Effect of slag composition on desulfurization during recycling rejected electrolytic manganese metal by electroslag remelting

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Abstract. To reduce the Mn vaporization during recycling rejected electrolytic manganese metal by electroslag remelting, it is proposed to reduce the temperature of molten slag pool, but which leads to the degradation of slag desulfurization. The desulfurization by interaction between CaF 2–CaO–Al 2O 3–Na 2O slag and rejected electrolytic manganese metal scrap was studied from the view of thermodynamics in this study. The results show that sulfur distribution ratio decreases with increase of CaF 2 content, and increases with the increase of Na 2O content and temperature. Na 2O increases sulfur distribution ratio of slag by increasing CaO activity. Na 2O addition in CaF 2–CaO–Al 2O 3–Na 2O slag can enhance desulfurization ability of slag due to the larger sulfur distribution ratio and lower viscosity. Thus, sulfur content in test of slag T3 bearing 45.8 wt% CaF 2-23.2 wt% CaO-22.7 wt% Al 2O 3-8.3 wt% Na 2O is much lower than that of slag without Na 2O, implying that 45.8 wt% CaF 2-23.2 wt% CaO-22.7 wt% Al 2O 3-8.3 wt%Na 2O slag is the promising slag for recycling rejected electrolytic manganese metal by ESR.

Keywords: rejected electrolytic manganese metal / desulfurization / slag / electroslag remelting / thermodynamics and kinetics

1 Introduction

Mn is extensively used in alloy steel for control of microstructure and mechanical properties [1–3]. To improve the cleanliness of steel, the Mn added into steel should contain as few impurities as possible. High-purity Mn is commonly produced via hydrometallurgical and electrolytic processes. In order to transform the Mn into a brittle α-phase from a ductile γ-phase at a reasonable electric current efficiency, sulfur dioxide is used as an additive to the catholyte during the electrolytic process, but, which leads to the serious increase of the S content in the produced electrolytic Mn [4,5]. Because of excessive S content, it is impossible to use the rejected electrolytic manganese metal scrap (as shown in Fig. 1) in the steelmaking process. As a result, enormous Mn resources are wasted, and the rejected electrolytic manganese metal (EMM) scrap storage is also hazardous in terms of soil and water contamination.

For effective recycling of the rejected electrolytic manganese metal scrap, the electroslag refining (ESR) approach, which provided a very effective desulfurization, was successfully introduced [6–8]. Figure 2 depicts the schematic of the ESR furnace used for rejected EMM scrap refining. ESR furnace is made of copper, which avoids the pollution risks for the refractory lining with the refined EMM. During the refining, the current passes from the water-cooled electrode to the water-cooled baseplate, which generates the Joule heat in the highly resistive molten slag. With a vibrating feeder, the rejected EMM scrap is continuous poured into the water-cooled mold from its top outer edge. The scrap would be melted in a very short time after it enters the hot molten slag layer. A dense manganese droplet then sinks through the molten slag layer, creating a liquid metal pool at the mold bottom. The sulfur dissolved in the molten Mn transfers to the molten slag during the refining process [9–11].

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2 Experiment

The rejected EMM scrap used in present experiment contains 0.16 wt.% S and 0.124 wt.% T.O (total oxygen content). The component points of slag used for ESR are generally on the line between CaF₂ and 12CaO·7Al₂O₃ in the CaF₂–CaO–Al₂O₃ ternary phase diagram. Thus, the mass ratio of CaO and Al₂O₃ was designed to be 1:1 in the present experiment. The reagent-grade powders of CaF₂, CaCO₃, Al₂O₃ and Na₂CO₃ were used as raw materials. The CaO powders were obtained from the reagent-grade CaCO₃ that were calcined at 1273 K for 10 h in a muffle furnace. To avoid the hydrolysis of CaF₂ powders at high temperature, the CaF₂ and Al₂O₃ powders were heated to 573 K with 10 h holding for dehydration. The NaCO₃ powders were heated to 373 K with 10 h holding for dehydration. Three types of slags with different compositions were accurately prepared by electronic balance with an accuracy of 0.1 mg, indicated as T1, T2 and T3, respectively. The well-blended powders were pre-melted at 1773 K for 5 min in a graphite crucible in the induction furnace in order to obtain homogeneous slag samples, and were quenched on a copper plate. The quenched slag was then carefully crushed and ground. The chemical compositions of the pre-melted slag determined by X-ray fluorescence spectroscopy are listed in Table 1.

According to the CaF₂–CaO–Al₂O₃ phase diagram [19], as shown in Figure 3, the melting point of slag T1 was below 1623 K, and melting point of slag T2 was lower than that of slag T1. The experimental temperature was set at 1673 K and 1723 K, at which the slag existed as liquid phase. Heat tests were performed in a vertical tube furnace with MoSi₂ bars as heating elements. The experimental setup is shown in Figure 4. High-purity Ar gas was blown into the furnace with a flow rate of 3.4 × 10⁻³ m³/s. To avoid the erosion of crucible by fluoride slag, the BN crucible (ID = 30 mm) was selected. Figure 5 shows that fluoride slag hardly corrodes BN crucible. Around 30 g synthetic slag and 40 g rejected EMM scrap were charged into the BN crucible and melted in the furnace. After 30 min holding at 1673 K or 1723 K, the crucible was taken out from furnace and quenched quickly. The sulfur contents of Mn ingots were determined by C–S analyzer. It should be noted that the sulfur content in slag after test was not determined because the severe fluoride and Na₂O vaporizations from slag bearing fluoride and Na₂O result in the change of slag amount [20,21].

3 Results and discussion

3.1 Change of sulfur content in Mn ingot

The sulfur contents in Mn ingots after tests with varying slags are listed in Table 2. It indicates that sulfur content increases with CaF₂ content in slag increasing from 32.1 wt.% to 48.3 wt.%, and decreases with the Na₂O content in slag increasing from 0 wt.% to 8.3 wt.% Furthermore, sulfur content in the tests with higher temperature is lower.
3.2 Thermodynamic analysis on the desulfurization ability of slag

S reacts easily with manganese to form MnS, as the reaction (1) [22]:

$$\frac{1}{2} \text{Mn} + \frac{1}{2} \text{S} \rightleftharpoons \text{MnS}; \quad \log K = \frac{9433}{T + 5.19};$$

where $K$ is the equilibrium constant, and $T$ is the temperature (K). It is very important to determine the existence form of S for understanding desulfurization. According to reaction (1), the S content in equilibrium with liquid Mn is calculated, as shown in Figure 6. It indicates that MnS is completely decomposed in liquid Mn above 1673 K, implying that the S is completely dissolved in liquid Mn.

The desulfurization reaction of molten slag-liquid metal interaction is as follows:

$$\frac{1}{2} \text{O}_2 + \frac{1}{2} \text{S} \rightleftharpoons \frac{1}{2} \text{S}_2;$$

where $(\text{O}_2)_{\text{slag}}$ and $(\text{S}_2)_{\text{slag}}$ represents the O$_2$ and S$_2$ in molten slag, respectively; $[\text{S}]_{\text{Mn}}$ and $[\text{O}]_{\text{Mn}}$ represents the S and O in liquid Mn, respectively.

In the investigated slag, CaO and Na$_2$O could participate in the desulfurization reaction, and the high CaO or Na$_2$O activity will contribute to desulfurization. The activities of CaO and Na$_2$O in molten slag were calculated by FactSage 7.0, as shown in Figure 7. With the increase of CaF$_2$ content, the CaO activity in CaF$_2$–CaO–Al$_2$O$_3$ slag (CaO/Al$_2$O$_3$ = 1:1 (mass ratio)) decreases, which is attributed to the decrease of CaO content. The CaO activity in slag T1 is higher than that in slag T2 (Fig. 7a), implying that the desulfurization ability of slag T1 is stronger than that of slag T2. It can be seen in Figure 7b that the CaO activity in CaF$_2$–CaO–Al$_2$O$_3$–Na$_2$O slag (CaF$_2$/CaO/Al$_2$O$_3$ = 2/1/1 (mass ratio)) increases with increase of Na$_2$O content. In CaF$_2$–CaO–Al$_2$O$_3$ slag, CaO combines with Al$_2$O$_3$ to form calcium aluminate. Na$_2$O addition can replace part of CaO combined with Al$_2$O$_3$ [23]. As a result, the free CaO content increases, and the CaO activity dramatically increases in slag bearing Na$_2$O. Meanwhile, CaO activity in slag increase with the increase of temperature (Fig. 7). The calculated activity of Na$_2$O in CaF$_2$–CaO–Al$_2$O$_3$–Na$_2$O slag at 1673 K or 1723 K is $0 \sim 3.883 \times 10^{-5}$ when the Na$_2$O content increases from 0 wt% to 12 wt%, which is much lower than CaO activity ($0.0173 \sim 0.0976$). Thus, from the view of thermodynamics, the desulfurization mainly depends on the CaO in CaF$_2$–CaO–Al$_2$O$_3$–(Na$_2$O) slag.

In order to quantitatively compare the difference on desulfurization ability of slag, the distribution ratio of sulfur ($L_S$) can be calculated by equation (3) [24,25]:

$$\log L_S = -935/T + 1.375 + \log f_{\text{S}0} + \log C_S - \log a_{\text{O}2},$$

where $f_{\text{S}0}$ is the activity coefficient of S in liquid Mn and $f_{\text{S}0} \approx 1$; $C_S$ is the sulfide capacity of slag; $a_{\text{O}2}$ is the activity of oxygen. The sulfide capacity of slag is calculated by equation (4) according to the optical basicity (A) [26]:

$$\log C_S = 12.0A - 11.9.$$
The optical basicity can be acquired according to equation (5):

\[ \Lambda = \sum A_i X_i. \]  

(5)

In which \( A_i \) is the optical basicity of the \( i \)th component, which can be obtained in reference [26, 27]; \( X_i = (V_i/2) \cdot x_i \cdot Z_i / \Sigma [(V_i/2) \cdot x_i \cdot Z_i] \), \( V_i \) is the charge number of negative ion of the \( i \)th component, \( x_i \) is the mole fraction of the \( i \)th component, \( Z_i \) is the number of negative ions. The optical basicities of investigated slags are shown in Table 1. It indicates that the optical basicity decreases with the increase of CaF\(_2\) content in CaF\(_2\)–CaO–Al\(_2\)O\(_3\) slag, and increases with the increase of Na\(_2\)O content in CaF\(_2\)–CaO–Al\(_2\)O\(_3\)–Na\(_2\)O slag.

\[ q_{(O)} \] can be calculated by equation (7) according to Mn deoxidation reaction (6) [22]:

\[ [\text{Mn}]_{\text{Mn}} + [\text{O}]_{\text{Mn}} = (\text{MnO})_{\text{slag}}, \]  

(6)
Fig. 7. CaO activity in (a) CaF₂–CaO–Al₂O₃ slag (CaO/Al₂O₃ = 1) with varying CaF₂ content and (b) CaF₂–CaO–Al₂O₃–Na₂O slag (CaF₂/CaO/Al₂O₃ = 2/1/1) with varying Na₂O content.

Fig. 8. Distribution ratios of sulfur in (a) CaF₂–CaO–Al₂O₃ slag (CaO:Al₂O₃ = 1:1) with varying CaF₂ content and (b) CaF₂–CaO–Al₂O₃–Na₂O slag (CaF₂:CaO:Al₂O₃ = 2:1:1) with varying Na₂O content.

Fig. 9. Viscosities of (a) CaF₂–CaO–Al₂O₃ slag (CaO:Al₂O₃ = 1:1) with varying CaF₂ content and (b) CaF₂–CaO–Al₂O₃–Na₂O slag (CaF₂:CaO:Al₂O₃ = 2:1:1) with varying Na₂O content.
\[ \log K = \log \frac{a_{(MnO)}}{a_{(Mn)}} = 14.880/T - 6.67 \]  
(7)

where \(a_{(Mn)}\) is the Mn activity in molten Mn, which is unity (\(a_{(Mn)} \approx 1\), pure substance as standard state) in the present study; \(a_{(MnO)}\) is the MnO activity in molten slag, which can be obtained by equation (8):

\[ a_{(MnO)} = \gamma_{(MnO)} \cdot x_{(MnO)}, \]  
(8)

where \(\gamma_{(MnO)}\) and \(x_{(MnO)}\) is the activity coefficient and mole fraction in molten slag, respectively. There is no MnO in the original slag. It is assumed that all the oxygen in rejected EMM scrap (0.124 wt% T.O) enters the molten slag in the form of MnO, the mole fraction of MnO in molten slag increased to ~0.0074. According to the equation (7), the calculated oxygen activity in molten Mn is ~0.0001.

Combining equations (3) and (4), the distribution ratio of sulfur \(L_S\) was calculated, as shown in Figure 8. It indicates that \(L_S\) decreases with increase of CaF\(_2\) content, and increases with the increase of Na\(_2\)O content and temperature, which is consistent with the change of CaO activity in molten slag. This implies that the CaO plays the dominant role in desulfurization. Na\(_2\)O increases sulfur distribution ratio of slag by increasing CaO activity. The sulfur content in liquid Mn decreases with increase of Na\(_2\)O content and the viscosity of slag T3 is the lowest.

Furthermore, sulfur content in liquid Mn decreases with the temperature increasing (Tab. 2) due to better thermodynamic condition. Viscosity has an important effect on the mass transfer, and was calculated by FactSage 7.0. Figure 9 shows viscosity of slag decreases with the increase of CaF\(_2\) content or Na\(_2\)O content, and the viscosity of slag T3 is the lowest. Lower viscosity contributes to the mass transfer for desulfurization by slag-metal interaction, implying that the better dynamic condition is acquired. Based on the above thermodynamic analysis and experimental results (Tab. 2), slag T3 shows the strongest desulfurization ability due to the larger sulfur distribution ratio and lower viscosity, which is promising slag for recycling rejected electrolytic manganese Metal by ESR.

4 Conclusions

The following conclusions can be drawn from the present study:

- In CaF\(_2\)-CaO-Al\(_2\)O\(_3\)-Na\(_2\)O slag, sulfur distribution ratio decreases with increase of CaF\(_2\) content, and increases with the increase of Na\(_2\)O content and temperature, which is consistent with the change of CaO activity in molten slag. CaO in slag plays the dominant role in desulfurization. Na\(_2\)O increases sulfur distribution ratio of slag by increasing CaO activity.

- Na\(_2\)O addition in CaF\(_2\)-CaO-Al\(_2\)O\(_3\)-Na\(_2\)O slag can enhance desulfurization ability of slag due to the larger sulfur distribution ratio and lower viscosity. The sulfur content in test with slag T3 is much lower than that with slag T1 and slag T2, implying that slag T3 is the promising slag for recycling rejected electrolytic manganese metal by ESR.

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