]. In this study, the focus was on evaluation of corrosion of MgO-C material with altered CaO/Al₂O₃ (C/A) ratio in the slag. This study helps to better understand the effect of C/A and SiO₂ in secondary metallurgy slag on refractory corrosion in magnesia-carbon refractory material.

MATERIALS AND METHODS

The MgO-C samples with 13 wt% of residual carbon based on phenolic resin with adding of Carborex P and 2 wt% of metallic aluminium as an antioxidant, see Table 1. Before the corrosion test, the MgO-C samples catted off from industrial refractory brick with the size 30x30x100 mm. In the upper part of each sample drilled a
25 mm deep hole for installation of Al₂O₃ holder. After cementing of the Al₂O₃ holder into sample body, the MgO-C samples were dried 12 hours at 120 °C.

Table 1. The constituent of MgO-C refractory (wt%).

<table>
<thead>
<tr>
<th>MgO</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>C</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.5</td>
<td>0.6</td>
<td>1.2</td>
<td>0.6</td>
<td>0.1</td>
<td>13</td>
<td>2</td>
</tr>
</tbody>
</table>

The target slags were mixed from industrial slag formers: lime and alumina carrier. The partial size of the slag formers was under 100 μm. All the slags were dried in a desiccator for 24 hours at 120 °C before and after mixing.

According to the CaO/Al₂O₃ (C/A) ratio the slags can be divided into: High-Al₂O₃, Cleanness, and Desulfurization slag. Table 2. C/A ratio is the parameter, determine the task of the secondary metallurgical slag. Slag compositions with C/A-ratio < 1 appear after deep deoxidised steel and steels with high aluminium content. In the case of C/A= 1, the slag has a refining function to agglomerate non-metallic inclusions out of the steel. Slag with C/A > 1 and up to 2 has desulphuration function in steel production processing. The increased MgO content in the High-Al₂O₃ slag is related to its content in the alumina carrier. Also the Table 2 contains the viscosity values of these three slags at 1650 °C from the previous publication [30].

Table 2. Chemical composition of ladle slags (wt%) and viscosity values (mPa*s) at 1650 °C.

<table>
<thead>
<tr>
<th>High-Al₂O₃</th>
<th>Cleanness</th>
<th>Desulfurization</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>30.09</td>
<td>43.33</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>53.86</td>
<td>43.33</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.05</td>
<td>1.08</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>13.91</td>
<td>11.00</td>
</tr>
<tr>
<td>MgO</td>
<td>0.99</td>
<td>1.16</td>
</tr>
<tr>
<td>MnO</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>CaO/Al₂O₃</td>
<td>0.56</td>
<td>1.00</td>
</tr>
<tr>
<td>Viscosity (mPa*s)</td>
<td>1777.24</td>
<td>100.29</td>
</tr>
</tbody>
</table>

The MgO-C corrosion test carried out according to the Finger Testing method, a schematic description of setup is shown in Fig. 1. A pre-dried slag of about 1000 g, melted in a graphite crucible (130 mm height x 80 mm inner diameter) in an induction furnace. After reaching the target temperature, the melt is held for at least 30 minutes at the constant temperature for the homogenization.

At the other hand, the MgO-C sample was carbonised in a metal box under graphite powder for 60 minutes at 1000 °C. Right after carbonisation, the MgO-C samples were immersed into the molten slag for 60 minutes.

At the end of holding time, the MgO-C samples were removed from the slag and cooled in the air, see Fig. 2. The slag solidified on the sample immediately when the sample left the molten slag, and forming a dense layer on the MgO-C surface. Afterward, the samples were embedded epoxy resin and cut crosswise to a thickness of 10 millimetres for optical and SEM- analyse.

Fig. 2. Finger testing: a) immersion of MgO-C sample in molten slag; b) cooling of samples in the air.

RESULTS AND DISCUSSION

Surface analyses of MgO-C

Fig. 3 represents photos of the MgO-C refractory samples immersed in the molten slag at 1650 °C for 60 minutes. After the finger testing experiments, the slag layer was observed to adhere on the surface of the refractories. The thickness of the refractory surface adhered slags was related to wettability of the refractory to the slags, hence, the factors such as the temperature, the roughness, and the porosity of the refractory, and the thermophysical properties of the slags, i.e. surface tension and viscosity of the slag could play an influential role. The present investigation focused on the utilization of a singular type of refractory material as the immersion sample. Consequently, the primary roughness and porosity were assumed to be identical among the specimens. As a result, the depth of corrosion emerged as the determining factor influencing the thickness of the adhered slags. The subsequent analysis considered the influence of viscosity and surface tension on the corrosion process, with specific attention given to the anticipated viscosity value.

The upper part of the refractory material above the slag was oxidised. Compared to the primary MgO-C refractory, the areas that were not in contact with the slag turned from dark to grey. The protective gas employed in the experiments, namely Argon 5.0, contained a minor concentration of oxygen (2-3 ppm oxygen). The oxygen content within the gas initially interacted with the carbon residing on the surface of both the refractory material and the graphite crucible, fostering a reducing atmosphere characterized by the presence of CO gas. Subsequently, the CO gas further reacted with carbon, ultimately yielding CO₂ gas.

Furthermore, a part of the slag was found to be pulled up to the non-immersed part of the refractory to the decarbonised layer. The height of the pulled up liquid slag (h) can be expressed by Jurin’s law [31] as depicted in Equation 2. Clearly, the factors such as surface tension, contact angle, and density of the liquid slag could directly affect the h, consequently they also affect the contact area between liquid slags and refractory, namely the corrosion area. The degraded MgO from the side of refractory to the side of liquid slags could change the factors (surface tension, density, and also the contact angle).

\[
 h = \frac{2\gamma \cos \theta}{\rho g r_0}
\]

Equation 2

where h is the height of the top of the layer to the liquid surface (m); \( \theta \) is the contact angle of the liquid on the crucible wall; \( \gamma \) is the surface tension of the liquid (mN·m⁻¹); \( \rho \) is the density of the liquid (kg·m⁻³); g is the gravitational acceleration and \( r_0 \) is the crucible radius (m).
Photographs immersed MgO-C refractory in the slag melts: a) High-Al₂O₃ b) Cleanliness, and c) Desulfurization

**Microstructure analyse**

Fig. 4 shows the MgO-C sample after contact with the molten High-Al₂O₃ slag. This slag has a high viscosity of 1777 mPa*s at 1650 °C. Because of this high slag viscosity, no visible slag infiltration can be seen. Cracks and ducts in the refractory remain free of slag since the high viscosity of the slag prevents the infiltration of slag into the refractory. Nevertheless, the residual slag build-up on the refractory is up to 2.3 mm.

This is a partially dissolved surface layer of the refractory as well as a cured slag layer on the surface. The slag layer is very dense, which during cooling caused numerous pores and slag cracking. The slag contains high amounts of magnesia spinel, which also increases the risk of slag infiltration into the refractory. The large amount of Al₂O₃ in the slag can break up the MgO grains to form more spinel, which makes the infiltration into the refractory even worse. The SEM-EDX analysis found a large amount of magnesia spinel in the slag and on the refractory surface.

Fig. 5 shows the refractory material in a cleanliness slag. Its viscosity at 1650 °C is seventeen times less (100 mPa*s) than the previous High-Al₂O₃ slag. These values are sufficient to infiltrate the slag into the refractory material, through the capillaries, and to crack the grains. The total slag layer on the refractory surface was 1.7 mm. Also a massive of the solid particles of MgO in the slag were found. This suggests that the slag in this composition cannot dissolve MgO grains due to its saturation in the slag. Such solid dendrites can be released when the slag is cooled on a hot refractory, when the MgO solubility in the slag decreases as the temperature decreases.

Fig. 6 shows MgO-C after contacting with the desulphurising slag. The depth of the slag layer is 1.57 mm due to the low viscosity 70mPa*s of the slag. In picture b), a spherical reduced iron with a diameter of 0.91 micrometre is observed. Although this slag does not contain more than one percent FeO, it is reduced to pure iron and agglomerated into a single sphere on contact with the refractory carbon. Due to the low viscosity this slag is infiltrated deep into the refractory. Infiltration is more active in areas where there is no carbon. These are often splits in the MgO grains, where the slag is infiltrated by the droplet effect. As the slag contains a large amount of CaO, its maximum allowable solubility in the slag drops and it is isolated separately as CaO solid.
CONCLUSIONS

In present work, the effect of different slags on the MgO-C refractory was investigated. The different C/A-ratio in the slag affected the capability of the slag to dissolve the MgO-grain, and prevented slag infiltration into the refractory:

1. Slag infiltration into the MgO-C refractory was not detected at a viscosity of more than 100 mPa*s.

2. Although high-Al2O3 was reacted with the refractory, it could dissolve the MgO grains to form MgAl2O4.

3. Cleanliness slag has low viscosity values, which lead them infiltrate deeper into the MgO-C refractory. At the same time, dissolution of MgO grains was not possible due to their saturation in the slag.

4. The desulfurized slag has the lowest viscosity index, because of its infiltration into the refractory the deepest. Solid CaO is released from the solidified slag as it is saturated with it.

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