

STUDY ON THE BEHAVIOR OF MAGNESIUM IN MOLTEN SALT ELECTROLYSIS IN-SITU DESULFURIZATION DURING HOT METAL PRETREATMENT

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A desulfurization method based molten salt electrochemistry using magnesite-based desulfurizer for hot metal pretreatment was investigated. The feasibility of desulphurization of hot metal by magnesium produced from magnesite-based desulfurizer through high temperature molten salt electrolysis was studied with one scheme of the desulfurizing agent constitutions. Through theoretical analysis, the conditions of the two different desulfurization processes, and the theoretical values of the critical current density at which mutual transition between the two desulfurization processes were specified. For the two different desulfurization processes, a kinetic model for desulfurization of hot metal by using magnesite-based desulfurizer through high temperature molten salt electrolysis was established. Through kinetic modeling, the behavior of magnesium and its main role on desulfurization were investigated.

Key words: hot metal pretreatment; in-situ desulfurization; magnesium-based desulfurizer; molten; salt electrochemistry; current density - temperature

INTRODUCTION

In the modern steel production process, the hot metal pretreatment process plays an irreplaceable role in metallurgical process, especially in the clean steel smelting process because it can reduce the burden of removal of sulfur and other harmful impurities in converter and improve the quality of steel. Pretreatment of molten iron with magnesium metal is one of the most widely used desulfurization methods for hot metal pretreatment [1]. However, due to special properties of the magnesium metal as active alkali metal, it brings additional economic burden to the storage, transport and use process of the magnesium metal. In recent years, the development of molten salt electrochemistry has opened up new ideas for the application of magnesium metal in hot metal desulfurization. A series of breakthroughs in related fields have provided the possibility to develop a short flow process which can directly utilize the rich magnesite resources in Liaoning area, China, for desulphurization of hot metal pretreatment. Previous studies have also made an effective exploration on the application of magnesium in-situ desulfurization in hot metal pretreatments. [2-3]

THE BEHAVIOR OF MAGNESIUM IN DESULFURIZATION PROCES

Thus, in the author's opinion, both types of desulfurization should be considered, which could be distin-

guished as primary and secondary reactions and neither can be ignored completely. The experimental results showed that the relationship between the primary.

(1) Magnesium precipitates on the cathode forming three-dimensional instantaneous nucleation. Initially, due to high solubility of magnesium in carbon saturated molten iron the magnesium nucleated on the cathode does not have enough time to gather to form bubbles but directly dissolved into the molten iron and reacted with sulfur in the molten iron. Therefore, the main desulfurization reaction occurred during this period is single phase desulfurization reaction.

(2) When the current efficiency is high, the nucleation rate on the cathode is much larger than that of mass transfer rate of magnesium in the molten iron bath. When the concentration of magnesium in the area around the electrode is higher than the equilibrium concentration, the primary nuclei of magnesium on the cathode began to gather and develop into small magnesium vapor bubbles on the cathode. Then, the multi-phase desulfurization reaction occurred on two-phase interface during the rising of the grown magnesium bubbles [5-6]. At the same time magnesium dissolved into the molten iron was reacting with sulfur in the process of magnesium bubble floating up. In this case, the multi-phase desulfurization reaction by the magnesium vapor played a major role, whereas the single phase desulfurization reaction by the dissolved magnesium plays a secondary role.

(3) When the current efficiency is low, the mass transfer rate of magnesium is lower than the nucleation rate of magnesium on the cathode in the molten iron bath, only

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when the concentration of magnesium in the hot metal reached the equilibrium concentration of the desulfurization reaction and the sulfur content is low enough by reacting with the dissolved magnesium, the primary nuclei of magnesium on the cathode will begin to grow up into vapor bubbles that then rose up. In this case, single phase desulfurization reaction by the dissolved magnesium played a major role in desulfurization while the multi-phase desulfurization reaction by the magnesium vapor played a secondary role in desulfurization [7].

EXPERIMENTAL

The molten salt system used in the experiment was a MgF_2-CaF_2-LiF system. The molten iron was made from the pig iron produced by blast furnace of Ansteel, which had sulfur content of 150 ppm. The initial sulfur content in molten iron was adjusted by adding FeS. The pig iron was melted in an inhouse high temperature furnace with a maximum heating temperature being 1 773 K. Alumina crucible and tube, graphite crucible, graphite electrode, and tungsten rods used in the experiments were purchased from external suppliers. 200 g salt mixture and 300 g pig iron were used for each experiment.

The experimental procedure is as follows: 200 g desulfurization agent (MgF_2-CaF_2-LiF system) after drying at 573 K for 2h, 300 g pig iron and an appropriate amount of FeS were put in an alumina-graphite crucible assembly and experimental set-up schematically shown in Figures 1 and 2, respectively. When the furnace was heated to 1 473 K, the molten salt system of the desulfurizer changed into molten state. When the temperature reached 1 573 K, pig iron was melted into molten iron. Because the density of the molten iron is much greater than that of the molten salt, a bath with two layers of melts was formed in the crucible. The hot metal stays at the bottom with the molten desulfurizer floating on top of the molten iron. Then, an electrolysis device was connected and the graphite electrode (cathode) was inserted into the molten bath. The insertion depth of the

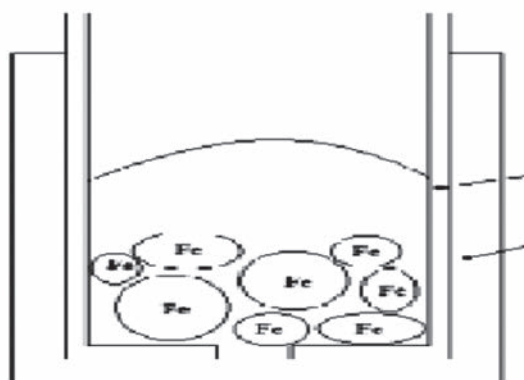


Figure 1 Sketch of experimental crucible assembly

electrode was recorded so as to calculate the work area according to the known diameter of the cathode. The electrode was lifted or lowered in steps with one step of 7 mm. After electrolysis system was switched on, the cathode was slowly lowered down. When the electrode initially touched the surface of the molten salt indicated by the ammeter, it was further lowered by four steps so that the electrode insertion depth was determined, i.e., 28 mm. Then, based on the electrode diameter of 12 mm the electrode work area was calculated to be around 10 cm^2 . When the desired heating temperature was well maintained, started the electrolysis process.

RESULTS AND DISCUSSION

Effect of current density on desulfurization

When the initial sulfur content in hot metal was 1 500 ppm and temperature was kept at 1 623 K and with a constant anode work area of 10 cm^2 the experimental results are shown in Figure 3. The horizontal axis is the desulfurization time and the vertical axis is the desulfurization ratio, which is the percentage of the change in the sulfur content (i.e., sulfur removed) divided by the initial sulfur content.

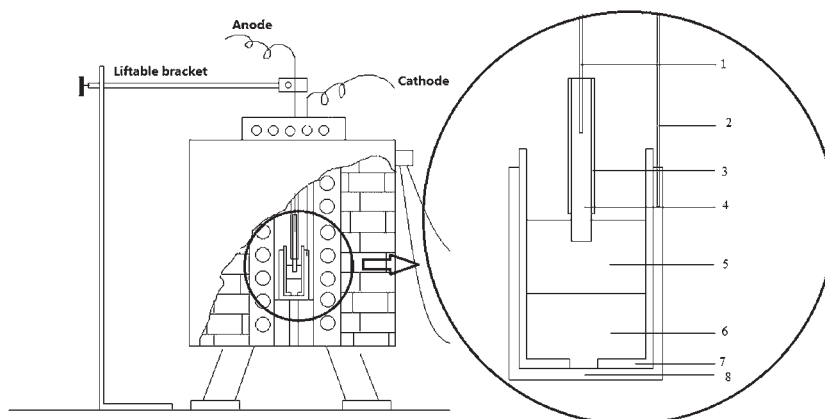


Figure 2 Schematic diagram of experimental set-up

1. Conductive wire of graphite anode; 2. Conductive tungsten rod of graphite cathode; 3. Corundum casing; 4. Graphite anode; 5. Molten salt; 6. Liquid iron; 7. Corundum crucible with bottom hole; 8. High purity graphite crucible

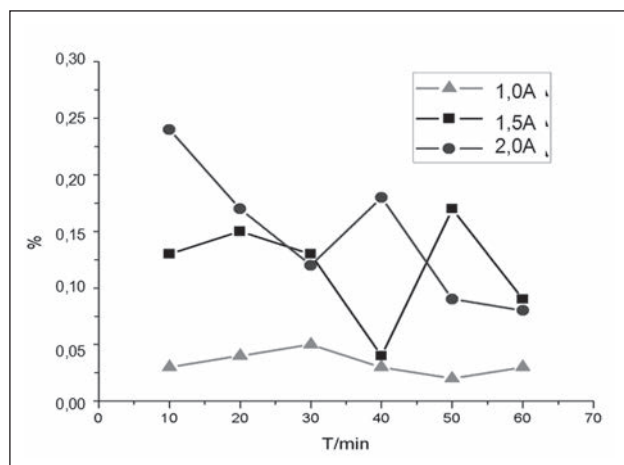


Figure 3 The influence of current density on desulfurization for the same anode work surface

As can be seen from Figure 3, the desulfurization ratio increases with the increase of the current density when the initial sulfur content and temperature are constant. Nevertheless, it is worth noting that the overall desulfurization ratio at the current density of $0,1 \text{ A/cm}^2$ is much lower than that of the current density of $0,15 \text{ A/cm}^2$ and $0,2 \text{ A/cm}^2$. One of the possible reasons is that the mechanism of desulfurization by magnesium may change during the desulfurization process at a certain current density level between $0,1 \text{ A/cm}^2$ and $0,15 \text{ A/cm}^2$ at the electrolysis temperature. The overall trend of the desulfurization ratio at the current density of $0,15 \text{ A/cm}^2$ is similar to that of $0,2 \text{ A/cm}^2$ with the increase of electrolysis time in that, for example, the desulfurization ratio generally decreases first, then increases and then decreases. In contrast, the variation of the desulfurization ratio at $0,1 \text{ A/cm}^2$ is in a more narrow range than that at $0,15 \text{ A/cm}^2$ and $0,2 \text{ A/cm}^2$, but still shows a similar trend of first rising and then descending. Figure 3 also shows that single phase desulfurization plays a major role at current density $0,1 \text{ A/cm}^2$, because the diffusion of magnesium and sulfur is relatively slow in single-phase desulfurization process, and the overall desulfurization ratio is smaller than that with multi-phase desulfurization process at current densities $0,15 \text{ A/cm}^2$ and $0,2 \text{ A/cm}^2$. In this case, as the amount of magnesium continues to increase leading to speed-up of the diffusion, the desulfurization ratio increases at the time between 10 and 30 min. Therefore, the desulfurization ratio shows a rising trend in the early stage of electrolysis at $0,1 \text{ A/cm}^2$. But as the desulfurization process proceeds, the sulfur content gradually decreases. As a result, the sulfur diffusion rate eventually decreases and, then, the desulfurization ratio began to exhibit a downward trend. In addition, the low formation rate of magnesium is one of the reasons why the desulfurization ratio is much lower than the cases with current densities $0,15 \text{ A/cm}^2$ and $0,2 \text{ A/cm}^2$.

In the other two cases (the current density of $0,15 \text{ A/cm}^2$ and $0,2 \text{ A/cm}^2$) the amount of magnesium increases at the initial stage because of the large current density. At the

initial stage, the diffusion of magnesium begins to occur and the single-phase desulfurization is dominant. As the sulfur content decreases, the efficiency of the single-phase desulfurization decreases. Therefore, a downward trend of the desulfurization ratio curve appears in the early period of the electrolysis process as shown in Figure 3. After that, the rate of formation of magnesium is faster than that of diffusion. After a period of time, the magnesium in the vicinity of the electrode reaches supersaturation and starts to gather into the nucleation, and the multi-phase desulfurization takes place during the magnesium vapor bubbles rising up. Therefore, the desulfurization ratio increases again. It can be seen from the curves of $1,5 \text{ A}$ and 2 A in Figure 3 that at the current density of $0,2 \text{ A/cm}^2$, the time of multi-phase desulfurization is shorter than that at the current density of $0,15 \text{ A/cm}^2$. This is because the faster magnesium formation with the larger current density to reach the supersaturation; the earlier the multi-phase desulfurization occurs. Then, the desulfurization ratio curve begins to decrease again along with the decrease of the sulfur content. It is worth noting that this multi-phase desulfurization doesn't necessarily mean large macro-scale magnesium vapor bubbles exist in the molten iron bath. It is likely that some tiny bubbles form from nucleation on the electrode but are quickly consumed for desulfurization and thus are depleted in the molten iron bath. In addition, this result further indicates that the multi-phase desulfurization rate is faster than the single-phase desulfurization rate. In the single-phase desulfurization process the diffusion of magnesium and sulfur is very slow whereas in the multi-phase desulfurization process the kinetic conditions of desulfurization reaction have been substantially improved due to the stirring effect of the rising bubbles, which promotes the occurrence and progress of desulfurization.

Effect of temperature on desulfurization

Figure 4 shows the effect of temperature on desulfurization ratio for the initial sulfur content of 1500 ppm , the current intensity of 2 A and anode surface area being 10 m^2 (i.e., current density of $0,2 \text{ A/cm}^2$). It can be seen from Figure 4 that at 1673 K the desulfurization ratio rises in the early period and then decreases in the late period, which is rather similar to the case with 1 A and 1623 K shown in Figure 3. This indicates that the desulfurization mechanism under the condition of $0,2 \text{ A/cm}^2$ and 1673 K is similar to that in the case of $0,1 \text{ A/cm}^2$ and 1623 K . A reasonable explanation could be that the formation rate of magnesium is lower than the mass transfer rate at a low current density of $0,1 \text{ A/cm}^2$ and a low temperature of 1623 K , and under this condition the single-phase desulfurization plays a primary role in the whole desulfurization process. However, at a large current density and a high temperature, both the formation rate and the diffusion rate of magnesium are high. If the formation rate of magnesium is lower than or the same to the diffusion rate of magnesium, the ma-

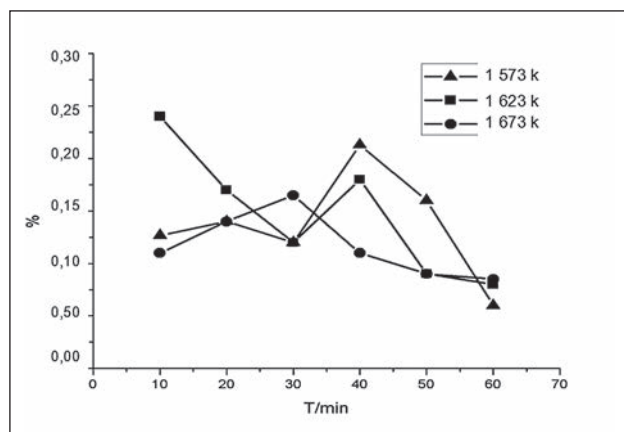


Figure 4 The influence of temperature on desulfurization

major desulfurization process is still single-phase desulfurization. Furthermore, since the diffusion rate of magnesium is larger at 1673 K than that at 1623 K, the overall desulfurization ratio at a higher temperature is obviously larger than that at a lower temperature.

From Fig 4 it can be seen further that at temperatures of 1573 K and 1623 K the overall trend of the desulfurization ratio is still first decreasing, then increasing and finally decreasing. According to the previous analysis (c.f., Figure 3, at 1573 K and 1623 K multi-phase desulfurization reaction has occurred. By comparing the curves corresponding to 1623 K and 1573 K in Figure 4, it is found that when the current density is the same, that is, the rate of production of magnesium is the same, a higher temperature accelerates the mass transfer of magnesium at the same current density and thus the desulfurization ratio at 1623 K is larger than that at 1573 K in the early stage of the electrolytic process. Furthermore, the multi-phase desulfurization at 1573 K and 1623 K occurs at nearly the same time because of the similar formation rate of magnesium at the same current density. In addition, the electrolysis temperature has a certain effect on the mass transfer rate of magnesium. The higher the temperature the faster the mass transfer of magnesium into the molten iron. Therefore, the time for the single-phase desulfurization to proceed will be relatively long. This is the reason why the desulfurization ratio at 1573 K is larger than that at 1673 K in the late stage of the electrolysis process. These results once again verified the hypothesis that there are two types of mechanisms of desulfurization of pig iron by magnesium produced from the magnesium oxide electrolytic process in high temperature molten salt melts. Figure 4 provides a side evidence showing that the desulfurization efficiency of the multi-phase desulfurization reaction by the magnesium vapor is much higher than that of the single-phase desulfurization reaction solely by the dissolved magnesium.

CONCLUSIONS

From the results of the present experimental study and theoretical analysis on the desulfurization of hot

metal by magnesium produced from magnesite-based desulfurizer through high temperature molten salt electrolysis, the following conclusions can be drawn:

(1) The critical transition current density of two types of

desulfurization mechanisms is $I_{crit} = \frac{C_{Mg,sat} n F D_R}{l}$.

n : electron number in Reaction

D_R : diffusion coefficient

F : Ladin constant

c : content of reaction particles on the electrode surface
 l : length)

(2) The desulfurization mechanisms are controlled by current density and temperature. Increase of the current intensity over the critical value (I_{crit}) causes the transition of the main form of desulfurization from single-phase desulfurization to multiphase desulfurization.

(3) If the temperature rises to a certain level, the mass transfer rate of magnesium is accelerated to greater than the formation (nucleation) rate of magnesium, the main form of desulfurization will be changed from multiphase desulfurization to single-phase desulfurization.

(4) The multiphase desulfurization reaction is faster and more efficient than the single-phase desulfurization reaction.

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Note: Responsible for English language is professor YH Pan from University Anshan, China