Article

Influence of Pulse Current on Inclusion Properties of Alumina in Molten Steel

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Abstract: In the process of metal purification, the study of controlling the morphology and size distribution of non-metallic inclusions in steel based on electric fields has attracted extensive attention. However, the action mechanism of electric fields on inclusions in liquid steel has not been clearly identified. In this paper, the influence of pulse current on the quantity, size, and distribution of alumina inclusions in liquid steel was explored through a high-temperature energization experiment, and the action mechanism of pulse current was expounded based on the angle of interface free energy. The results show that the number of small alumina inclusions in the steel after electric pulse treatment (the pulse current density was 0.1–3 A/cm², the frequency was 100 Hz, and the pulse waveform was a square wave) was significantly increased compared with the sample without electric pulse treatment, and the particle size was concentrated at 2–5 µm, and the inclusions were concentrated in the upper and lower parts of the sample. However, in the samples without electrification treatment, the large particles of inclusions are the majority, the particle size was concentrated at about 10 µm, and the inclusions were concentrated in the upper and middle parts of the samples. When the pulse current was applied to the molten steel, the interfacial free energy of the internal system of liquid steel alumina inclusion was reduced, the nucleation of alumina inclusion was promoted, the aggregation growth between alumina particles was inhibited, and then the migration and distribution of inclusions were also affected. The experimental results could provide technical support for high-quality steel smelting production to a certain extent.

Keywords: non-metallic inclusion; interface free energy; pulse current; nucleation and growth

1. Introduction

The sources of alumina inclusions (or composite inclusions) in tundish molten steel include deoxidation products, secondary oxidation, and refractory materials that are eroded and peeled off. During the casting process of aluminum-killed steel, the whereabouts of the formed deoxidation products (alumina inclusions) in the molten steel of the tundish can be divided into three situations. Firstly, it may be removed by tundish slag adsorption or captured by the ceramic filter (tundish metallurgy technology) in the process of floating. Secondly, it can be attached and deposited on the inner wall of the immersed nozzle, resulting in nozzle clogging, and finally, it may also enter the mold with molten steel, making the quality of the billet deteriorate [1–5]. Increasing demand for high-quality steel grades has resulted in more strict requirements for the number and size of inclusions in steel, and the existing inclusion removal technology can no longer meet the demand. Therefore, it is urgent to further research and develop new technologies for inclusion removal. In the tundish, the nucleation, collisional growth, and floating of the deoxygenated products occurred continuously, or nearly simultaneously. Once the nucleation and growth behavior of alumina inclusion in molten steel can be controlled, it can be “fully” removed by using tundish metallurgical technology, which can fundamentally cut off the source of alumina and thus reduce the alumina inclusion in molten steel.
Extensive studies have shown that the shape, particle size, and distribution of inclusions in molten steel can be controlled by applying an electric field to molten steel. Zhang and Qin et al. [6–8] treated liquid steel with a pulsed current, which effectively controlled the morphology and distribution of inclusions in liquid metal, thus improving the mechanical properties and corrosion resistance of the steel. Piak and Kim et al. [9–11] verified the charging behavior of oxide particles in cryogenic liquid metal, and treated the liquid metal with an electrostatic field to separate it from oxide particles. Zhang et al. [12,13] and Wang et al. [14] controlled the migration of the inclusions in molten steel by electromagnetic separation technology, so that the metal could be purified. However, the mechanism of the action of electric fields on oxide particles in liquid metals has not been clearly identified.

In recent years, the research on improving the microstructure and properties of metal materials based on electric pulse (ECP) technology has become the focus. The mechanism of ECP is that current can change the Gibbs free energy and solid-liquid interface energy of the system, thus affecting the nucleation and growth processes during metal solidification [15–18].

To sum up, the nucleation, collisional growth, and migration behavior of alumina inclusions are affected when the molten steel in the tundish is treated with a pulse current. Combined with the tundish metallurgical technology, it is fully removed in advance to avoid increasing the source of alumina due to subsequent unsteady production (secondary oxidation, clogging of nozzle, etc.), which improves the number and distribution of alumina inclusions in the slab. Therefore, in this paper, the ECP experiments were carried out to explore the effect of pulse currents on the number, size, and shape distribution of alumina inclusions in molten steel, and to explain the action mechanism of pulse currents on inclusions in steel.

2. Experiment Schemes

2.1. Experimental Materials

The steel used in the experiment was cold heading steel of grade SWRCH22A, and the chemical composition is shown in Table 1. The crucible made of pure corundum was used to hold molten steel, and the graphite crucible was covered for protection. The experimental electrodes were pure molybdenum rods or high-melting-point metal rods with a diameter of 10 mm. The protective atmosphere used in the experiment was high-purity argon with a purity of 99.99%.

| Table 1. Chemical composition of SWRCH22A steel, wt%.
|-----------------|-----|-----|-----|-----|-----|
|                 | C   | Si  | Mn  | P   | S   | Als |
|-----------------|-----|-----|-----|-----|-----|-----|
|                 | 0.220| 0.032| 0.854| 0.025| 0.018| 0.035|

2.2. Experimental Device and Scheme

The experimental equipment is shown in Figure 1. The experimental equipment is mainly composed of the high-temperature tubular resistance furnace, the temperature measurement and temperature control system, the external power supply system, the argon gas protection system, and the water cooling system. The additional power supply equipment includes: a multi-function pulse power supply (output voltage 0–36 V, output frequency 0–500 KHz), and a Pratt and Whitney multi-function oscilloscope.
In the experiment, the steel ingot was heated and melted in the furnace under the protection of argon gas; the temperature was raised to and then kept constant at 1580 °C. In the constant temperature stage, a pulse power supply was introduced for the experiment using electrification treatment, and the electrification treatment time was 30 min. Then, when the temperature in the furnace dropped to 1300 °C, the crucible was quickly lowered into the water tank for water quenching. Several groups of experiments were carried out in the up-and-down energization experiment on liquid steel. The blank sample was not electrified, and other operating conditions were consistent with the energization experiment. The specific parameters of the pulse current were as follows: the current density was 0.1–3 A/cm², the frequency was 100 Hz, and the pulse waveform was a square wave. The energized samples and the control samples were axially sectioned to prepare metallographic samples. The schematic diagram of the sampling location and size is shown in Figure 2. The number and particle size of the inclusions on the surface of the samples were statistically analyzed using an Olympus DXS510 microscope and a scanning electron microscope equipped with INCA software (Oxford Instruments INCA steel, BEIJING HONGCHANG TECHNOLOGY CO. LTD., Beijing China). The composition of the inclusions was determined by SEM-EDS analysis.

Figure 1. Electrification experimental device. Annotations: 1 furnace body, 2 MoSi₂ rod, 3 crucible, 4 energized electrode, 5 air vent, 6 pulse power supply.

Figure 2. Schematic diagram of sampling position and size of metallographic samples.
2.3. Experimental Results and Discussion

Figure 3 shows the microscopic morphology of the distribution of inclusions inside the sample after electrification treatment and non-electricity treatment. As can be seen from the figure, compared with the unenergized samples, the inclusions in the samples after pulse current treatment increased significantly, and the inclusions tended to be fine. A large number of inclusions gathered in the upper part of the energized sample (near the positive electrode); fewer inclusions were distributed in the middle, and more inclusions also appeared in the lower part of the sample (near the negative electrode). However, there were few inclusions in the upper part of the non-energized sample. The inclusions distributed in the middle of the sample were similar to the results obtained by the energized treatment, while there were almost no or very few inclusions in the lower part (caused by the natural floating of inclusions).

![Figure 3. Micro morphology of inclusion distribution in the sample after electrified and non-electrified treatment.](image)

The number and size distribution of inclusions in different parts (upper, middle, lower) in Figure 3 were statistically analyzed, as shown in Figure 4. Figure 4a shows the area occupied by the inclusions in different parts (400 µm × 400 µm), and Figure 4b shows the number (quantity) of the inclusions in different parts (400 µm × 400 µm). According to the figure, the number of non-metallic inclusions (or the proportion of inclusions in the statistical area) in the sample treated by pulse current is more than that in the sample without electrification treatment. Moreover, after pulse-current treatment, the number of inclusions (or the proportion of inclusions in the statistical area) in the upper and lower parts of the sample is more. However, the number of inclusions in the middle part is basically consistent with the result without electrification treatment.
Figure 4. Statistical analysis of inclusions in the sample after electrification and non-electricity treatment. (a) Inclusion area statistics (b) Inclusion number statistics.

Microscopic analysis of inclusions in the energized and non-energized samples was carried out, as shown in Figure 5. The inclusions in the sample were mainly alumina and a small amount of magnesia alumina spinel (Figure 5). In addition, the alumina inclusions in the samples after electrification treatment were obviously finer, the particle size was concentrated in 2–5 µm, and the shape tended to be spherical. The particle size of inclusion in the sample without electrification treatment was relatively large, and the particle size was concentrated at about 10 µm. The inclusion size statistics are shown in Table 2. The statistical results in Table 2 show that the formation of small particle inclusions in the steel is promoted by the pulse current, and the particle size of the small particle inclusions is concentrated at 2–5 µm.

Figure 5. Cont.
Figure 5. Microscopic analysis of inclusions in the sample without electrification and after electrification treatment. (a) Microscopic analysis of the inclusions inside the sample after no electrification treatment. (b) Microscopic analysis of inclusions inside the sample after electrification treatment.

Table 2. Statistical analysis of inclusion size with and without electric field.

| Model Inclusion (µm) | ECP | No ECP |
|----------------------|-----|--------|
| 2–5                  | 260 | 38     |
| 5–10                 | 98  | 152    |
| 10–20                | 4   | 19     |
| >20                  | 0   | 2      |

The molten steel was rapidly water quenched at high temperatures, and there was basically no alumina inclusion precipitation in the molten steel during solidification. Therefore, it can be considered that the quantity, particle size, and morphology of alumina inclusions in molten steel were changed by pulse current treatment based on the current effect. Zhang et al. [15,16] believed that the free energy of the system could be changed by using a pulse current to treat liquid metal, which reduced the interface free energy between solid inclusions and liquid metal, thus affecting the distribution state of the solid-metal inclusions in liquid steel. Monaghan et al. [19,20] confirmed that under the action of electric fields, the interfacial tension between refractory and slag first decreased and then increased with the increase in voltage. Figure 6 shows the arrangement of positive and negative ions and the change of interfacial tension generated by the electric field acting on the solid-liquid interface. As can be seen from Figure 6, when a positive voltage is applied, the interfacial tension decreases with the increase in voltage [20].

Figure 6. Schematic diagram of the arrangement of positive and negative ions and the change of interfacial tension generated by the electric field acting on the solid-liquid interface.
In addition, the author studied the influence of electric fields on the wettability between alumina and molten iron through an electrowetting experiment, and discussed the influence of electric fields on the interfacial free energy between alumina and molten iron in combination with Young’s equation theory and the Young–Pullman equation. The results showed that electric fields could significantly reduce the interfacial free energy between solid and liquid and promote two-phase wetting [21,22]. Therefore, the interfacial free energy between the alumina phase and the molten steel phase can be reduced when a pulsed current is applied to the molten steel system rich in alumina inclusion, thus affecting the nucleation and growth processes of inclusions in the steel. The nucleation of deoxidized products (alumina inclusion) in molten steel can be divided into homogeneous nucleation and heterogeneous nucleation. According to the theory of homogeneous nucleation, when a spherical deoxidizing product with radius \( r \) is generated, the change of thermodynamic free energy \( \Delta G \) can be deduced by Equation (1):

\[
\Delta G = 4\pi r^2 \gamma_{SL} + \frac{4}{3} \pi r^3 \Delta G_V
\]

where, \( \gamma_{SL} \) is the interface free energy of the interface between molten steel and the deoxidation product, \( \text{erg/cm}^2 \); \( \Delta G_V \) is the change of volume free energy during the generation of the deoxidation product, so the critical radius \( r^* \) for the generation of stable crystal nucleus can be expressed by Equations (2) and (3):

\[
\Delta G^*_{Ho} = \frac{16}{3} \pi \gamma_{SL} (\Delta G_V)^{-2}
\]

\[
r^* = -2\gamma_{SL}/\Delta G_V
\]

According to Equations (2) and (3), the smaller the interfacial free energy \( \gamma_{SL} \) between molten steel and alumina, the smaller the critical radius \( r^* \); that is, the easier the nucleation of alumina. When pulse current acts on molten steel, the interfacial free energy \( \gamma_{SL} \) between molten steel and alumina inclusions is reduced, the nucleation of alumina is promoted, and the number of inclusions in molten steel is increased. For heterogeneous nucleated alumina, the critical free energy \( \Delta G^*_{He} \) required to form a stable core is shown in Equation (4).

\[
\Delta G^*_{He} = \Delta G^*_{Ho} \times \left( \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right)
\]

where, \( \theta \) is the wetting angle between the alumina phase and the steel liquid phase. Because the wettability between alumina and liquid steel is improved by pulse current, the wettability angle \( \theta \) between alumina and liquid steel is reduced. According to Equation (4), \( \Delta G^*_{He} \) is significantly reduced, which makes the heteronucleation of alumina easier.

The aggregation and growth of deoxidizing products can be caused by the interaction between particles or by the collision and volume diffusion between particles in the process of floatation. According to the growth rate formula of deoxidation products [23,24], the average growth radius of deoxidation products is deduced as shown in Equation (5):

\[
r_{cv}^3 = \frac{4}{9} \times \frac{2\gamma_{SL} V_m C_O D}{RT(C_P - C_O)} t
\]

where, \( V_m \) is the molar volume of the deoxidation product; \( C_O \) is the concentration of constituent elements of deoxidation products in liquid steel at the interface between liquid steel and deoxidation products; \( C_P \) is the concentration of constituent elements of the deoxidation product; \( D \) is the diffusion coefficient of the constituent elements of deoxidation products in liquid steel; \( R \) is a constant; \( T \) is the temperature of molten steel; and \( t \) is the time required for the inclusions to aggregate and sinter and grow. According to Equation (5), the smaller the interface free energy \( \gamma_{SL} \) of molten steel and the deoxidized product alumina is, the smaller \( r_{cv} \) is; that is, the less likely the deoxidized product is to aggregate and grow.
addition, the free energy change $\Delta G_{\text{coh}}$ per unit area during the collision and aggregation of two solid inclusions is shown in Equation (6), which is substituted into Young’s equation $\gamma_{\text{LG}} \cos \theta = \gamma_{\text{SG}} - \gamma_{\text{SL}}$ to obtain Equation (7).

$$\Delta G_{\text{coh}} = \gamma_{\text{SS}} - 2\gamma_{\text{SL}}$$  \hspace{2cm} (6)

$$\Delta G_{\text{coh}} = \gamma_{\text{SS}} - 2\gamma_{\text{SG}} + 2\gamma_{\text{LG}} \cos \theta$$  \hspace{2cm} (7)

where $\gamma_{\text{SS}}$ is the interface energy between two solid phases, $\gamma_{\text{SL}}$ is the interface energy between solid and liquid, $\gamma_{\text{SG}}$ is the interface energy between gas and solid, $\gamma_{\text{LG}}$ is the surface free energy of the liquid, and $\theta$ is the contact angle between the solid and liquid. According to Equation (7), if $\Delta G_{\text{coh}}$ is negative, the deoxidation products can aggregate and grow again. On the contrary, if $\Delta G_{\text{coh}}$ is positive, the deoxidation products are not easy to aggregate and grow. For the same deoxidation product, the larger the wetting angle $\theta$ between the inclusion and molten steel is, the more the free energy of the collision system between the two inclusions decreases, which makes it more favorable for the deoxidation product to aggregate and grow. By introducing the pulse current into the liquid steel, the interface free energy $\gamma_{\text{SL}}$ between alumina and liquid steel is reduced, and the wetting angle $\theta$ between them is reduced, so the accumulation and growth of alumina inclusion are inhibited. In addition, the finer the inclusion, the more significant the effect of interfacial tension. In order to reduce the free energy of the interface, small particle inclusions tend to reduce their own area and tend to be spherical, as shown in Figure 5. Therefore, the interfacial free energy of the molten steel alumina inclusion system is changed by the introduction of a pulse current, which affects the nucleation and aggregation growth process of alumina inclusion.

Based on the electric pulse experiment, the quantity, size, and distribution of alumina in molten steel can be significantly changed by energizing the electrode up and down. Through the introduction of an electric current field, the interfacial free energy of the system inside the molten steel-alumina inclusion was changed, the nucleation of the alumina inclusion was promoted (providing energy, and reducing nucleation work, which was beneficial to the nucleation of alumina), the aggregation growth between alumina particles was inhibited, and the migration and distribution of the inclusion were also affected.

Continuous casting is the last step in the refining and purification of steel, and the tundish is the best place to control and remove inclusions. The size, shape, and distribution of non-metallic inclusions in molten steel can be improved by introducing a pulse current into the continuous casting tundish and combining it with the tundish metallurgy technology, so that the inclusions can float onto the tundish covering agent or be adsorbed by the ceramic filter as soon as possible, which can prevent the clogging of the submerged nozzle caused by unstable casting in the later period ([Al] in the steel is oxidized twice or $\text{Al}_2\text{O}_3$ precipitates due to the temperature drop at the nozzle). In addition, small inclusions enter the slab (treated by pulse current) as nucleation particles to refine the grain, which is of great significance for the production of high-quality clean steel.

3. Conclusions

The effect of the applied current field on the non-metallic inclusions in the aluminum-killed steel was explored through the electric pulse experiment, and the action mechanism of the pulsed current on the molten steel-alumina inclusion system was expounded based on the interface free energy. The following conclusions were drawn:

1. The results show that the number of small alumina inclusions in the steel after electric pulse treatment (the pulse current density was 0.1–3 A/cm$^2$, the frequency was 100 Hz, and the pulse waveform was a square wave) was significantly increased compared with the sample without electric pulse treatment, and the particle size was concentrated at 2–5 $\mu$m, and the inclusions were concentrated in the upper and lower parts of the sample. However, in the samples without electrification treatment, the large particles of inclusions were the majority, and the particle size is concentrated at
about 10 µm, and the inclusions are concentrated in the upper and middle parts of the samples.

(2) When the pulse current was applied to the molten steel, the interfacial free energy of the internal system of liquid steel alumina inclusion was reduced, the nucleation of alumina inclusion was promoted, the aggregation growth between alumina particles was restrained, and then the migration and distribution of inclusions were also affected.

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