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Generation Mechanism of MgO and Al₂O₃ Inclusions in 51CrV4 Spring Steel Based on the Ion–Molecule Coexistence Theory

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Received: 1 July 2019; Accepted: 24 July 2019; Published: 26 July 2019

Abstract: The presence of MgO·Al₂O₃ inclusions in 51CrV4 spring steel is detrimental to the alloy’s castability and fatigue properties. To effectively suppress these inclusions during production, accretions were collected from the immersion nozzle, and the MgO·Al₂O₃ inclusions in the steel billet were investigated. The generation mechanism of the inclusions was evaluated based on the ion–molecule coexistence theory, and the mass action–concentration model of CaO–SiO₂–Al₂O₃–MgO–FeO–MnO slag was developed. Industrial experiments showed that nozzle clogging was primarily caused by MgAl₂O₄ spinel inclusions, and the MgO·Al₂O₃ spinel inclusions in the steel billet were investigated by non-aqueous electrolysis. The model calculation results indicate that the Mg content increased with an increasing basicity, CaO/Al₂O₃ ratio, and Al content during the ladle furnace (LF) process. In contrast, the Mg content decreased with increasing CO pressure under Ruhstahl-Hausen vacuum degassing process (RH) conditions.

Keywords: MgO·Al₂O₃ inclusions; mass action–concentration model; slag basicity; CaO/Al₂O₃ ratio; ion–molecule coexistence theory

1. Introduction

In recent years, the increasing demand for alloyed steels with excellent properties has led to efforts to enhance the castability, surface quality, toughness, and fatigue behaviors of alloyed steels [1–4]. Due to the addition of Cr and V, 51CrV4 spring steel exhibits an excellent intensity, fatigue performance, and hardenability; thus, it has attracted considerable attention for use in large damping springs, suspension springs, and flat springs [5,6]. During the production of 51CrV4 steel, a high-basicity slag is adopted, as it is conducive to the removal of inclusions in bulk steel, desulfurization, and reducing the total oxygen content, but results in the formation of detrimental MgO·Al₂O₃ inclusions [7–9]. These inclusions have a steady face-centered cubic structure with a high melting point and are hard and un-deformable [10]. They tend to accumulate on the submerged entry nozzle (SEN) [2,11,12], resulting in nozzle clogging during casting. Furthermore, the accretions on the SEN might desquamate and become entrapped in the solidified shell, resulting in serious decreases in the internal quality [13]. Therefore, MgO·Al₂O₃ inclusions are detrimental to the final 51CrV4 product and its castability. Although a small amount of dissolved Ca can modify the MgO·Al₂O₃ spinel inclusions [9,14–17], the Ca treatment has a limited effect on large clusters of MgO·Al₂O₃ inclusions [18].

The generation and control of MgO·Al₂O₃ inclusions in stainless steels have been extensively investigated, because these inclusions are harmful to both the surface quality and forming properties of the final products [2,8,19–22]. They are thought to be generated from sources of Mg in liquid steel
via the reduction of MgO in slag or MgO-based refractory [8,23–25]. Many studies have found that the compositions of top slag and refractory material strongly affect the inclusion composition [16,17,21,26–37], as summarized in Table 1.

Table 1. The relationships between compositions of slag or refractory and inclusions.

| Steels                      | Slag/Refractory | Inclusions          | Main Finding                                                                 | Ref. |
|-----------------------------|-----------------|---------------------|-------------------------------------------------------------------------------|------|
| High strength alloyed       | CaO-SiO$_2$–Al$_2$O$_3$–MgO | MgO-Al$_2$O$_3$      | log($X_{MgO}/X_{Al}_2O_3$) of inclusions and log($a_{MgO}/a_{Al}_2O_3$) in slag exhibiting a good linear relation. | [16] |
| High strength alloying      | CaO-SiO$_2$–Al$_2$O$_3$ | MgO-Al$_2$O$_3$–CaO | MgO-Al$_2$O$_3$ inclusions can be modified to liquid ones by high-basicity slag | [17] |
| Ferritic stainless steel    | CaO–Al$_2$O$_3$–MgO | MgO-Al$_2$O$_3$     | log($X_{MgO}/X_{Al}_2O_3$) of inclusions and log($a_{MgO}/a_{Al}_2O_3$) in slag showing a good linear relation. | [21] |
| Al-killed ferritic stainless steel | CaO–SiO$_2$–Al$_2$O$_3$–MgO | MgO-Al$_2$O$_3$ | MgO contents in inclusions decreased with the declining of CaO/SiO$_2$ and CaO/Al$_2$O$_3$ ratio. | [26] |
| Mn and V alloyed steel      | CaO–SiO$_2$–Al$_2$O$_3$–MgO–CaF$_2$ | Spinel | The generation behavior of inclusion was influenced by aMgO in the initial slag. | [27] |
| Al-killed steel             | CaO–SiO$_2$–Al$_2$O$_3$–MgO–FeO | MgO-Al$_2$O$_3$ | The content of FeO in slag plays an important role in the formation of MgO-Al$_2$O$_3$ inclusions. | [28] |
| Bearing steel               | CaO–SiO$_2$–Al$_2$O$_3$–MgO | CaO–SiO$_2$–Al$_2$O$_3$–MgO | Thermodynamic for the formation of spinel inclusions was made. | [29] |
| Fe–Mn–S–C–Al steel          | CaO–Al$_2$O$_3$–SiO$_2$–CaF$_2$–MgO/FeO–C refractory | Mg$_2$Al$_2$O$_4$ | The calculated results at different composition of slag and steel were in good agreement with the experimental results. | [30] |
| Extra-low-oxygen steel      | MgO-based refractory and MgO bearing slag | MgO-Al$_2$O$_3$ spinel | MgO-based refractory supplied more Mg into liquid steel than refining slag. | [31] |
| AI deoxidized molten steel  | MgO–C refractory | MgO-Al$_2$O$_3$ | An internal oxidation–reduction occurs in the MgO–C refractory at elevated temperature. | [32] |
| AI-killed molten steel      | Mg–Cr refractory | MgO-Al$_2$O$_3$ spinel | Mg and Cr dissolved from the refractory, and lead to the increasing contents of Mg and Cr in the liquid steel. | [33] |
| Fe–Al alloy                 | MgO-based refractory | MgO-Al$_2$O$_3$ spinel | The generation of a spinel layer at the interface was attributable to oxidation–reduction reactions and phase transformation. | [34] |
| Steels                      | MgO-based refractory | Spinel | Improving the resistance of MgO-based refractory to slag penetration is good to improve steel cleanliness. | [35] |
| AI-killed steel             | MgO refractory | Spinel | The decomposing of MgO refractory plays a key role in the dissolution of MgO refractory in Al-killed steels. | [36] |
| 304 stainless steel         | CaO–Al$_2$O$_3$-based slag | Spinel | A thermodynamic model was developed to predict slag–steel–inclusion reactions. | [37] |

Compared to stainless steels, the suppression of MgO-Al$_2$O$_3$ inclusions in alloyed spring steels has the potential to provide a superior castability and fatigue performance. In this study, the generation mechanism of MgO-Al$_2$O$_3$ inclusions in 51CrV4 spring steel refined by CaO–SiO$_2$–Al$_2$O$_3$–MgO–FeO–MnO slag was investigated, based on the ion–molecule coexistence theory (IMCT) combined with industrial experiments, and influential factors were discussed.

2. Experimental and Methods

2.1. Nozzle Clogging

Nozzle clogging is occasionally observed during the production of 51Cr4V steel. To understand the causes of nozzle clogging, accretions taken from the SEN were identified by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The XRD analysis indicated that the accretions primarily consisted of MgAl$_2$O$_4$ (Figure 1).
The smelting process of 51CrV4 spring steel can be described as BOF→LF→RH→calcium treatment (soft blow)→slab continuous casting. During basic oxygen furnace (BOF) tapping, Al ingots were employed for preliminary deoxidation and V–Fe and Cr–Fe as the alloying elements. When the ladle reached the ladle furnace (LF) station, a high-basicity slag was used, and Al particles were added into liquid steel for final deoxidation. During the LF process, V–Fe and Cr–Fe were added to final composition adjustment. After degassing in Ruhstahl-Hausen vacuum degassing process (RH) for 20 min, the Ca–Si wire was fed to modify the inclusions and the removal of inclusions by soft blowing about 15 min was done. Finally, the liquid steel was sent to the continuous casting (CC) platform. The average compositions of 51CrV4 spring steel and refining slag are given in Tables 2 and 3, respectively.

2.2. Types of MgO·Al2O3 Spinel Inclusions in 51CrV4 Spring Steel

The smelting process of 51CrV4 spring steel can be described as BOF→LF→RH→calcium treatment (soft blow)→slab continuous casting. During basic oxygen furnace (BOF) tapping, Al ingots were employed for preliminary deoxidation and V–Fe and Cr–Fe as the alloying elements. When the ladle reached the ladle furnace (LF) station, a high-basicity slag was used, and Al particles were added into liquid steel for final deoxidation. During the LF process, V–Fe and Cr–Fe were added to final composition adjustment. After degassing in Ruhstahl-Hausen vacuum degassing process (RH) for 20 min, the Ca–Si wire was fed to modify the inclusions and the removal of inclusions by soft blowing about 15 min was done. Finally, the liquid steel was sent to the continuous casting (CC) platform. The average compositions of 51CrV4 spring steel and refining slag are given in Tables 2 and 3, respectively.
Table 2. Average composition of 51CrV4 spring steel (wt%).

| C   | Si  | Mn  | P  | S  | Al  | Cr  | V  | Fe  |
|-----|-----|-----|----|----|-----|-----|----|-----|
| 0.51| 0.23| 0.94| 0.01|0.008|0.024|1.02|0.16| balance |

Table 3. Average composition of refining slag (wt%).

| CaO | SiO₂ | MgO | FeO | MnO | Al₂O₃ | CaO/Al₂O₃ |
|-----|------|-----|-----|-----|-------|-----------|
| 50.19| 8.2  | 7.49| 0.35| 0.18| 33.59 | 1.49      |

Three types of MgO-Al₂O₃ spinel inclusions in the steel billet were evaluated via non-aqueous electrolysis: Independent MgO-Al₂O₃ inclusions (Figure 3a); modified MgO-Al₂O₃ spinel inclusions primarily containing Mg, Ca, Al, and O (Figure 3b), which was the dominant inclusion type; and modified spinel inclusions mainly consisting of Al, Ca, and O (Figure 3c). The spinel-type inclusions exhibited three-dimensional shapes with spherical morphologies, and the energy spectra given in Figure 3 are all for point A.

Figure 3. Images and energy spectra of MgO-Al₂O₃ spinel-type inclusions extracted by non-aqueous electrolysis: (a) Independent MgO-Al₂O₃ inclusions; (b) modified spinel inclusions containing Mg, Ca, Al, and O; (c) modified spinel inclusions consisting of Al, Ca, and O.
To assess the inclusions during the LF refining process, RH, and calcium treatment, respectively, the steel specimens taken with pail samplers were also investigated before and after LF and RH after polishing; the schematic diagram of sampling locations is given in Figure 4.

The evolution of mean mass fraction of inclusions in the specimens is shown in Figure 5. Figure 5 indicated that no MgO·Al₂O₃ spinel inclusions were found before LF; MgO·Al₂O₃ inclusions containing small amounts of CaO began to form after LF. The number of MgO·Al₂O₃ spinel inclusions increased after RH, and the dominant inclusion type was MgO–Al₂O₃–CaO, which was attributed to the calcium treatment after RH. Therefore, the inclusions transformed through Al₂O₃ → MgO·Al₂O₃ → MgO–Al₂O₃–CaO during the refining process.

2.3. Generation Mechanism of MgO·Al₂O₃ Inclusions

There are four possible Mg sources in liquid steel (Figure 6) [8,13,25,26,38–40]: (1) The reduction of MgO in slag by Al in liquid steel; (2) the reduction of MgO in slag by C under RH conditions; (3) the reduction of MgO in the refractory by Al in liquid steel; and (4) the reduction of MgO in the refractory by C under RH conditions.

The reduced Mg in liquid steel is oxidized into MgO and reacts with Al₂O₃ to generate MgO·Al₂O₃ inclusions via the following reactions:

\[ 2[\text{Al}] + 3(\text{MgO}) = (\text{Al}_2\text{O}_3) + 3[\text{Mg}] \], \hspace{1cm} (1) \\
\[ [\text{C}] + (\text{MgO}) = [\text{Mg}] + \text{CO}_{(g)} \], \hspace{1cm} (2) \\
\[ [\text{Mg}] + [\text{O}] = (\text{MgO}) \], \hspace{1cm} (3)
and

\[(\text{MgO}) + (\text{Al}_2\text{O}_3) = (\text{MgO}\cdot\text{Al}_2\text{O}_3).\]  

(4)

Therefore, to suppress the formation of MgAl\(_2\)O\(_4\) inclusions during steel production, it is essential to study the generation mechanism of inclusions along with the factors influencing their formation. However, it is difficult to determine the activity of each constituent in a complex refining slag. The IMCT provides an effective way to obtain the activity of a complicated slag [41–56]. In the IMCT, the defined mass action–concentration (MAC) is consistent with the classical concept of activity in the slag. The MAC model based on the IMCT has been successfully applied to describe the manganese distribution, phosphate capacity, sulfide capacity, and so on [41–56].

![Figure 4. Schematic diagram of sampling locations.](image)

The evolution of mean mass fraction of inclusions in the specimens is shown in Figure 5. Figure 5 indicated that no MgO·Al\(_2\)O\(_3\) spinel inclusions were found before LF; MgO·Al\(_2\)O\(_3\) inclusions containing small amounts of CaO began to form after LF. The number of MgO·Al\(_2\)O\(_3\) spinel inclusions increased after RH, and the dominant inclusion type was MgO–Al\(_2\)O\(_3–\text{CaO}\), which was attributed to the calcium treatment after RH. Therefore, the inclusions transformed through Al\(_2\)O\(_3\) → MgO·Al\(_2\)O\(_3\) → MgO–Al\(_2\)O\(_3–\text{CaO}\) during the refining process.

![Figure 5. Evolution of mean mass fraction of inclusions.](image)

2.3. Generation Mechanism of MgO·Al\(_2\)O\(_3\) Inclusions

There are four possible Mg sources in liquid steel (Figure 6) [8,13,25,26,38–40]: (1) The reduction of MgO in slag by Al in liquid steel; (2) the reduction of MgO in slag by C under RH conditions; (3) the reduction of MgO in the refractory by Al in liquid steel; and (4) the reduction of MgO in the refractory by C under RH conditions.

![Figure 6. Diagram showing the four potential sources of Mg in liquid steel.](image)

2.4. MAC Model of the Constitutional Units in Slag Systems

Based on the assumptions inherent in the IMCT, the dominant features of the MAC model for the activities of the structural units in the slag can be summarized as follows:

1. The constitutional units in the slag consist of simple ions, ordinary molecules, and complicated molecules;
2. Complex molecules are generated by the reactions of bonded ion couples and simple molecules under kinetic equilibrium;
3. The activity of each constituent in the slag equals the MAC of the structural unit at the steelmaking temperature;
4. The chemical reactions comply with the law of mass conservation.

The calculations were based on actual production involving CaO–SiO\(_2–\text{Al}_2\text{O}_3–\text{MgO–FeO–MnO}\) slag systems. The initial numbers of moles for each composition in 100g of CaO–SiO\(_2–\text{Al}_2\text{O}_3–\text{MgO–FeO–MnO}\) slag were \(a = n_0^{\text{CaO}}, b = n_0^{\text{SiO}_2}, c = n_0^{\text{Al}_2\text{O}_3}, d = n_0^{\text{MgO}}, e = n_0^{\text{FeO}},\) and \(f = n_0^{\text{MnO}}\) respectively.

The balanced mole number of each constituent unit in the slag was defined as \(n_i\), and \(N_i\) denotes the MAC of each constitutional unit. The MAC is equivalent to the classical definition of activity based on the IMCT and can be obtained as follows:

\[N_i = \frac{n_i}{\sum n_i}\]  

(5)

where \(\sum n_i\) is the total balanced mole number of each constitutional unit.

According to the IMCT, at an elevated temperature, the slag system contains four simple ions (Ca\(^{2+}\), Mg\(^{2+}\), Fe\(^{2+}\), Mn\(^{2+}\), and O\(^{2−}\)) and two ordinary molecules (Al\(_2\)O\(_3\) and SiO\(_2\)). Based on the reported phase diagrams, 25 types of complex molecules can be generated at the steelmaking temperature [57,58]. The above mentioned structural units and their parameters are listed in Table 4.
The MACs for all the complex molecules can be determined using the reaction equilibrium constants $K_i$, $N_1(N_{CaO})$, $N_2(N_{SiO_2})$, $N_3(N_{Al_2O_3})$, $N_4(N_{MgO})$, $N_5(N_{FeO})$, and $N_6(N_{MnO})$, which are listed in Table 5.

The mass conservation equations for the CaO–SiO$_2$–Al$_2$O$_3$–MgO–FeO–MnO slag equilibrated with bulk steel can be built based on the definitions of $n_i$ and $N_i$ for each structural unit as follows:

\[ a = \sum n_i(0.5N_1 + N_2 + 3N_3 + 2N_4 + 3N_5 + \frac{N_6}{2} + N_7 + 2N_8 + 3N_9 + N_{10} + 3N_{11} + 12N_{12} + N_{13} + N_{14} + N_{15}) \]  
\[ + 2N_{25} + N_{26} + 2N_{27} + 3N_{28} + N_{29} + N_{30}) \]  
\[ b = \sum n_i(N_2 + 2N_7 + 2N_8 + N_9 + N_{10} + 2N_{16} + 2N_{17} + N_{18} + N_{20} + N_{22} + N_{23}) \]  
\[ + N_{25} + 2N_{26} + 2N_{27} + 2N_{28} + N_{29} + 2N_{30} + 5N_{31}) \]  
\[ c = \sum n_i(N_3 + N_{11} + 7N_{12} + N_{13} + 2N_{14} + 6N_{15} + 3N_{16} + N_{19} + N_{21} + N_{24} + N_{25}) \]  
\[ + N_{26} + 2N_{31}) \]  
\[ d = \sum n_i(0.5N_4 + 2N_{17} + N_{18} + N_{19} + N_{27} + N_{28} + N_{29} + N_{30} + 2N_{31}) \]  
\[ e = \sum n_i(0.5N_4 + N_{20} + N_{21}) \]
and
\[
f = \sum_{i=1}^{31} n_i (0.5N_6 + N_{22} + 2N_{23} + N_{24}). \quad (11)
\]

Based on the theory that the total MAC of each constitutional unit in CaO–SiO\(_2\)–Al\(_2\)O\(_3\)–
MgO–FeO–MnO slag with a fixed amount is equal to unity, Equation (12) can be derived as follows:
\[
\sum_{i=1}^{31} N_i = 1. \quad (12)
\]

Equations (5)–(12) represent the MAC calculation model for each constitutional unit in
CaO–SiO\(_2\)–Al\(_2\)O\(_3\)–MgO–FeO–MnO slag systems. The activity of each constituent in the slag at
the refining temperature can then be obtained.

### Table 5. Reaction formulas, Gibbs free energy, and mass action–concentrations (MACs) [56,59–64].

| Reaction Formulas                  | \(\Delta G^0/\text{J mol}^{-1}\) | MACs                                      |
|-----------------------------------|----------------------------------|-------------------------------------------|
| \((\text{Ca}^{2+} + \text{O}^{2-}) + \text{SiO}_2\) = \((\text{CaO-SiO}_2)\) | \(-21757 - 36.197T\) | \(N_7 = K_1 N_1 N_2\)                     |
| 3/(\text{Ca}^{2+} + \text{O}^{2-}) + 2/(\text{SiO}_2) = (3\text{CaO-2SiO}_2) | \(-236972.9 + 9.62967T\) | \(N_6 = K_2 N_1^2 N_3\)                   |
| 2/(\text{Ca}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = (2\text{CaO-SiO}_2) | \(-102900 - 24.267T\) | \(N_6 = K_1 N_1 N_2\)                     |
| 3/(\text{Ca}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = (3\text{CaO-SiO}_2) | \(-118826 - 6.694T\) | \(N_{10} = K_4 N_1 N_2\)                   |
| 3/(\text{Ca}^{2+} + \text{O}^{2-}) + 2/(\text{AlO}_2) = (3\text{CaO-AlO}_2) | \(-21757 - 29.287T\) | \(N_{11} = K_3 N_1 N_3\)                   |
| 12/(\text{Ca}^{2+} + \text{O}^{2-}) + 7/(\text{AlO}_2) = (12\text{CaO-7AlO}_2) | \(-617977 - 612.119T\) | \(N_{12} = K_2 N_1^2 N_3^2\)               |
| \((\text{Ca}^{2+} + \text{O}^{2-}) + (\text{AlO}_2) = (\text{CaO-AlO}_3)\) | \(-59413 - 59.413T\) | \(N_3 = K_3 N_1 N_3\)                     |
| \((\text{Ca}^{2+} + \text{O}^{2-}) + 2/(\text{AlO}_2) = (\text{CaO-2AlO}_3)\) | \(-16736 - 25.522T\) | \(N_{14} = K_3 N_1 N_3^2\)                 |
| \((\text{Ca}^{2+} + \text{O}^{2-}) + 6/(\text{AlO}_2) = (\text{CaO-6AlO}_3)\) | \(-22594 - 31.798T\) | \(N_{15} = K_3 N_1 N_3^3\)                 |
| 3/(\text{AlO}_2) + 2/(\text{SiO}_2) = (3\text{AlO}_2-2\text{SiO}_2) | \(-4351 - 10.64T\) | \(N_{16} = K_10 N_2 N_3^3\)                |
| 2/(\text{Mg}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = (2\text{MgO-SiO}_2) | \(-56902 - 3.347T\) | \(N_{17} = K_11 N_1 N_4\)                  |
| \((\text{Mg}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = (\text{MgO-SiO}_2)\) | \(-23849 - 29.706T\) | \(N_{18} = K_12 N_2 N_4\)                  |
| \((\text{Mg}^{2+} + \text{O}^{2-}) + (\text{AlO}_2) = (\text{MgO-AlO}_3)\) | \(-18828 - 6.276T\) | \(N_{19} = K_13 N_3 N_4\)                  |
| \((\text{Fe}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = \text{FeO-SiO}_2\) | \(-9395 - 0.227T\) | \(N_{20} = K_14 N_1 N_3^2\)                |
| \((\text{Fe}^{2+} + \text{O}^{2-}) + (\text{AlO}_2) = \text{FeO-AlO}_3\) | \(-59204 + 22.343T\) | \(N_{21} = K_15 N_1 N_3^2\)                |
| \((\text{Mn}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = \text{MnO-SiO}_2\) | \(-38911 + 40.041T\) | \(N_{22} = K_16 N_2 N_6\)                  |
| \((\text{Mn}^{2+} + \text{O}^{2-}) + (\text{AlO}_2) = \text{MnO-AlO}_3\) | \(-36066 - 30.669T\) | \(N_{23} = K_17 N_2 N_6^2\)                |
| \((\text{Mn}^{2+} + \text{O}^{2-}) + (\text{AlO}_2) = \text{MnO-AlO}_3\) | \(-45116 + 11.81T\) | \(N_{24} = K_18 N_2 N_6^3\)                |
| \((\text{Mn}^{2+} + \text{O}^{2-}) + (\text{AlO}_2) + \text{SiO}_2\) = \((\text{MnO-2AlO}_2-5\text{SiO}_2)\) | \(-116315 - 38.911T\) | \(N_{25} = K_{19} N_2 N_6^3\)               |
| \((\text{Ca}^{2+} + \text{O}^{2-}) + (\text{AlO}_2) + 2/(\text{SiO}_2) = \text{CaO-AlO}_2-2\text{SiO}_2\) | \(-4148 + 73.638T\) | \(N_{26} = K_20 N_1 N_2 N_3\)               |
| 2/(\text{Ca}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = \text{CaO-2SiO}_2\) | \(-73638 - 63.597T\) | \(N_{27} = K_21 N_1^2 N_2 N_4\)             |
| 3/(\text{Ca}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = \text{CaO-2SiO}_2\) | \(-205016 - 31.798T\) | \(N_{28} = K_22 N_1^2 N_2 N_4\)             |
| \((\text{Ca}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = \text{CaO-2SiO}_2\) | \(-124683 + 3.766T\) | \(N_{29} = K_23 N_1 N_2 N_4\)               |
| \((\text{Ca}^{2+} + \text{O}^{2-}) + \text{SiO}_2 = \text{CaO-2SiO}_2\) | \(-80333 - 51.882T\) | \(N_{30} = K_24 N_1 N_2 N_4\)               |
| 2/(\text{Mg}^{2+} + \text{O}^{2-}) + 2/(\text{AlO}_2) + 5/(\text{SiO}_2) = \text{MgO-2AlO}_2-5\text{SiO}_2\) | \(-14422 - 14.808T\) | \(N_{31} = K_25 N_1 N_2 N_4^2\)             |

### 3. Results and Discussions

#### 3.1. Effect of Slag Composition on Mg Content in Liquid Steel

After final deoxidation with Al, the dissolved Mg is supplied by the reduction of MgO in slag by
dissolved Al via the following reaction [65]:
\[
2[\text{Al}] + 3(\text{MgO})_s = (\text{Al}_2\text{O}_3)_s + 3[\text{Mg}], \quad \Delta G^0 = 296752.4 + 21.697T (\frac{\text{J}}{\text{mol}}). \quad (13)
\]
The equilibrium constant $K$ for the above process is given by

$$K = \frac{(a_{Al_2O_3,slag}a_{Mg}^3)}{(a_{3MgO,slag}a_{2Al}^2)} = \frac{(a_{Al_2O_3,slag}f_{Mg}^3[\%Mg]^3)}{(a_{3MgO,slag}f_{Al}^2[\%Al]^2)} = \exp\left(-\frac{\Delta G^0}{RT}\right) \quad (14)$$

where $a_{MgO,slag}$ and $a_{Al_2O_3,slag}$ are the activities of MgO and Al$_2$O$_3$ in slag relative to the pure solid state, respectively; $a_{Mg}$ and $a_{Al}$ are the activities of Mg and Al in liquid steel relative to a 1% mass concentration, respectively; and $f_{Mg}$ and $f_{Al}$ are the activity coefficients of Mg and Al in molten steel, respectively. $R$ is the ideal gas constant, whose value is 8.314 J/(mol·K).

The interaction coefficients $e_{ij}$ are given in Table 6. The relationship between the activity coefficient $f_i$ and temperature can be described as follows [66]:

$$\lg f_i(T) = \left(\frac{2538}{T} - 0.355\right)\lg f_i(1873 \text{ K}) \quad (15)$$

where

$$\lg f_i(1873 \text{ K}) = \sum e_{ij}[\%j]. \quad (16)$$

| $e_{ij}$ | C | Si | Mn | P | S | Al | Cr | V |
|---------|---|----|----|---|---|----|----|---|
| C       | 0.14 | 0.08 | –0.012 | 0.051 | 0.046 | 0.043 | –0.024 | –0.077 |
| Mg      | –0.24 | –0.09 | –0.0065 | –0.033 | –1.38 | –0.12 | 0.05 | – |
| Al      | 0.091 | 0.0056 | 0.0065 | 0.033 | 0.030 | 0.045 | 0.012 | 0.06 |

By substituting the values of $f_{Mg}$ and $f_{Al}$ at 1853 K (0.781 and 1.198, respectively) into Equation (14), the effect of the slag composition on the content of Mg at 1853 K is obtained as follows:

$$[\%Mg] = 1.44 \times 10^{-3.17}N_{MgO}\left(\frac{[\%Al]}{N_{Al_2O_3}}\right)^{\frac{1}{3}} \quad (17)$$

Based on the constituents of refining slag shown in Table 3, the compositions of MgO, FeO, and MnO were fixed at 7.5 wt%, 0.35 wt%, and 0.2 wt%, respectively, in subsequent calculations.

Equation (17) gives the thermodynamic model of MgO in slag reduced by Al. Based on the MAC model, $N_{MgO}$ and $N_{Al_2O_3}$ at various basicities and CaO/Al$_2$O$_3$ ratios were calculated, and the relationship between Al and Mg content was obtained (Figure 7). The content of Mg in liquid steel increased dramatically with increasing Al content (Figure 7a,b). When the CaO/Al$_2$O$_3$ ratio was fixed at 1.5, and the Al content remained the same, the Mg content increased slightly with increasing basicity, and the increasing trend was enhanced when the Al content increased (Figure 7a). When the basicity ($B$) was fixed at 6, the Mg content was clearly affected by the CaO/Al$_2$O$_3$ ratio; a higher CaO/Al$_2$O$_3$ ratio in slag corresponded to a higher Mg content in liquid steel (Figure 7b). This suggests that the effect of slag on liquid steel became stronger as the basicity and CaO/Al$_2$O$_3$ ratio increased.

In industrial production, the CaO/Al$_2$O$_3$ ratio of the refining slag was 1.49, the content of acid-soluble aluminum was 0.024 wt%, and the basicity was 6.12. Based on the IMCT, the calculated equilibrium Mg was about 0.82 ppm, which was lower than the measured value 1.4 ppm. It is because that the effect of the lining has not been taken into account, and this will be discussed in the next section.
began to occur during LF process (Figure 5). In order to verify the model ... inclusions. The trend of the model calculation is in agreement with the industrial test results. After Ca treatment, the supply of Mg, and the increasing trend is closely related to the slag compositions, especially the thermodynamic model of MgO in the refractory reduced by Al can be obtained at high Al content, the MgO in the lining can be reduced, and can further lead to the generation of 3.2. Effect of Lining on the Mg Content in Liquid Steel

Currently, MgO is a common component in refractory materials. When the bulk steel has a high Al content, the MgO in the lining can be reduced, and can further lead to the generation of MgO·Al2O3 spinel inclusions. For the refractory, $N_{\text{MgO}} = 1$. According to Equation (17), the following thermodynamic model of MgO in the refractory reduced by Al can be obtained at $T = 1853$ K:

$$\%\text{Mg} = 1.44 \times 10^{-3.12}(\%\text{Al})^2 \cdot \frac{\%\text{C}}{N_{\text{Al}_2\text{O}_3}}.$$

(18)

Based on Equation (18), the relationship between Mg and Al content was obtained (Figure 8). The influence of liquid steel on the refractory increases with an increasing content of Al, which leads to the supply of Mg, and the increasing trend is closely related to the slag compositions, especially the CaO/Al2O3 ratio, as shown in Figure 8b. For a fixed Al content, the Mg content is higher when the effect of the slag is considered compared to when this effect is ignored. This is attributed to the fact that the slag can absorb Al2O3 inclusions, and its ability to absorb inclusions increases with increasing basicity, resulting in an increased Mg content (Figure 8a).

According to the calculation result based on the IMCT, in industrial production, the equilibrium Mg content was 3.2 ppm. Although the real balance is not reached, it indicated that the MgO-based
refractory has a greater potential to supply more Mg into liquid steel than refining slag, which has been verified by Liu [31]. Due to the simultaneous effect of slag and refractory, the Mg content in bulk steel has the enough chance to reach 1.4 ppm. Based on the reported phase stability diagram of Al₂O₃, MgO-Al₂O₃, and MgO [16,17,24,67], and calculated stability diagram of Mg–Al–O system in liquid steel [13,68], the [Mg%] and [Al%] mainly existed in the spinel generation zone, which is the dominating reason for the generation of MgO-Al₂O₃ inclusions. It shows a good agreement with the fact that No MgO-Al₂O₃ spinel inclusions were found before LF, and the MgO-Al₂O₃ inclusions began to occur during LF process (Figure 5). In order to verify the model at real equilibrium conditions, the laboratory experiment will be carried out in the future work.

3.3. Effect of C on the Mg Content Under RH Conditions

The reduction of MgO by C under RH conditions can be written as the following [69]:

\[
(MgO) + [C] = [Mg] + CO\,_{(g)}; \Delta G^0 = 722976.29 - 281.59T \left( \frac{1}{\text{mol}} \right),
\]

with

\[
K = \frac{P_{CO}^{a_{Mg}}}{a_{MgO}^{a_C}} = \frac{f_Mg^{[\%Mg]}P_{CO}}{f_C^{[\%C]}N_{MgO}}.
\]

Substituting \( f_C = 1.107, f_Mg = 0.781 \), and \([\%C] = 0.51\) into Equation (20) gives the following formula for slag at 1853 K:

\[
[\%Mg] = 0.72 \times 10^{-5.67} \frac{N_{MgO}}{P_{CO}}.
\]

For the refractory, \( N_{MgO} = 1 \), which gives,

\[
[\%Mg] = 0.72 \times 10^{-5.67} \frac{1}{P_{CO}}
\]

where \( P_{CO} \) is the pressure of CO. Equations (21) and (22) represent the theoretical models for the reduction of MgO by C under RH conditions. Based on the IMCT, the effect of C on Mg content under RH conditions at different \( P_{CO} \) values was obtained. The content of Mg increases dramatically with decreasing \( P_{CO} \), when C reduces the MgO in slag or lining, and the reduction of MgO in the lining is more crucial. When \( \log(P_{CO}/\text{Pa}) \) reached 3.7 (i.e., \( P_{CO} = 5066.25 \text{ Pa} \), \([\%Mg] \) was about 0. Therefore, when the CO pressure was sufficiently high, the reduction of MgO in the slag or lining was insignificant. Figure 9 shows the effects of basicity and the CaO/Al₂O₃ ratio in the slag on the Mg content. For a fixed CO pressure, the effect of basicity and the CaO/Al₂O₃ ratio on Mg resulting from the reduction of MgO by C in the slag can be ignored.

![Figure 9](image_url)

**Figure 9.** Effects of C on Mg content under RH conditions at different \( P_{CO} \): (a) Effect of basicities at a fixed CaO/Al₂O₃ ratio; (b) effect of CaO/Al₂O₃ ratios at a fixed basicity.
In actual production, the $P_{CO}$ was about 67 Pa. In this case, the Mg content balanced with lining and slag can reach up to 17 ppm and 5 ppm, respectively, based on the IMCT. Therefore, the supply of Mg into bulk steel under RH conditions is more crucial. In this study, the number of MgO-Al$_2$O$_3$ spinel inclusions and the mass fraction of MgO in MgO-Al$_2$O$_3$ spinel inclusions (Figure 5) increased after RH. These were attributed to the fact that, under RH conditions, the MgO in the slag or lining was partly reduced by C to generate MgO-Al$_2$O$_3$ inclusions; on the other hand, the excess Mg can also combine with MgO-Al$_2$O$_3$ to increase the mass fraction of MgO in MgO-Al$_2$O$_3$ inclusions. The trend of the model calculation is in agreement with the industrial test results. After Ca treatment, some of the inclusions were not modified and existed as independent spherical MgO-Al$_2$O$_3$ inclusions, while others were partly modified (Figure 3). To inhibit the formation of undesirable MgO-Al$_2$O$_3$ spinel inclusions, the pressure of CO could be adjusted to decrease inclusion generation. Furthermore, the appropriate application of Ca treatment can ensure that MgO-Al$_2$O$_3$ spinel inclusions are completely modified into liquid MgO-Al$_2$O$_3$-CaO-type inclusions.

4. Conclusions

The causes of nozzle clogging during casting and the existent forms of MgO-Al$_2$O$_3$ spinel inclusions in the steel billet were investigated. Based on the IMCT, the MAC model of CaO-SiO$_2$-Al$_2$O$_3$-MgO-FeO-MnO slag was developed, and the generation mechanism of MgO-Al$_2$O$_3$ inclusions, along with the influential factors, were clarified. The conclusions of the present study are as follows:

1. The XRD and SEM/EDS analyses indicated that the nozzle clogging for 51CrV4 spring steel production was primarily due to the presence of MgAl$_2$O$_4$ spinel inclusions;
2. Three types of MgO-Al$_2$O$_3$ spinel inclusions were observed in steel billets by non-aqueous electrolysis: Pure MgO-Al$_2$O$_3$ inclusions; modified MgO-Al$_2$O$_3$ spinel inclusions containing Mg, Al, Ca, and O, which was the dominant inclusion type; and modified spinel inclusions primarily containing Al, Ca, and O. The assessment of the inclusions in the specimens before and after LF and RH indicated that the inclusions transformed through Al$_2$O$_3$→MgO-Al$_2$O$_3$→MgO-Al$_2$O$_3$-CaO during the refining process;
3. The generation mechanism of MgO-Al$_2$O$_3$ inclusions in 51CrV4 spring steel refined by CaO-SiO$_2$-Al$_2$O$_3$-MgO-FeO-MnO slag was evaluated based on the IMCT combined with industrial results. The effects of slag composition, refractory, and RH conditions on the content of Mg in liquid steel were determined. Model calculation results indicated that the Mg content increased with an increasing basicity, CaO/Al$_2$O$_3$ ratio, and Al content during LF, with the CaO/Al$_2$O$_3$ ratio being the most critical factor. In contrast, under RH conditions, the effects of basicity and the CaO/Al$_2$O$_3$ ratio were insignificant, and the partial pressure of CO was the dominant factor.

Author Contributions: Methodology, D.Z. and J.L.; formal analysis, H.Z.; investigation, Z.X.; writing—review and editing, J.L.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 51704105, No. 51874214, No. 51604198).

Acknowledgments: The authors would like to thank the National Natural Science Foundation of China (Grant No. 51704105, No. 51874214, No. 51604198). The resources were partially provided by the State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology.

Conflicts of Interest: The authors declare no conflicts of interest.

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