Evolution of Oxide Inclusions in G20CrNi2Mo Carburized Bearing Steel during Industrial Electroslag Remelting

Shijian LI,1) Guoguang CHENG,1)* Zhiqi MIAO,1) Weixing DAI,1) Lie CHEN2) and Zhiquan LIU2)
1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083 China.
2) Xining Special Steel Group, Co., Ltd, Xining, 810005 China.
(Received on January 30, 2018; accepted on June 4, 2018; J-STAGE Advance published date: July 21, 2018)

Industrial experimental and thermodynamic analyses were carried out to investigate the evolution of oxide inclusions from consumable electrode to droplet and refined ingot during electroslag remelting (ESR) of G20CrNi2Mo carburized bearing steel. All the oxide inclusions in electrode were CaO–MgO–Al2O3, most of which compositions were located in the liquid region. During droplet formation, most electrode inclusions were absorbed by molten slag, and it was inferred that the Ca content in metal film obviously decreased. A few inclusions were still remained in the liquid steel mainly owing to low interfacial energy. In addition, pure Al2O3 inclusions smaller than 2 μm were generated in droplet, indicating that significant Al-oxidation occurred. The ingot inclusions were low-MgO-containing MgO–Al2O3, Al2O3-based irregular CaO–MgO–Al2O3 and spherical CaO–Al2O3, all of which compositions were outside of the liquid region, indicating that no ingot inclusions could be identified as the relics of that in electrode. Thermodynamic calculations showed that the dissolved Ca and Mg reduced by Al at slag/metal interface could not transfer into the metal pool. FactSage™ 7.0 was used to elucidate the formation of inclusions in metal pool, and the results were basically in accordence with the experimentally observed inclusions, showing that a quasi-thermodynamic equilibrium could be established.

KEY WORDS: bearing steel; electroslag remelting; oxide inclusion; evolution mechanism; thermodynamics.

1. Introduction

G20CrNi2Mo is a typical carburized bearing steel, widely used in various facilities requiring high contact fatigue strength and excellent mechanical properties.1) In China, it is utilized in the railway wagon bearings. With the railway speed-up and heavier load of the train, a higher requirement for the superior quality of G20CrNi2Mo has been put forward in recent years. However, the presence of non-metallic inclusions, particularly the large and low-melting-point ones, can exert a detrimental effect on the fatigue life of bearing steel.2–4) Inclusions can easily initiate fatigue cracks at interfaces between inclusions and steel, which might be the origins of fatigue fractures.5) During traditional secondary refining, large inclusions are occasionally formed owing to technology instability. Because electroslag remelting can eliminate large inclusions and effectively improve solidification structure of target steel,6,7) steel plants in China generally utilize it to produce G20CrNi2Mo. Although the oxygen content of bearing steel usually increases after ESR, its fatigue life obviously increases owing to the presence of fine inclusions. Since ESR is the last adjustable step in controlling steel cleanliness, a thorough understanding of inclusion evolution during ESR is of great importance for producing superior steel.

During past decades, several researchers have contributed to analyzing inclusions behavior.8–16) Although conflicting viewpoints have been presented on which position (i.e., the electrode tip, droplet, or metal pool) played the dominant role in inclusion removal,8–10) a basic agreement has been reached, that is inclusions are mainly removed at the electrode tip.11–13) Li et al.11) counted the number of inclusions in melted and un-melted zones of electrode tip and showed that melted zones presented far fewer inclusions. Fu et al.12) commented on the removal mechanism of oxide inclusions in electrode and indicated that the inclusions could be spontaneously absorbed by molten slag. Mitchell13) pointed out that physical solution of electrode inclusion played a minor role in overall inclusion removal, and no ingot inclusions were relics of that in electrode. Almost all ingot inclusions nucleated and grew in the mushy zone. In addition, Reyes-Carmona et al.14) found that electrode inclusions were almost entirely removed when the droplets were completely formed. The ingot inclusions were more strongly influenced by deoxidation practice. These studies described well the behavior of inclusions during ESR, but most of them were carried out within laboratory scale and focused on that when oxygen content was decreased. It was noted that oxygen content usually increased during electroslag
remelting of bearing steel. Therefore, more detailed analysis about the inclusions behavior during industrial process should be concerned.

In the present study, the characteristics of inclusions in electrode, droplet and refined ingot of G20CrNi2Mo were systematically investigated by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS). The evolution mechanism including the dissolution and removal of electrode inclusions, and the formation of inclusions in droplet and metal pool was proposed in detail.

2. Experimental

2.1. Experimental Procedure and Sampling

Carburized bearing steel G20CrNi2Mo was produced by the process of 70-ton electric arc furnace (EAF) melting → 70-ton ladle furnace (LF) refining → 70-ton vacuum degassing (VD) refining → continuous casting → ESR. Two 2200×250×280-mm billets were utilized as the consumable electrodes.

A schematic of ESR furnace with the capacity to refine 2400 kg ingot is illustrated elsewhere.17) Table 1 lists the furnace specifications and technology parameters. About 75 kg of slag was prepared by mixing CaF₂, CaO, Al₂O₃ and MgO, and pre-melted by a Fe–Al electrode. About 50 g of slag was then taken for chemical analysis. A graphite electrode was used for arcing. After the slag was completely remelted, the consumable electrode was switched into a copper mold. Thirty minutes later, the refining proceeded to a quasi-steady state, at which another slag sample was taken from the slag pool for chemical analysis.

To investigate the characteristics of droplet inclusions, the electrode was quickly withdrawn from the slag pool when exchanging electrodes and then quenched with water immediately. The morphology of electrode tip is shown in Fig. 1(a). The remnant was cooled to room temperature, and one droplet was removed from the area indicated by the square, as shown in Fig. 1(b).

After the ingot was cooled, one 20-mm-high slice was cut from 70 mm from the bottom of the ingot. Then, two steel cuttings and 15×15×15-mm cubic samples were cut from the center and edge of the slice for chemical analysis and microscopic observation.

2.2. Chemical Analysis and Microscopic Observation

Chemical analyses were performed at the National Analysis Center for Iron and Steel (NACIS), China. The concrete methods of analyzing steel and slag were described in Ref. 17).

The characteristics of electrode and ingot inclusions including the composition, number and size were examined on a cubic of cross-section by SEM, EDS equipped with an automated particle explorer (INCA, Oxford Instruments, UK). The area scanned by INCA was 30 mm² and detection limit of inclusions diameter was 1 μm. To reveal the three-dimensional morphologies of typical inclusions, the mirror face of another cubic sample was eroded by AA type electrolytic solution containing 1.0 g of tetramethyl ammonium chloride, 10 mL of diacetone and 90 mL of methanol.18) Characteristics of droplet inclusions were detected by SEM-EDS manually because the droplet surface was curved.

3. Experimental Results

3.1. Chemical Compositions of Slag and Steel

Table 2 lists the chemical compositions of slag pre-melted and at the beginning of normal refining, respectively. From Table 2, the Al₂O₃ and CaF₂ contents decreased while the CaO content increased, mainly due to the reaction between CaF₂ and Al₂O₃, yielding AlF₃, as follows:

\[ 3(CaF_2) + (Al_2O_3) = 3(CaO) + 2AlF_3 \]  

In addition, the SiO₂ and MnO contents increased owing to the oxidation of Si and Mn during refining, which is supported by the differences between the Si and Mn contents of the electrode and that of ingot, as listed in Table 3. As the reaction proceeded, the FeO content also increased, which

| Table 1. Furnace specifications and ESR parameters. |
|--------------------------------------------------|
| Mold height                                      | 2 000 mm  |
| Mold diameter                                    | 470 mm    |
| Slag weight                                      | 75 kg     |
| Ar flow rate                                     | 100–140 L·min⁻¹ |
| Secondary voltage                               | 50–60 V   |
| Alternating current                             | 8 500–9 500 A |
| Average melting rate                            | 6.3 kg·min⁻¹ |

| Table 2. Chemical compositions of slag premelted and at beginning of refining, wt.%. |
|-----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Remelting stage                   | CaF₂           | CaO            | Al₂O₃          | SiO₂           | MgO            | MnO            | FeO            | Pre-melted      |
|                                   | 47.34          | 8.25           | 38.23          | 0.80           | 5.20           | 0.056          | 0.12           | Beginning       |
|                                   |                |                |                |                |                |                |                | 44.26           |
|                                   | 10.19          | 37.74          | 2.60           | 0.28           |                |                |                | 48.63           |
|                                   | 8.00           | 5.20           | 0.05           | 0.005          | 0.0040         | 0.0012         |                | 0.10            |
|                                   | 0.12           |                |                |                |                |                |                | 0.28            |

| Table 3. Chemical compositions of electrode and refined ingot, wt.%. |
|-----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Position                          | C              | Si             | Mn             | Cr             | Ni             | Mo             | Als            | Ca             | Mg             | N              | O              |
| Electrode                         | 0.21           | 0.33           | 0.63           | 0.50           | 1.80           | 0.25           | 0.040          | 0.0008         | 0.0005         | 0.0040         | 0.0012         |
| Ingot                             | 0.22           | 0.25           | 0.60           | 0.50           | 1.80           | 0.25           | 0.030          | 0.0003         | 0.0002         | 0.0041         | 0.0020         |
was the main cause of Al oxidation and increased oxygen content.\(^{19}\) Furthermore, the Ca and Mg contents decreased from 8 and 5 ppm in the electrode to 3 and 2 ppm in the refined ingot, which will be discussed later.

### 3.2. Characteristics of Inclusions in Electrode, Droplet and Ingot

#### 3.2.1. Inclusions in Consumable Electrode

Typical three-dimensional morphologies and SEM-mappings of electrode inclusions are presented in Fig. 2. All the inclusions can be categorized as either high- or low-CaO-containing (i.e., > or <40 mol.% CaO) CaO–MgO–Al\(_2\)O\(_3\). High-CaO-containing CaO–MgO–Al\(_2\)O\(_3\) inclusions showed a melting point below 1 873 K, as shown in Fig. 2(a). Clearly, few MgO was distributed in this type of inclusions while CaO was almost homogeneously distributed throughout the whole region. The high-CaO-containing inclusions presented spherical in morphology and were mostly larger than 5 μm in diameter.

Low-CaO-containing inclusions showed a higher melting point (above 1 873 K), as shown in Fig. 2(b). The shared features of this inclusion are high MgO concentration in the inner part whereas high CaO concentration in the outer part. This kind of inclusion could be described as MgO–Al\(_2\)O\(_3\) as the core, surrounded by an outer CaO–Al\(_2\)O\(_3\) layer. Similar results in Al-killed steel were also obtained by Kang et al.\(^{20}\) Jiang et al.\(^{21}\) Yang et al.\(^{22}\) Deng et al.\(^{23}\) and Yoshioka et al.\(^{24}\) It is concluded that this type of CaO–MgO–Al\(_2\)O\(_3\) inclusions were formed by Ca substitution for part of Mg in MgO–Al\(_2\)O\(_3\) inclusions.

#### 3.2.2. Inclusions in Droplet and Refined Ingot

Figure 3 shows the typical morphologies of droplet

![Fig. 3. Morphologies of typical inclusions in droplet.](image)

**Fig. 3.** Morphologies of typical inclusions in droplet.
Fig. 4. Elemental mappings of typical inclusions in refined ingot. (Online version in color.)
inclusions. Most of inclusions are pure Al₂O₃ less than 2 μm in size, and the shape of the inclusions is nearly globular, as shown in Figs. 3(a)–3(c). The inclusions were newly-generated due to the slag/metal reactions at the electrode tip. In addition, a few inclusions were inherited from the electrode, as shown in Fig. 3(d), indicating that not all the electrode inclusions could be removed during droplet formation.

Typical morphologies and SEM-mappings of inclusions in ingot are shown in Fig. 4. The inclusions could be visually classified as low-MgO-containing MgO–Al₂O₃, Al₂O₃-based irregular CaO–MgO–Al₂O₃ and CaO–Al₂O₃, and spherical CaO–Al₂O₃.

The elemental mappings of MgO–Al₂O₃ inclusion are given in Fig. 4(a). Mg, Al and O were all evenly distributed throughout the whole inclusion. Figures 4(b) and 4(c) show elemental mappings of Al₂O₃-based irregular CaO–MgO–Al₂O₃ and CaO–Al₂O₃ inclusions (comprising most of inclusions in the refined ingot), both of which were smaller than 5 μm. Elemental mappings of spherical CaO–Al₂O₃ inclusions in ingot are shown in Fig. 4(d). Although they are very similar to those of high-CaO-containing CaO–Al₂O₃ inclusion in electrode shown in Fig. 2(a), the CaO content of spherical inclusions in the ingot was much lower than that in electrode.

3.2.3. Composition and Size Distribution of Inclusions

To more accurately determine the inclusion characteristics, the composition distribution of oxide inclusions was marked onto the CaO-MgO-Al₂O₃ ternary phase diagram at 1 873 K, as calculated by FactSage™ 7.0. Inclusions larger than 10 μm were composed of 12CaO·7Al₂O₃, which is considered to be extremely detrimental to the fatigue life.

The composition distribution of droplet inclusions is shown in Fig. 5(b). We observed 200 fields for a total area about 10.0 mm² under 2 000× magnification. The number density of Al₂O₃ was estimated to exceed 10 per mm². The average CaO content of inclusions inherited from electrode decreased and the melting point increased compared to that in electrode.

The composition distribution of inclusions in refined ingot is shown in Fig. 5(c), from which it can be seen that the inclusions were Al₂O₃-based ones, i.e., CaAl₄O₇, Ca₂Mg₂Al₂O₇, MgO-Al₂O₃, and CaAl₄O₇. The melting point of all the inclusions exceeded 1 873 K. The average compositions of electrode and ingot inclusions are given in Fig. 6. The average Al₂O₃ content increased from 38.81% in electrode to 77.07% in ingot, while the average CaO content decreased from 44.41% in electrode to 10.15% in ingot. The variation of CaO in inclusions is consistent with that of Ca from electrode to ingot.

The size distribution of inclusions in the electrode and ingot are shown in Fig. 7. The number densities of the electrode and ingot inclusions were 3.40 and 4.73 per mm², corresponding well with the variation of total oxygen con-
tent. But the number density of inclusions larger than 5 \( \mu \text{m} \) was 1.09 per mm\(^2\) in the electrode and but only 0.24 per mm\(^2\) in refined ingot, showing that ESR was excellent for eliminating large inclusions. Although the total oxygen content increased after ESR, the average size of inclusions obviously decreased, which is favorable for fatigue life.

4. Discussions

According to the above results, it was suggested that the inclusions varied from low-melting-point CaO–MgO–Al\(_2\)O\(_3\) in the electrode to pure Al\(_2\)O\(_3\) in the droplet and high-melting-point Al\(_2\)O\(_3\)-based CaO–(MgO)–Al\(_2\)O\(_3\) in the ingot. To understand the reasons for such variation, thermodynamic calculations were performed and discussed in the following section.

4.1. Behavior of Inclusions in Consumable Electrode

During ESR, electrode tip is remelted layer by layer owing to resistance heat of molten slag, thereby continuously forming thin (50–200 \( \mu \text{m} \)) metal film. It has been reported that the temperature of metal film was close to the liquidus temperature of steel (1 785 K, calculated by FactSage\textsuperscript{TM} 7.0) and the superheat could not exceed 20–30 K.\textsuperscript{26,27} Thus, the temperature of metal film is supposed to be 1 815 K more or less. The Equilib module of FactSage\textsuperscript{TM} 7.0 was employed to investigate the behavior of electrode inclusions during heating, as shown in Fig. 8.

From the equilibrium point of view, the most stable phase was low-melting-point CaO–MgO–Al\(_2\)O\(_3\) in the electrode, which is basically consistent with our observed results. From the solidus temperature of steel (1 750 K) to the temperature of metal film, the dissolved Mg content noticeably increased, while the Ca content slightly increased owing to limited dissolution of CaO–MgO–Al\(_2\)O\(_3\) inclusions. At 1 815 K, the equilibrium contents of dissolved Ca and Mg were 1.38 ppm and 3.70 ppm, respectively. When the contents of total Ca and Mg were 8 and 5 ppm, liquid CaO–Al\(_2\)O\(_3\) was the most stable phase, which has also been confirmed by several researchers.\textsuperscript{20,28,29} Therefore, according to thermodynamic calculation, most Mg in steel would be soluble in steel, while 6.62 ppm of Ca was supposed to be in the form of liquid CaO–Al\(_2\)O\(_3\) inclusions at 1 815 K.

As proposed by Fu,\textsuperscript{12} inclusions tend to move to the slag/metal interface with the update of metal film, and thereafter be absorbed by the molten slag spontaneously. Therefore, it is concluded that the Ca content obviously decreased in the metal film. As listed in Table 3, the Ca content decreased from 8 ppm in electrode to 3 ppm in ingot, mainly due to that most CaO–MgO–Al\(_2\)O\(_3\) inclusions in electrode has been absorbed at the slag/metal interface of electrode tip. Only a few globular inclusions existed in the droplet, proving the accuracy of this viewpoint.

Note that interfacial properties will influence the behavior of inclusions removal. Liquid CaO–Al\(_2\)O\(_3\) inclusions do wet to molten steel well,\textsuperscript{24,30–33} and the electrode melted rather quickly, so not all the inclusions could reach the slag/metal interface.\textsuperscript{13} Therefore, the smaller liquid inclusions were unlikely absorbed by the molten slag. It is observed that the CaO content in inclusions remaining in the droplet decreased, mainly owing to the thermodynamic driving force. That is, with the temperature increasing, the dissolved Ca content in metal film increased. Consequently, the CaO
content in inclusions showed a downtrend.

4.2. Formation of Inclusions in Droplet and Refined Ingot

As mentioned in Section 3.2.2, pure Al$_2$O$_3$ inclusions smaller than 2 μm were generated in the droplet. **Figure 9** shows the behavior of Al$_2$O$_3$ in metal film. As proposed in our previous study,[17] the Al content decreased from 0.04 wt.% in the electrode to 0.03 wt.% in the metal film owing to the oxygen supply by molten slag. Consequently, about 0.019 wt.% of Al$_2$O$_3$ was generated at the slag/metal interface of electrode tip. The Al-oxidation caused by slag/metal reaction was expressed as Eq. (2).

$$2\text{[Al]} + 3\text{(FeO)} = (\text{Al}_2\text{O}_3) + 3\text{[Fe]}$$

$$10^\log K = \frac{45130}{T} - 12.21^{14,35} \quad \text{......... (2)}$$

Simultaneously, most newly-generated Al$_2$O$_3$ inclusions were immediately absorbed by the molten slag. Only few could be remained in the metal film. Because contact time between the slag and steel at the electrode tip only lasted less than a second, the remaining Al$_2$O$_3$ did not have enough time to react with the dissolved Ca and Mg, thus presenting globular morphology and small size. Van Ende et al.[37] investigated the Al$_2$O$_3$ inclusion morphology at the onset of deoxidation, and also found that the inclusions were globular. A similar finding was also reported by Wakoh et al.[38]

The liquid metal leaving the electrode tip contained the generated Al$_2$O$_3$ and a small amount of inclusions inherited from the electrode. When droplets passed through the slag pool, they were superheated by approximately 100–150 K,[13] even reaching the temperature above 2000 K. Although the residence time was very short (0.2–0.5 seconds), inclusions inherited from electrode may further dissolve, since no inclusions in ingot could be identified as relics of that in electrode.

When droplets entered into the metal pool, they immediately mixed with the bulk and underwent a period of cooling. In order to better understand the behavior of inclusions, the temperature distribution of metal pool was first determined by commercial software Meltflow-ESR (developed in cooperation between Prof. Alec Mitchell, University of British Columbia, Canada, and Innovative Research, Inc., Plymouth, Minnesota, USA). The height and radius of the slag pool were set as 0.14 m and 0.235 m, respectively. The depth of metal pool was about 0.13 m, as calculated by Meltflow-ESR. The top surface of the slag pool was defined as zero datum, and the schematic diagram is shown in **Fig. 10**.

**Figure 11** depicts the temperature distribution of half the metal pool, from which it is clear that the temperature in the radial direction was rather evenly distributed while that in axial direction showed a downtrend. At slag/metal pool interface, the temperature distribution was uneven, and the highest temperature was about 1980 K, at which further study should be conducted to determine whether the dissolved Ca and Mg reduced by Al at the interface could transfer into the metal pool. Combining Eqs. (3), (4), and (5), the equilibrium contents of Ca and Mg at the slag/metal pool interface could be calculated as follows:.

$$2\text{[Al]} + 3\text{[O]} = (\text{Al}_2\text{O}_3)$$

$$\log K_\text{Al} = \frac{64000}{T} - 20.57^{39} \quad \text{......... (3)}$$

$$\log K_{\text{Ca}} = \frac{4700}{T} + 4.28^{39} \quad \text{......... (4)}$$

![Image](image_url)
\[ [\text{Ca}] + [\text{O}] = (\text{CaO}) \]
\[ \log K_{\text{Me}} = \frac{7220}{T} + 3.292 \]  

(5)

It has been reported that both the first- and second-order coefficients should be considered in order to accurately calculate the activities of Ca and Mg in molten iron.\textsuperscript{40} The interaction coefficients used in the study are listed in Tables 4 and 5.

The activities of Al\textsubscript{2}O\textsubscript{3}, MgO and CaO in the CaF\textsubscript{2}-containing slag were calculated by Factsage\textsuperscript{TM} 7.0. \textbf{Figure 12} shows the equilibrium Ca and Mg contents calculated for different Al contents. With the content of Al increasing, the Ca and Mg contents also increased. At 0.03 wt.% Al, the equilibrium contents of dissolved Ca and Mg were 0.53 ppm and 0.35 ppm, respectively. The Ca and Mg contents in the melt film were 1.38 ppm and 3.70 ppm. Therefore, it is inferred the Al-reduced Ca and Mg could not transfer into the metal pool. As listed in Table 3, the Mg content decreased from 5 ppm in the electrode to 2 ppm in the ingot, mainly because part of the dissolved Mg was oxidized owing to the low MgO-activity and oxygen supply by molten slag. It is noted that the mechanism governing the Mg-decrease was different from that governing the Ca-decrease which was mainly attributed to the absorption of CaO-containing inclusions at the electrode tip.

The aforementioned analysis demonstrated that the inclusions in droplet were mainly pure Al\textsubscript{2}O\textsubscript{3} owing to the short contact time between slag and steel, and most Mg was soluble in droplet. At slag/metal interface, part of Mg would be oxidized and surplus Mg would precipitate in the form of MgO-containing inclusions in metal pool. Therefore, the MgO content of inclusions in ingot obviously increased compared to that in droplet, as shown in Figs. 5(b) and 5(c).

During steady state remelting, the steel solidification rate is nearly equal to the melting rate of electrode. Therefore, it could be interpreted that the metal pool is static and its shape remained unchanged. Factsage\textsuperscript{TM} 7.0 with FToxid and FSstel databases was used to investigate the formation of inclusions in metal pool, as shown in \textbf{Fig. 13}. CaAl\textsubscript{4}O\textsubscript{7} inclusions began to precipitate at 1 953 K, and the amount largely increased with the temperature decreasing, achieving its maximum at 1 943 K. Then, the amount slightly decreased with temperature further decreasing. From the temperature distribution of metal pool, certain amount of CaAl\textsubscript{4}O\textsubscript{7} inclusions were thought to be generated in the high-temperature zone near the slag/metal pool interface. In the low-temperature area below 1 943 K, nearly no additional CaAl\textsubscript{4}O\textsubscript{7} could precipitate.

With regard to CaO–MgO–Al\textsubscript{2}O\textsubscript{3} inclusions, CaMg\textsubscript{2}Al\textsubscript{16}O\textsubscript{27} began to precipitate at 1 943 K and its content increased with temperature decreasing. At the solidus temperature of steel, the amount reached its maximum. That is to say, CaMg\textsubscript{2}Al\textsubscript{16}O\textsubscript{27} could precipitate throughout nearly the entire metal pool. In addition, some spinel inclusions may be generated at 1 913 K and gradually increase with temperature decreasing, reaching its maximum at 1 815 K. As described in Fig. 5(c), most inclusions in the refined ingot were located in region [1–3, 5–7, 9], most of which are

![Equilibrium contents of dissolved Mg and Ca at slag/metal pool interface.](image)

\[ \text{Equilibrium contents of dissolved Mg and Ca at slag/metal pool interface.} \]

---

**Table 4.** First-order interaction coefficients in molten iron.\textsuperscript{41}

| e\textsuperscript{j} | C | Si | Mn | Al | S | Mg | Ca | Cr | O |
|---------------------|---|----|----|----|---|----|----|----|----|
| Al                  | 0.091 | 0.056 | –   | 0.045 | 0.030 | –1.03 | –0.047 | 0.012 | –34 740/T+11.95 |
| Mg                  | –0.31 | –0.096 | –    | –0.27 | –1.38 | –    | –    | 0.022 | –289\textsuperscript{42} |
| Ca                  | –0.34 | –0.096 | –0.0156 | –0.072 | –336 | –    | –    | 0.014 | –780\textsuperscript{43} |
| O                   | –0.45 | –0.13 | –0.021 | –3.90 | –0.133 | –190\textsuperscript{42} | –310\textsuperscript{43} | –0.0459 | –1 750/T+0.734 |

**Table 5.** Second-order interaction coefficients in molten iron.\textsuperscript{40}

\[
\begin{array}{c}
\kappa_{\text{Al}}^{\text{O}} = -2.419 \times 10^9 + 6.080 \times 10^7 / T \\
\kappa_{\text{Si}}^{\text{Al}} = 36 100 - 1.013 \times 10^6 / T \\
\kappa_{\text{Mn}}^{\text{Al}} = 1.809 \times 10^9 - 5.075 \times 10^7 / T \\
\kappa_{\text{O}}^{\text{Al}} = -2.077 \times 10^8 - 4.864 \times 10^9 / T \\
\kappa_{\text{Si}}^{\text{O}} = -1.904 \times 10^4 + 4.222 \times 10^3 / T \\
\kappa_{\text{Mn}}^{\text{O}} = 70 500 - 1.696 \times 10^4 / T \\
\kappa_{\text{Al}}^{\text{Mn}} = 2.143 \times 10^5 - 5.156 \times 10^3 / T \\
\kappa_{\text{Al}}^{\text{Si}} = -2.513 \times 10^4 + 5.573 \times 10^3 / T \\
\kappa_{\text{Al}}^{\text{Cr}} = -230 \\
\kappa_{\text{Cr}}^{\text{Si}} = -107 + 275 000 / T \\
\kappa_{\text{Cr}}^{\text{Mn}} = 70 500 - 1.696 \times 10^4 / T \\
\kappa_{\text{Cr}}^{\text{Al}} = -107 + 275 000 / T \\
\kappa_{\text{Cr}}^{\text{O}} = -0.023 - 13.78 / T \\
\kappa_{\text{Si}}^{\text{Cr}} = 127.3 + 327 300 / T \\
\kappa_{\text{Al}}^{\text{Si}} = -260 \\
\end{array}
\]
spinel, CaMg$_2$Al$_{16}$O$_{27}$ and CaAl$_2$O$_3$. The theoretical results are basically consistent with the experimentally observed inclusions. Therefore, it is indicated that a quasi-equilibrium state could be established in the metal pool.

5. Evolution Mechanism of Oxide Inclusions from Electrode to Refined Ingot

According to the experimental results and subsequent analyses, the evolution of oxide inclusions from the electrode to droplet and refined ingot is illustrated in Fig. 14. The proposed mechanism could be classified into three steps:

1. In the metal film of electrode tip, most low-melting-point CaO–MgO–Al$_2$O$_3$ inclusions were absorbed by the molten slag, but a few inclusions were still remained in the molten steel owing to low interfacial energy. In addition, the oxygen supplied from the molten slag significantly induced Al-oxidation, thereby forming pure Al$_2$O$_3$ inclusions at the slag/metal interface. Although most of the inclusions were prone to be absorbed by the slag again, a few ones were remained in the steel. Contact time between the slag and the metal film was very short, so the remaining Al$_2$O$_3$ did not have enough time to react with the dissolved Ca and Mg, and therefore presented globular in the droplet.

2. When the droplets detached from the electrode tip, they contained a few electrode-inherited inclusions and pure Al$_2$O$_3$. When the droplets passed through the slag pool, the CaO–MgO–Al$_2$O$_3$ inclusions would further dissolve, since no inclusions in refined ingot could be identified as the relics of that in electrode.

3. When the droplets entered into the metal pool, they immediately mixed with the bulk volume. The Al$_2$O$_3$ acted as heterogeneous nuclei on which inclusions could precipitate, while some inclusions precipitated as a result of homogeneous nucleation. In the high-temperature zone of metal pool, the CaAl$_4$O$_7$ was initially generated and its content quickly reached its maximum. Then, the high-melting-point CaO–MgO–Al$_2$O$_3$ inclusions began to precipitate and their content increased during cooling. It is inferred that most of inclusions in metal pool precipitated at the temperature above liquidus temperature of steel. To summarize, owing to the absorption of inclusions in electrode and the oxygen supply by the molten slag, the original equilibrium in metal film was disrupted, and a new quasi-equilibrium state was established in the metal pool.

6. Conclusions

Industrial experimental and thermodynamic analyses were undertaken to elucidate the evolution of oxide inclusion during industrial ESR process. The following conclusions were obtained:

1. All the inclusions in electrode were CaO–MgO–Al$_2$O$_3$, most of which compositions were located in the liquid region. At the electrode tip, most inclusions were absorbed by the molten slag, but a few were remained in the steel owing to the low interfacial energy. It was inferred that the Ca content obviously decreased in the metal film.

2. Pure Al$_2$O$_3$ inclusions were generated in droplet owing to the oxygen supply by the molten slag. Low-MgO-containing MgO–Al$_2$O$_3$, Al$_2$O$_3$-based irregular CaO–(MgO)–Al$_2$O$_3$, and spherical CaO–Al$_2$O$_3$ inclusions were generated in the metal pool, all of which compositions were located out of liquid region.

3. Thermodynamic calculations showed that the dissolved Ca and Mg reduced by Al at the slag/metal interface could not transfer into the metal pool. The results calculated by FactSage$^\text{TM}$ 7.0 were basically in accordance with the experimentally observed inclusions, indicating that a quasi-thermodynamic equilibrium could be established in the metal pool.
Acknowledgments

The authors wish to express their gratitude to Xining Special Steel Plant as well as to the National Natural Science Foundation of China (Grant No. 51674024) for their financial support.

REFERENCES

1) Z. Y. Li: Special Steel Technol., 16 (2011), 10.
2) J. Monnot, B. Heritier and J. Y. Conge: American Society for Testing and Materials, Philadelphia, PA, (1988), 156.
3) T. Fujimatsu, M. Nagao, M. Nakasaki and K. Hiraoka: Sanyo Tech. Rep., 13 (2006), 62.
4) X. D. Miao, C. M. Yu, C. M. Shi, J. F. Du, H. G. Zhu and G. G. Cheng: J. Univ. Sci. Technol. Beijing, 29 (2007), 771.
5) M. Nagao, K. Hiraoka and Y. Unigame: Sanyo Tech. Rep., 12 (2005), 42.
6) A. Rücker and H. Pfeifer: Magnetohydrodynamics, 45 (2009), 29.
7) V. Weber, A. Jardy, B. Dussoubs, D. Ablitzer, S. Ryberon, V. Schmitt, S. Hans and H. Poisson: Metall. Mater. Trans. B, 40 (2009), 271.
8) O. Madono: Proc. 2nd Int. Symp. on Electroslag Remelting Technology, Air Force Materials Laboratory Manufacturing Technology Division, Pittsburgh, (1969), 48.
9) M. Hasegawa and K. Takeshita: Tetsu-to-Hagané, 62 (1976), 201.
10) Z. B. Li, Y. D. Li, Y. W. Ye and Z. C. Song: Iron Steel, 1 (1966), 20.
11) Z. B. Li, W. H. Zhou and Y. D. Li: Iron Steel, 15 (1980), 20.
12) J. Fu: Acta Metall. Sin., 15 (1979), 526.
13) A. Mitchell: Ironmaking Steelmaking, 1 (1974), 172.
14) F. R. Carmona and A. Mitchell: ISIJ Int., 32 (1992), 529.
15) C. B. Shi, X. C. Chen, H. J. Guo, Z. J. Zhu and R. Hao: Steel Res. Int., 83 (2012), 472.
16) A. Mitchell, F. R. Carmona and E. Samuelsson: Trans. Iron Steel Inst. Jpn., 24 (1984), 547.
17) S. J. Li, G. G. Cheng, Z. Q. Miao, L. Chen, C. W. Li and X. Y. Jiang: ISIJ Int., 57 (2017), 2148.
18) K. Oikawa, H. Ohtani, K. Ishida and T. Nishizawa: ISIJ Int., 35 (1995), 403.
19) S. J. Li, G. G. Cheng, L. Yang, L. Chen, Q. Z. Yan and C. W. Li: ISIJ Int., 57 (2017), 713.
20) Y. J. Kang, F. Li, K. Morita and S. C. Du: Steel Res. Int., 77 (2006), 785.
21) M. Jiang, X. H. Wang, B. Chen and W. J. Wang: ISIJ Int., 50 (2010), 95.
22) S. H. Yang, Q. Q. Wang, L. F. Zhang, J. S. Li and K. Peaselee: Metall. Mater. Trans. B, 43B (2012), 731.
23) Z. Y. Deng and M. Y. Zhu: ISIJ Int., 53 (2013), 450.
24) T. Yoshioka, K. Nakahata, T. Kawamura and Y. Ohsiba: ISIJ Int., 56 (2016), 1973.
25) K. Riyahimalayeri, P. Ölund and M. Selleby: Ironmaking Steelmaking, 40 (2013), 470.
26) M. E. Fraser and A. Mitchell: Ironmaking Steelmaking, 3 (1976), 279.
27) A. Mitchell, J. Szekely and J. F. Elliott: Electroslag Refining, Iron and Steel Institute, London, (1973), 1.
28) H. Todoroki and K. Mizuno: ISS Trans., 30 (2003), 60.
29) H. Todoroki and K. Mizuno: ISIJ Int., 44 (2004), 1350.
30) K. Ogino, S. Haru, T. Miwa and S. Kimoto: Tetsu-to-Hagané, 65 (1979), 2012.
31) J. Wikström, K. Nakajima, H. Shibata, A. Tilliander and P. Jönsson: Ironmaking Steelmaking, 35 (2008), 595.
32) A. L. Kundu, K. M. Gupta and P. K. Rao: Metall. Mater. Trans. B, 20 (1989), 581.
33) B. H. Reis, W. V. Bielefeldt and A. C. F. Vilela: ISIJ Int., 54 (2014), 1584.
34) The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking: Steelmaking Data Sourcebook, Gordon and Breach Science Publishers, New York, (1988), 45.
35) C. R. Taylor and J. Chipman: Trans. AIME, 154 (1943), 228.
36) M. Ettiene: Ph.D. thesis, University of British Columbia, (1970), https://open.library.ubc.ca/cIRcle/collections/ubctheses/831/items/1.0079023, (accessed 1970-11-23).
37) M. A. Van Ende, M. X. Guo, J. Proost, B. Blanpain and P. Wollants: ISIJ Int., 51 (2011), 27.
38) M. Wakoh and N. Sano: ISIJ Int., 47 (2007), 627.
39) H. Itoh, M. Hino and S. Ban-ya: Mater. Trans. B, 28B (1997), 953.
40) L. F. Zhang, Y. Ren, H. J. Duan, W. Yang and L. Y. Sun: Metall. Mater. Trans. B, 46B (2015), 1809.
41) H. Suito and R. Inoue: ISIJ Int., 30 (1996), 536.
42) R. Inoue and H. Suito: Metall. Mater. Trans. B, 25B (1994), 235.
43) H. Itoh, M. Hino and S. Ban-ya: Tetsu-to-Hagané, 83 (1997), 695.