Mechanism of Reaction between Refractory Materials and Aluminum Deoxidised Molten Steel

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The conditions of formation of inclusions in steel during ladle refining in MgO-C lined ladles were investigated. From the experimental results as well those of a thermodynamic study conducted in parallel, the following conclusions can be made about the reaction mechanism between the MgO-C refractory and aluminum deoxidised molten steel:

- an internal oxidation-reduction occurs in the MgO-C refractory and aluminum deoxidised molten steel during ladle refining;
- the formation of a thin oxide layer at the interface is due to the reaction between magnesium vapour and aluminum dissolved into the molten steel and the CO(g) generated by the reaction between MgO and C in the crucible walls;
- the oxide inclusions formed in the steel have been shown to consist mainly of MgO, Al2O3 or a mixture of them;
- some of the finest inclusions are believed to be formed as secondary inclusions during cooling and solidification of the steel, and are connected only with the diffusion of magnesium from the crucible to the molten steel.

Thermodynamic calculations indicate that during vacuum refining, as the pressure decreases, the chemical compatibility of carbon-bonded magnesia for ladle lining decreases.

KEY WORDS: aluminum killed steel; reoxidation; inclusions; refractory; low carbon steel; magnesia graphite.

1. Introduction

It is well known that the reactions between refractories and molten steel and slag are closely related to product quality. The use of MgO-C lined ladles for refining of steel in steelmaking processes has received increasing attention over the last years. The thermodynamic calculations indicate that MgO is stable in contact with carbon for \( P_{CO} = 1.013 \times 10^{2} \text{N} \cdot \text{m}^{-2} \) and \( P_{\text{re}} = 1.013 \times 10^{2} \text{N} \cdot \text{m}^{-2} \) at 2123 K. If either or both of the products of the reaction, Mg(g) or CO(g), are swept away, e.g. by operating at reduced pressures or under flow conditions, the reaction MgO(s) + C(s) = Mg(g) + CO(g) can be made to proceed at a lower temperature.\(^1\) According to Schwerdtfeger\(^2\) and Brabie\(^3\) CO(g) and Mg(g) formed within the brick will diffuse via pores to the steel side where they can react with the molten steel.

Some authors\(^4,5\) argued that superior resistance of carbon-bearing MgO refractories in a Basic Oxygen Furnace vessel is due to the nonwetting character of the carbon or to the flow of CO gas that could retard the slag penetration. According to Kim and Lu\(^6\) and Watanabe et al.\(^7\) the beneficial effects of the presence of carbon in Basic Oxygen Furnace magnesite bricks are mainly due to the formation of a dense MgO layer behind the hot face. As the reduction proceeds in the brick, porosity will increase and Mg(g), formed in the brick, will be reoxidised near the surface. A dense layer of magnesia will form and prevent further slag penetration into the brick. Therefore, the Basic Oxygen Furnace process itself is consistent with the criterion of the optimum use of carbon refractories. In Argon Oxygen Decarburisation processes and ladle furnaces for refining of steel the situation is quite different, as the oxygen partial pressure at the hot face is much lower and the conditions for dense magnesia formation do not exist within the brick. The producers of very clean steel often claim the presence of magnesium compounds (MgO or MgO-Al2O3) as inclusions in the steel. This is connected to the reaction between refractories and the steel during ladle refining of molten steel in MgO-C lined ladles.

Important industrial information for preventing the formation of the above inclusion types can be obtained by understanding of the reaction mechanisms at the metal–refractory interface during steel refining in MgO–C lined ladles.

2. Experimental Procedure

The crucibles (25 mm OD × 15 mm ID × 40 mm depth) were cut from a commercial MgO-C brick with the following chemical composition: MgO = 97.3%, CaO = 2%; SiO2 = 0.3%; Al2O3 = 0.1%; Fe2O3 = 0.2%; carbon retained = 12.5%. Refractory crucibles were placed in a larger graphite crucible and heated to 1873 K for 45 min before the test. Aluminum killed steel was made before the experiments from commercial pure iron (C = 0.004%; Si = 0.01%, Mn = 0.16%; P = 0.004%, S = 0.002%) with the addition of 0.02%, 0.065% and 0.14% metallic aluminum. Rods of each alloy were obtained by suction of the melt into 5mm silica tubes. A test crucible containing 50 g steel was placed in a larger graphite
crucible and held at 1873 K in argon atmosphere for 30 and 60 min, respectively. Before each experiment the furnace was refilled many times with argon and during the experiments it was flushed with 3 l/min of argon gas. The inert cylinder gases used for the experiments were dried by passage through silica gel. After the experimental runs, the appearance and the microstructure of a cross-sectional steel sample surface were examined under an optical microscope, a scanning electron microscope (SEM) and by an electron probe microanalyser (EPMA).

3. Experimental Results

Figure 1 shows the microstructure of the MgO-C crucible/steel interface when aluminium deoxidised molten steel is held in MgO-C crucible at 1873 K for and 60 min. The layer buildup was a network of particles and was found to consist of pure MgO or MgO·Al₂O₃, based on the results of SEM investigations shown in Fig. 2. Magnesium and/or aluminium and oxygen react to form a dense layer of oxide and, as the reduction reaction continues, there is a pressure buildup behind this layer. Some magnesium condensed on the colder parts of the furnace. The oxide layers often appeared very fragmented and this could be the result of high Mg(g) and CO evolution. The morphology of the surface structure, however, may also have changed during cooling. On the other hand, a complex magnesium–calcium silicate slag is formed during heating and maintaining the crucible at 1873 K. Such slag could be a medium possibly transporting large amounts of MgO which reacted with carbon in our experiments. It should be noted that the layer formed at the interface contains some CaO and SiO₂ together with the MgO and Al₂O₃, which could be due to volatilisation and oxidation reactions.

Microscopic observations of the steel samples showed that inclusions formed were not always distributed homogeneously throughout the sample structures. A cross section of a sample could be divided into two types of regions: areas with clusters of MgO·Al₂O₃, mixed oxides and the nonclustered area, where the inclusions were very small and their sizes were mainly under 3 microns. It should be noted that most of the clusters were located along the crucible wall (Fig. 3).

The initial aluminum content and the holding time were found to have a pronounced effect not only on the formation of clusters, but also on the composition and morphology of the inclusions. Typical inclusions are shown in Fig. 3. The SEM analyses showed that the inclusions consisted of MgO, Al₂O₃ or a mixture of them. Spinel inclusions occurred in three main forms: as isolated particles, as clusters, or in association with sulphides. As the molten steel did not contain magnesium, the magnesium content in the inclusions could be connected only to the diffusion of magnesium from the crucible into the molten steel.

Chemical analyses prove that the concentrations of carbon in the melt increases, while the aluminum content decreases. The total oxygen content was around 35:10⁻⁴ o/o. The magnesium content of the steel samples was around 4:10⁻⁴ o/o, which is far below the calculated equilibrium concentration of magnesium in the melts. This indicates that magnesium must evaporate from the molten steel and condense on the crucible and furnace walls.

4. Discussion

4.1. Estimation of Inclusion Composition

The equilibrium constant of magnesium and oxygen reported in the literature⁸⁻¹¹ varies from 5.8×10⁻¹⁰ to 7.73×10⁻⁴. In the following calculations the value reported by Nadif and Gatellier¹¹ will be used. There is believed to be an equilibrium between MgO in slag and [Mg] and [O] in molten steel, according to the reaction:

\[ \text{MgO(s)} = [\text{Mg}] + [\text{O}] \]  

for which the equilibrium constant is given by:

\[ \log K_{\text{MgO}} = \log (a_{\text{MgO}}) = 8.24 - 26110/T \]  

where \( a_{\text{MgO}} \) is the activity of magnesium oxide,
the standard state being the pure substance in the solid state.

At 1873 K a value of $K_MgO=1.99\cdot10^{-6}$ is calculated.

According to our calculations the partial pressure of magnesium at the refractory interface should be $0.091\cdot10^5$ N·m$^{-2}$ at 1873 K which, together with the relation (3)$^{12}$:

$$\%Mg=0.031P_{Mg} \ldots \ldots \ldots (3)$$
gives a dissolved magnesium content of $28.2\cdot10^{-4}$ %, that corresponds to a dissolved oxygen of $7\cdot10^{-4}$ %.

The formation of spinel is practically a very significant aspect of the reaction between MgO-C refractory and aluminum deoxidised molten steel. As the magnesium gas diffuses into the molten steel the following reaction is taking place:

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

for which the equilibrium constant is written as:

$$\log K_{\text{spinel}}= \log (a_{\text{Mg}}a_2^{\text{Al}}a_4^{\text{O}})/(a_{\text{MgO} \cdot \text{Al}_2\text{O}_3})$$

According to Hauck et al.$^{10}$ an equilibrium constant of $5.6\cdot10^{-21}$ is calculated for the formation of the spinel when the activities of magnesium, aluminum and oxygen are in mass percentage, the standard state being the infinitely dilute solution of Fe-Mg, Fe-Al and Fe-O systems. The solid state of MgO-Al$_2$O$_3$ is taken as reference state. Taking into account the mass contents of 0.0028% of magnesium and 0.007% of oxygen an aluminum content of 0.0028% can be in equilibrium with the MgO-Al$_2$O$_3$. The dissolved aluminum content in the molten steel during the experiments was always higher than the above value. SEM investigations confirm the existence of such inclusions in the steel samples (Fig. 3).

Spinel can also be formed according to the reaction:

$$3[\text{Mg}]+4\text{Al}_2\text{O}_3(s)=2[\text{Al}]+3\text{MgO} \cdot \text{Al}_2\text{O}_3 \ldots \ldots \ldots (5)$$

According to Itoh et al.$^9$ at higher Mg level Al$_2$O$_3$ can react to form MgO according to the following reaction:

$$3[\text{Mg}]+\text{Al}_2\text{O}_3(s)=2[\text{Al}]+3\text{MgO} \ldots \ldots \ldots (6)$$

Microscopic observations of the samples showed that the inclusions found in the samples were very small. SEM and EPMA analyses showed that the inclusions consisted of MgO or Al$_2$O$_3$ or mixtures of them, but not of stoichiometric MgO in spinel composition. As the master alloys did not contain any magnesium, the presence of MgO in the inclusions should indicate the result of the contamination by the refractories/steel reaction. This was in good agreement with the inclusions analysed from the steel samples before melting when no MgO content was found. Many of the inclusions were probably formed during cooling or solidification of the steel.

### 4.2. On the Formation of an Oxide Layer at the Interface

According to Pickering and Batchelor$^1$ and to Watanabe et al.$^7$ at high temperature the reaction MgO(s)+C(s)=Mg(g)+CO(g) proceeds to the right and Mg(g) is diffusing towards the free surface of the sample where it encounters a higher $P_0$, and is oxidised to MgO, which condenses and forms a MgO layer.

At the same time, according to Schwertfiger,$^2$ Brabie$^3$ and Poirier et al.$^{13}$ CO(g) formed during MgO(s) reduction by carbon will diffuse to the interface where it will react with the molten steel forming MgO and Al$_2$O$_3$ according to the following reactions:

$$2[\text{Al}]+3\text{CO(g)}=\text{Al}_2\text{O}_3(s)+3[\text{C}] \ldots \ldots \ldots (7)$$

$$[\text{Mg}]+\text{CO(g)}=\text{MgO(s)}+[\text{C}] \ldots \ldots \ldots \ldots (8)$$

Reaction occurs in two stages. The first stage takes place immediately after the reactive 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. Eventually the layer is broken at a weak point and the oxide layer is entrapped into the molten steel (Fig. 2). Pickering and Batchelor observed the same phenomenon in their studies on the C-MgO reaction in BOF refractories. They pointed out that the layer is pierced at a weak point and magnesium metal vapour streams through the orifice to form a horn of MgO outside the brick. It must be noted that according to Watanabe et al., the thickness of the MgO layer would increase by cooling Mg(g) and CO(g), which coexist at high temperature.

The maximum value of \( P_{\text{CO}} \) at the interface can be calculated under the assumption that it is in equilibrium with [C] and [O] in the molten steel using the relation: \[ \%C \cdot \%O = 0.0025P_{\text{CO}}. \]
The initial carbon content of the melted steel was 0.004%.

As the steel is aluminium deoxidised, there is believed to exist an equilibrium between Al, O, and Al. The standard state being the infinitely dilute solution of Fe-Al and Fe-O, the dissolved oxygen could be calculated using the equilibrium constant: \[ K_{\text{Al}_2\text{O}_3} = 2.51 \times 10^{-14} \] to be 4 \( \times \) 10^{-4}, 1.8 \( \times \) 10^{-4} and 10^{-4}%, for 0.02, 0.065, and 0.14% Al, respectively. Now the \( P_{\text{CO}} \) can be calculated as 6.6 \( \times \) 10^{-8}, 2.9 \( \times \) 10^{-9} and 1.7 \( \times \) 10^{-9} \( \text{N} \cdot \text{m}^{-2} \), for the experimental aluminium contents, respectively. The above \( P_{\text{CO}} \) is less than the equilibrium partial pressure of the calculated carbon monoxide imposes by the refractory inside the crucible wall. The possibility of the reaction of CO with molten steel at the interface according to Eqs. (7) and (8) is increased and the carbon and oxygen dissolve into the steel. At that point the alumina and/or magnesium precipitate at the interface between the steel and crucible.

**Figure 4** summarises the mechanisms of the reaction between the molten steel deoxidised by aluminium and MgO-C refractories during the ladle refining.

5. **Conclusions**

Laboratory experiments were conducted to investigate the reaction between aluminium deoxidised molten steel 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 primarily forming Mg(g), SiO(g) and CO(g) which can react with molten steel.

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(g) generated by the reaction between MgO and C in the crucible walls.

The oxide inclusions in the steel have been shown to consist of MgO, Al2O3 or a mixture of them.

The composition range, origin and mechanism of formation of the oxide inclusions have been discussed and it is concluded that MgO and spinel could be formed. Some of the finest inclusions are thought 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 crucible to the molten steel.

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