J. Min. Metall. Sect. B-Metall. 58 (2) (2022) 275 - 284

Journal of Mining and Metallurgy, Section B: Metallurgy

DESULFURIZATION OF MOLTEN STEEL WITH MOLTEN SLAG USING THE ELECTROCHEMICAL METHOD

X.-Q. Wu [a], J.-F. Xu [a, b *], P.-W. Gu [a], J.-Y. Zhang [b]

[a] School of Iron and Steel, Soochow University, Suzhou, Jiangsu, China
[b] Shanghai Key Laboratory of Modern Metallurgy and Material Processing, Shanghai University, Shanghai, China

(Received 14 October 2021; Accepted 16 June 2022)

Abstract

The desulfurization in metallurgical process is electrochemical reaction in nature. Desulfurization using the electrochemical method was proposed with the CaO-MgO-Al_2O_3 molten slag covering molten steel. Effect of an applied external DC voltage, which varied from 0 to 8V, was discussed. The results indicated that sulfur in molten steel could be removed effectively with applied external voltage. According to the mechanism analyses of the desulfurization under the applied external voltage, kinetics formulae were developed, and the model calculated results that were in agreement with the experimental values. The transfer coefficient of sulfur in molten slag under electromigration conditions was approximately 2.09×10^{-5} $m\cdot s^{-1}\cdot V^{-1}$. The desulfurization of molten steel with molten slag can be promoted by increasing the applied voltage, reducing the partial pressure of atmospheric oxygen, strengthening the stirring intensity of the reaction system, and optimizing the composition and properties of the slag.

Keywords: *Desulfurization; Electrochemical; Kinetic; Electromigration; Mass transfer coefficient*

1. Introduction

As the requirements for high-quality steel products become more and more stringent, the detrimental effects of sulfur to steel have been widely recognized as a harmful impurity because it will negatively influence ductility, strength, and corrosion resistance of metal products. In order to achieve clean steel and alloy production with low sulfur content, extensive work has been carried out, and desulfurization of molten steel is one of important reactions in metallurgical process [1-3].

It is known that the transfer of sulfur from metal to slag is an electrochemical process involving exchange of electrons between the metal phase and the slag phase. Many investigations have been reported on desulfurization based on the ionic nature of slag, and many interesting phenomena were found [4]. King et al. [5] demonstrated that the transfer of sulfur from metal to slag involved an electrochemical mechanism, and indicated that the possibility of an externally-imposed current on sulfur transfer reaction. Ward et al. [6] studied the application of direct current (DC) power on electrochemical desulfurization of pig iron and found that the sulfur transfer rate increased on application of direct current. Nilas et al. [7] investigated the transition of sulphur between carbon containing iron melts and molten slags, and found the mutual action of silica reduction and sulphur transfer from the metal into the slag. Mclean et al. [8] reported that on application of electric current to the slag-steel system, not only there was an acceleration in sulfur transfer from metal to slag, but also that there was much lower sulfur content in the steel melt. Kim et al. [9] also confirmed that desulfurization of molten steel using molten slag could be enhanced by applying an electric field across the slag. Shi et al. [1] recently reviewed desulfurization in ESR, including its most relevant electrical/electrochemical aspects. All of these investigations confirmed that application of the electric energy could decrease the final sulfur content in molten metal, which was lower than that obtained by normal desulfurization. As discussed above, most of those studies focused on the electrochemical desulfurization in C-saturated molten metal, and graphite electrodes were used in some investigations, which would lead to high carbon content in molten metal. However, the carbon content of molten steel in the refining process is generally low. Few attempts have been

---

[*] *Corresponding author: xujifangsuda@163.com*

https://doi.org/10.2298/JMMB211014012W

made to quantitatively investigate on the basis of kinetics analysis, and the electromigration speed of sulfur ions under electric field needs to be further explored.

In the present work, the desulfurization process of molten steel with molten slag was studied. The electrochemical desulfurization between molten steel and molten CaO-Al_2O_3 based slag with the applied external DC voltage at 1823K was investigated. The Mo-ZrO_2 cermet electrodes were used in the preset work to keep the low carbon content in molten steel low which was more consistent with the actual situation of refining molten steel. A desulfurization kinetic model was developed, while the gradient of electrochemical potential was simultaneously taken into consideration. And it was also expected to obtain the transfer coefficient of sulfur in slag under electromigration conditions.

2. Experimental Apparatus and Procedures

2.1. Sample preparation

Table 1 provides the chemical compositions of the molten steel. In order to increase the level of sulfur to about 850 ppm, ferrous sulfide sticks were added in calculated amounts to the molten steel. It is known that the slag system is one of the major factors that influence the efficiency of desulfurization. The slag in the present work was developed from $7Al_2O_3 \cdot 12CaO$ refining slag with addition of 5%MgO. The CaO-Al_2O_3 based slag, which had a low melting temperature [10-11], a low viscosity, and a high sulfide capacity, was a basis of slags widely used in refining process. These synthetic-slag samples were prepared from chemical grade purity CaO (≥99.0 pct), Al_2O_3 (≥99.5 pct), and MgO (≥99.0 pct) powders. The slag in the experiments was prepared in the laboratory and the method of preparation was reported elsewhere [12]. Table 2 offers the analyzed chemical compositions and physicochemical parameters [13] of the homogeneous samples.

Table 1. *Chemical composition of the experimental steel before addition of S, wt.%*

C	Si	Mn	P	S	Al
0.0018	0.13	0.16	0.0015	0.0045	0.040

2.2. Experimental apparatus

The schematic diagram of the experiment apparatus, performed at 1823 K, is shown in Fig. 1. The furnace cover was sealed. The furnace had a maximum continuous temperature of 1873 K, where the temperature was controlled by a controller unit. The temperature was measured by the Pt-30Rh/Pt-6Rh thermocouple touching the crucible bottom from outside, whose accuracy was ±1 K of the measured temperature between 1073 K and 1973 K. Inert purified argon gas went through the furnace to protect the melt sample from oxidization while the furnace temperature was increasing. On the other hand, this also aimed at ensuring that the partial pressure of oxygen in the experimental atmosphere remained constant, to ensure that there was no influence of the change of the oxygen partial pressure on the electrochemical desulfurization process. An alumina crucible (80 mm outside dimensions × 72 mm inside dimensions × 80 mm height) with about 1000 g melt sample was placed into the center of the furnace, where was a uniform temperature zone. The alumina crucible was placed in a graphite crucible which was connected with a molybdenum wire in alumina tube and led to the ground, used to shield the interfering signals.

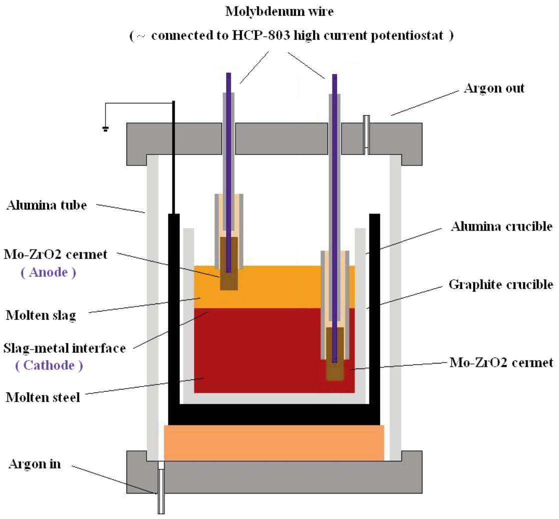

Figure 1. *The schematic diagram of the experiment apparatus*

The slag-metal interface functioned as cathode, and a Mo-ZrO_2 cermet electrode (10 mm outside

Table 2. *Chemical composition and physicochemical parameters of the slag sample*

composition (wt. %)			physicochemical parameters [13]			
CaO	MgO	Al_2O_3	melting point /°C	density /$g \cdot cm^{-3}$	conductivity /$S \cdot cm^{-1}$	dynamic viscosity /Pa·s
44.36	5.04	51.60	~1360	2.75(at 1823K)	0.37(at 1823K)	0.26 (at 1823K)

dimensions × 15 mm height) was inserted into molten steel and connected with a molybdenum wire in alumina tube. Another Mo-ZrO_2 cermet electrode in alumina tube, connected with a molybdenum wire, inserted into slag was used as anode. The insertion depth of the Mo-ZrO_2 electrode remained constant during the experiment. The resistance between the cathode and the anode was monitored with the Agilent 34405A multi-meter and it decreased sharply when the anode electrode contacts with the surface of the slag, and the depth of anode electrode dipped into slag was confirmed. The electrode described above was connected to HCP-803 high current potentiostat (Princeton Applied Research, USA) which controlled the potential between cathode and anode, and the current was measured.

2.3. Experimental procedure

When the temperature reached 1823K, it was kept at this value for 15 minutes, to make sure that the metal sample (about 1000 g) in the crucible was completely melted. A small amount of molten steel sample was taken out with a quartz tube. About 120 g synthetic-slag was added on the top of the molten steel. Slag was added on the top of the molten steel. Another sample was taken out 10 minutes after the slag melted. The external voltage was applied between the molten slag and molten steel at this moment. Samples were taken while experiment was done. The sulfur content in samples was analyzed by Carbon/Sulfur Determinator (CS600, LECO Co., USA). The total oxygen content in samples was analyzed by Nitrogen/Oxygen Determinator (TC-436, LECO Co., USA). After the measurements were completed, the slag samples were withdrawn and powdered with a mortar and pestle, and analyzed using the standard method of chemical analysis to check the composition of the slag.

3. Results

The relation between total sulfur content and reaction time in molten steel with and without external voltage is shown in Fig. 2. It is seen that desulfurization of molten steel was promoted by external voltage. The initial sulfur concentration of molten steel was about 850 ppm, and the sulfur content dropped rapidly after adding the slag. In the case of the experiment without external voltage, for the first 10 min, the total sulfur content in the molten steel decreased from 835 ppm to 660 ppm. The sulfur content dropped by 175 ppm, the average desulfurization rate is 17.5 ppm/min, and the efficiency for desulfurization was about 21%. The desulfurization rate decreased with the increase of the reaction time, and the final sulfur concentration decreased to 610 ppm for the next 60 min. The average desulfurization rate in this interval was about 0.83ppm/min, and the final efficiency for desulfurization was about 27%. In the case of the experiment with external voltage, for the first 10 min, the sulfur content dropped by 175-193 ppm, the average desulfurization rate was 17.5-19.3 ppm/min, and the efficiency for desulfurization was about 21-25%. The results indicated that the beginning of the experiment, the desulfurization reaction at the interface between slag and metal occurred fairly quickly, and the sulfur content dropped very rapidly at the early stages. After this period, the conditions of the kinetic and thermodynamic for desulfurization reaction deteriorated, the desulfurization reaction appeared to occur at a much slower rate and the average desulfurization rate had significantly slowed down. It was confirmed that longer reaction time did not help to further decrease the sulfur content effectively. Based on the composition of experimental and the thermodynamic data, thermodynamic software FACTSAGE (version 7.3) was used, and the desulfurization equilibrium between molten steel and molten CaO-Al_2O_3-MgO slag at 1823K was calculated as shown in Fig 2. The calculation results showed that the sulfur content in thermodynamic equilibrium under the experimental conditions was about 50 ppm, which was lower than the sulfur content during the experiment. The reason for this was that the desulfurization process was not only affected by thermodynamic conditions, but also limited by kinetic factors.

In the case of the experiment with external voltage of 2V, the sulfur content dropped by 70 ppm for the next 42 min, and the average desulfurization rate was about 1.67 ppm/min. In the case of the experiment with external voltage of 4V, the sulfur content dropped by 121 ppm for the next 42 min, and the average desulfurization rate was about 2.88 ppm/min. In the case of the experiment with external voltage of 8V, the sulfur content dropped by 193 ppm for the next 62 min, and the average desulfurization rate was about 4.60 ppm/min. The final sulfur content in molten steel (min [S]) and the average desulfurization rate as a function of the external voltage are shown in Fig 3. It was observed that there was a marked decrease in the final sulfur content in molten steel on application of external voltage, and the average desulfurization rate increased with the increase of the applied electric voltage. On application of external voltage, not only there was an acceleration in sulfur transfer from metal to slag, but also there was much lower sulfur content in molten steel than the sulfur content without considering the imposed electrical potential.

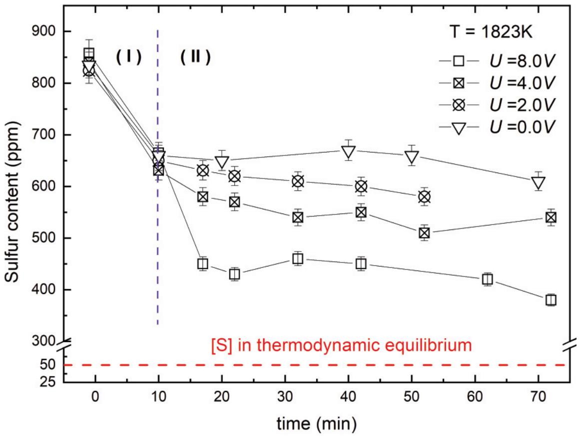

Figure 2. *Sulfur concentration of molten steel as a function of time for the experiment: (I) by slag equilibrium period and, (II) with the applied external voltage period*

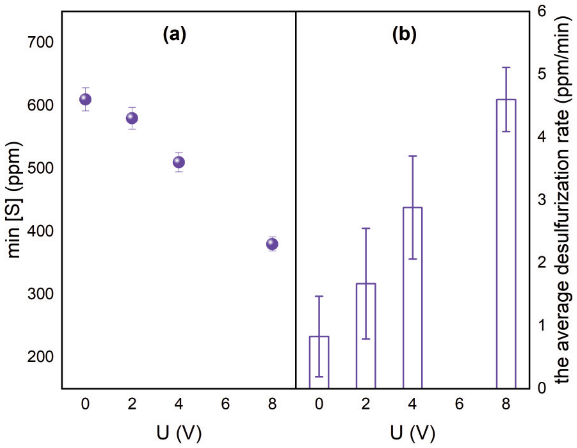

Figure 3. *The final sulfur content in molten steel and the average desulfurization rate as a function of the external voltage*

The application of external electric field between slag and steel also could enhance the deoxidation rate of molten steel [14-16]. The efficiency for deoxidization and the final oxygen content of molten steel as a function of the external voltage is shown in Fig 4. The initial total oxygen content of molten steel was about 100 ppm, which included soluble oxygen and inclusions. In the case of the experiment without external voltage, the total oxygen content in the molten steel decreased from 93 ppm to 69 ppm in 50 min. The oxygen content dropped by 24 ppm and the deoxidization rate was about 0.48 ppm/min. In the case of the experiment with external voltage of 2V, the oxygen content dropped by 46 ppm in 42 min with external voltage, and the deoxidization rate was about 1.10 ppm/min. In the case of the experiment with external voltage of 4V, the oxygen content dropped by 91 ppm in 42 min with external voltage, and the desulfurization rate was about 2.17 ppm/min. In the case of the experiment with external voltage of 8V, the oxygen content dropped by 88 ppm in 62 min with external voltage, and the desulfurization rate was about 1.42 ppm/min. It should be pointed out that the final oxygen content was higher than the soluble oxygen content in thermodynamic equilibrium, a certain amount of oxide inclusions existed in molten steel. The results indicated that the selected slag was a good oxygen ion carrier, and could remove oxygen from molten steel effectively. Due to the decrease in soluble oxygen content with external voltage, the total oxygen content decreased. The application of external voltage to the slag-steel system showed that, not only there was an acceleration in the deoxidization rate, but also lower oxygen content in molten steel. Both of the average deoxidization rate and the final oxygen content increased with the external voltage increasing. When the external voltage was 2, 4 and 8V, the final oxygen concentrations decreased to 46, 43 and 25 ppm, respectively, at the end of the corresponding experiments.

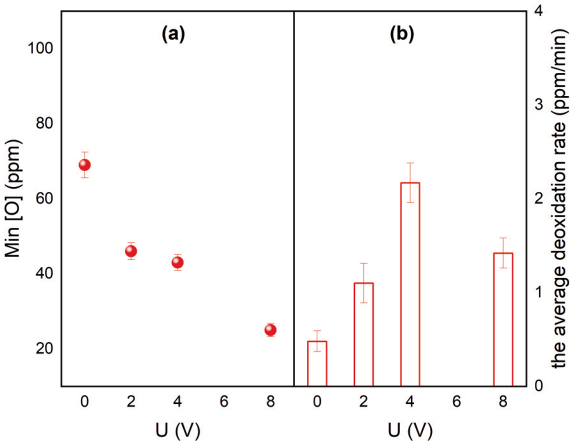

Figure 4. *The efficiency for deoxidization and the final oxygen content of molten steel as a function of the external voltage*

Fig. 5 shows the variations of the current during the desulfurization of molten steel with the different external voltage. As seen from the current-time plot of the electrochemical process, when the external voltage was 2, 4 and 8V, the initial current was about 850, 1800 and 3800 mA, respectively. Then the current gradually declined and, finally reached the steady background current nearly 500 mA. The initial current was approximately in linear correlation with the external voltage. The ionic nature of molten slag and the contact potential between different interfaces in the electrochemical system were considered to be the origin of the steady background current. In the case of the experiment with external voltage of 8V, the Mo-ZrO_2 cermet electrode was broken, and the current gradually reached nearly zero after 18 min.

Then another Mo-ZrO_2 cermet electrode in alumina tube, connected with a molybdenum wire, inserted into slag was used as anode, and the current rose to a peak value of 2000 mA. Due to the high experimental temperature made the control of the atmosphere more difficult, the oxygen content increased in the late stage of some experiments, and the metal-slag reaction was impacted, leading to the current curve ups and downs.

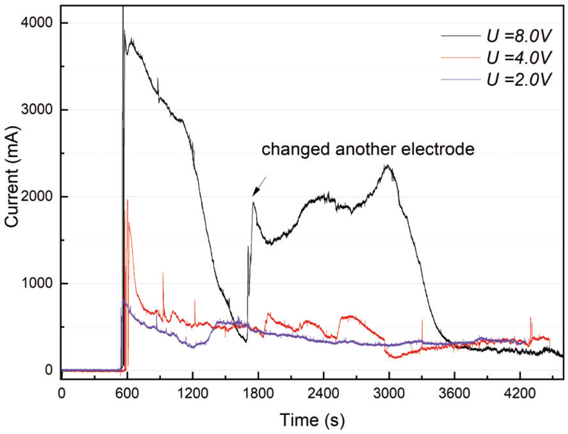

Figure 5. *I-s curves during electrochemical process with different external voltage*

It is known that the transfer of sulfur and oxygen from metal to slag is an electrochemical process involving exchange of electrons between the metal phase and the slag phase. The sulfur in molten steel will be exchanged with oxygen in the slag according to the reaction (In order to correlate the sulfide capacity to the sulfur distribution between the metal and slag phase at equilibrium, the following reaction should be considered):

$$[S] + (O^{2-}) = (S^{2-}) + [O] \qquad (1)$$

As described in previous publications [17], the sulfur partition ratio, LS, between slag and metal can be related to the sulfide capacity (CS). It is generally known that the following parameters are important for good sulfur removal from the metal to slag: liquid and fluid slag with a high dissolved lime content, higher temperature, which improves both thermodynamics and kinetics, lower oxygen content of the steel and oxidation state of the slag, higher decent slag volume. An important thermodynamic parameter, which influences the desulfurization process apart from slag composition, is the oxygen potential of the slag-steel system. The exchange of sulfur between molten metal and slag releases oxygen from the slag thereby decreasing it. The reduction of FeO, due to the low oxygen potential at the slag-metal interface, also releases oxygen. As the (FeO) concentration in the top slag is reduced, the interfacial oxygen content decreases [18]. If this concentration drops below the oxygen bulk concentration in the liquid steel, the direction of the oxygen flux reverses.

In the case of the experiment with application of external voltage between molten steel and slag, there was a marked increase in the rate of desulfurization and deoxidization on application of external voltage. The rate of sulfur and oxygen removal from molten steel to slag was accelerated, which could be attributed to two reasons. The first reason was that the transfer of sulfur and oxygen in liquid phase mass transfer was enhanced, and a rapid mass transfer caused by the external voltage led to an acceleration of the desulfurization and deoxidization rate. The second reason was that as the (FeO) concentration in the top slag was reduced [14], which could be concluded simply from the fact that the total iron content in the final slag decreased with the increase of the external voltage, the sulfur partition ratio between slag and metal increased, and the sulfur of molten steel decreased.

4. Desulfurization Kinetics

4.1. Kinetics mechanism analyses

To understand the mechanism of the desulfurization under the applied external voltage between molten steel and molten slag, the ion theory was used to describe the desulfurization process, and the corresponding schematic diagram is shown in Fig. 6. Under the applied external voltage, the desulfurization processes could be assumed to be composed of the following steps:

1) In molten steel, the dissolved sulfur atom in molten steel diffuses from the inside of molten steel towards the slag-steel interface.

2) At the cathode, the dissolved sulfur atom at the interface between steel and slag became sulfur ion after obtain the electron as follows:

$$[S] + 2e = (S^{2-}) \qquad (2)$$

3) In molten slag, sulfur ion diffusion in molten slag was driven by the electromigration, molecular diffusion, and mass convective. A part of sulfur dissolved in the molten slag, which was easily provided by the analysis of the samples sucked from the slag. Some parts diffused to the anode through the molten slag.

4) At the anode, the sulfur ion in molten slag became sulfur atom after losing the electron as follows:

$$(S^{2-}) = (S) + 2e \qquad (3)$$

Or gas-slag reaction occurs via the oxidation of sulfur ions at the atmosphere-slag interface as a result of their diffusion from molten slag layer to the atmosphere-slag interface and the exposition of the slag surface to atmospheric oxygen. This reaction is described as follows:

$$(S^{2-}) + 3/2O_2 = \{SO_2\} + (O^{2-}) \tag{4}$$

As for desulfurization processes, the dissolved sulfur atom in molten steel diffused to the slag-metal interface and became sulfur ion by the cathodic reaction. A part of sulfur dissolved in the molten slag, which was easily provided by the analysis of the samples sucked from the slag. Some parts diffused to the anode through the molten slag, reacted with atmospheric oxygen and removed to the atmosphere by the gas-slag reaction. The charges accumulated in the two electrodes could be removed through the external circuit.

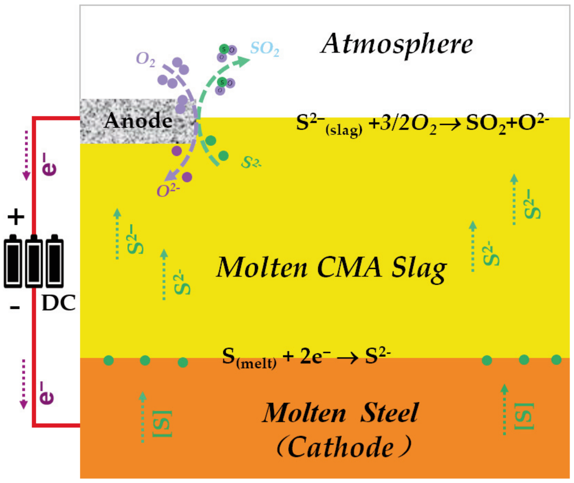

Figure 6. Schematic diagram of desulfurization process

4.2. Derivation of desulfurization kinetics equation

It is known that the course of heterogeneous reactions is limited by the transport of species to and from the phase boundary between molten steel and molten slag. It is known that the reaction rate between molten metal and molten slag at steel-making temperatures is mostly determined by the mass transport [19-21]. Regarding desulfurization in refining process, the reaction rate is dependent on how fast sulfur is transported from the metal phase to the metal-slag interface and how fast it is transported away from the interface into the slag phase. Phase boundary reactions themselves are fast compared to transport as can be concluded simply from the fact that the desulfurization rate rises when the gas injection rate is increased. Therefore, the kinetics of desulfurization is controlled by liquid phase mass transfer.

Under the conditions of high-temperature metallurgical reactions, the sulfur diffusion in molten steel and molten slag may be controlled by mass transfer step during the desulfurization process. It can be assumed that the concentrations of sulfur atom in molten steel $C^{s\text{-}s}_{[S]}$ (mol·m^{-3}) and sulfur ion in molten slag $C^{s-s}_{(S^{2-})}$ between the slag-steel interface are the same; the concentration of sulfur ion $C^{s-e}_{[S]}$ in the slag-electrode interface is equal to the sulfur concentration $C^{eq}_{(S)}$ in equilibrium with atmosphere.

$$C^{s-s}_{[S]} = C^{s-s}_{(S^{2-})} \tag{5}$$

$$C^{s-e}_{[S]} = C^{eq}_{(S)} \tag{6}$$

Because of the external voltage, sulfur ion diffusion in molten slag is driven by the electromigration, molecular diffusion and mass convective. In addition, the forced stirring is relatively weak under the present experimental conditions, and the flow velocity of molten slag under natural convection conditions is relatively small, the influence of mass convection on the mass transfer of sulfur ions in molten slag can be ignored.

The sulfur ion diffusion flux (j_{MD}, kg·m^{-2}·s^{-1}) in molten slag under molecular diffusion conditions can be described by the Fick's first law:

$$j_{MD} = D\frac{\partial C_{(S^{2-})}}{\partial x} \approx k_1\left(C^{s-s}_{(S^{2-})} - C^{s-e}_{[S]}\right) = k_1\left(C^{s-s}_{[S]} - C^{eq}_{(S)}\right) \tag{7}$$

The sulfur ion diffusion flux in molten slag under electromigration conditions can be described by the electric field strength (E, V·m^{-1}) and ion mobility (u, m^2·s^{-1}·V^{-1}), and the relationship between ion mobility (u) and diffusion coefficient (D, m^2·s^{-1}) can be expressed by the Einstein-Stokes relationship [8]:

$$u_i = D_i F / RT \tag{8}$$

$$j_E = zuE \cdot C^{s-s}_{(S^{2-})} = zD_{(S)}FE / RT \cdot C^{s-s}_{(S^{2-})} =$$
$$zD_{(S)}FE / RT \cdot C^{s-s}_{[S]} \tag{9}$$

Assigning $k_2 = zD_{(S)}FU/RTL$, the total mass transfer of sulfur ions in molten slag can be expressed as:

$$j^{slag}_{(S)} = j_{MD} + j_E = k_1 \cdot (C^{s-s}_{[S]} - C^{eq}_{(S)}) + k_2 \cdot C^{s-s}_{[S]} \tag{10}$$

where z is the number of transferred charges (here z=-2), $D_{(S)}$ is the diffusion coefficient of sulfur ion in molten slag, E is the electric field strength, k_1 is the mass transfer coefficient of sulfur ion in molten slag under molecular diffusion conditions, m·s^{-1}. k_2 is the mass transfer coefficient of sulfur ion in molten slag under electromigration conditions. F, R, and T are the Faraday constant (C·mol^{-1}), the universal gas constant and temperature of molten slag (J·mol^{-1}·K^{-1}), U is the applied voltage (V), L is the distance from anode to cathode (the slag-metal interface) (m).

The diffusion flux of sulfur from molten steel to slag-steel interface can be expressed by the Fick's first law with the concentrations of sulfur atom in molten steel body $C^{b}_{[S]}$ and sulfur ion the concentrations of sulfur atom in molten steel$C^{s-s}_{[S]}$and sulfur ion in molten slag $C^{s-s}_{(S^{2-})}$ between the slag-steel interface are the same in the slag-steel interface.

$$j^{(s-s)}_{[S]} = k_3\left(C^{b}_{[S]} - C^{s-s}_{[S]}\right) \qquad (11)$$

where k_3 is the mass transfer coefficient of sulfur ion in molten steel under molecular diffusion conditions.

According to the mass conservation law, the rate of change of the sulfur content in molten steel body is equal to the sulfur ion transfer mass in molten steel and the sulfur ion transfer mass in molten slag.

$$-V\cdot\frac{dC^{b}_{[S]}}{dt} = Aj^{s-s}_{[S]} = Aj^{slag}_{(S)} \qquad (12)$$

where V is the volume of molten steel (m^3), A is the area of slag-metal interface (m^2).

According to Equations (10), (11) and (12), the mass transfer of the sulfur is obtained:

$$-V\cdot\frac{dC^{b}_{[S]}}{dt} = Aj^{s-s}_{[S]} = Aj^{slag}_{(S)} \qquad (13)$$

$$-V\cdot\frac{dC^{b}_{[S]}}{dt} = -A\frac{(k_1+k_2)\cdot k_3\cdot C^{b}_{[S]} - k_1k_3C^{eq}_{(S)}}{\left(k_1+k_2+k_3\right)} \qquad (14)$$

$$\textit{Assigning}\ \beta_1 = \frac{(k_1+k_2)\cdot k_3}{\left(k_1+k_2+k_3\right)},\ \beta_2 = \frac{k_1k_3}{\left(k_1+k_2+k_3\right)}$$

$$\textit{then}\ \frac{\beta_2}{\beta_1} = \frac{k_1}{k_1+k_2}$$

$$\frac{dC^{b}_{[S]}}{dt} = -\beta_1\cdot\frac{A}{V}\cdot C^{b}_{[S]} + \beta_2\cdot\frac{A}{V}\cdot C^{eq}_{(S)} \qquad (15)$$

Under the initial conditions of $C^{b}_{[S]} = C^{0}_{[S]}$ at $t = 0$, the sulfur content in molten steel is given by the following equation.

$$C^{b}_{[S]} = \left(C^{0}_{[S]} - \frac{\beta_2}{\beta_1}C^{eq}_{(S)}\right)e^{-\beta_1\cdot\frac{A}{V}\cdot t} + \frac{\beta_2}{\beta_1}C^{eq}_{(S)} \qquad (16)$$

$$\ln\frac{C^{b}_{[S]} - \dfrac{\beta_2}{\beta_1}C^{eq}_{(S)}}{C^{0}_{[S]} - \dfrac{\beta_2}{\beta_1}C^{eq}_{(S)}} = -\beta_1\cdot\frac{A}{V}\cdot t \qquad (17)$$

Thus, the desulfurization kinetic equation under the applied external electrical field is obtained as Equation (17), with the adjusted parameters of β_1, β_2, $C^{eq}_{(S)}$. When the partial pressure of oxygen in the atmosphere is low, $C^{eq}_{(S)}$ is very low and could be considered approximately to be zero. In this case, Equation (17) will become as following:

$$C^{b}_{[S]} / C^{0}_{[S]} = e^{-\beta_1\cdot\frac{A}{V}\cdot t} \qquad (18)$$

4.3. Comparisons between measured and calculated desulfurization kinetic curves

In the case of the experiment without external voltage and the period (I) of the experiment with external voltage, k_2, the mass transfer coefficient of sulfur ion in molten slag under electromigration conditions (U=0), was zero. Then, $\beta_1=k_1k_3/(k_1+k_3)$, $\beta_2=k_1k_3/(k_1+k_3)$, and $\beta_2/\beta_1=1$, the desulfurization kinetic equation without the applied external voltage was obtained as:

$$\ln\frac{C^{b}_{[S]} - C^{eq}_{(S)}}{C^{0}_{[S]} - C^{eq}_{(S)}} = -\beta_1\cdot\frac{A}{V}\cdot t \qquad (19)$$

The area of slag-metal interface (A) was assumed to be the cross-sectional area of the alumina crucible, subtracted by areas occupied by two alumina protection tubes. Volume of the molten steel (V) was calculated from the density of and its mass used in the experiment. The lowest sulfur content in our sample is assumed to be $C^{eq}_{(S)}$ in the equation. The apparent rate constant (β_1) can be obtained by fitting the experimental data. The comparisons between calculated desulfurization kinetic curves by model and experimental data are given in Fig. 7. Therefore, β_1 of the case of the experiment without external voltage and the Period (I) of the experiment with external voltage were obtained, and are shown in Table 3.

The period (II) of the experiment with external voltage, $k_2 \neq 0$, Equation (17) was used to describe the desulfurization kinetic equation with the applied external voltage. The following assumptions were: i) the lowest sulfur content during the desulfurization with external voltage was assumed to be $C^{eq}_{(S)}$ in the equation, ii) the mass transfer coefficient of sulfur in molten slag under molecular diffusion conditions, k_1

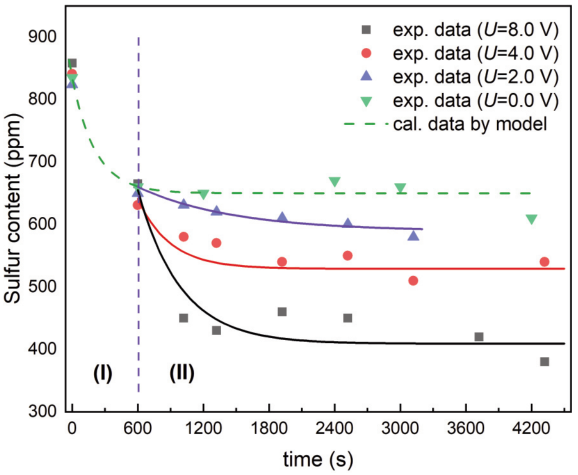

Figure 7. *Comparisons between calculated data by model and experimental data at different applied voltage*

Table 3. *Obtained values of parameters of the desulfurization by fitting the experimental results*

Exp.	Period	U	β_1	k_1	k_2	$2DF/RTL$	k_3
		(V)	($m\cdot s^{-1}$)	($m\cdot s^{-1}$)	($m\cdot s^{-1}$)	($m\cdot s^{-1}\cdot V^{-1}$)	($m\cdot s^{-1}$)
1	(I)	0.0	6.98×10^{-6}	1.27×10^{-5}	0.00×10^{-5}	2.09×10^{-5}	1.46×10^{-5}
2	(I)	0.0	6.58×10^{-6}		0.00×10^{-5}		
	(II)	2.0	9.41×10^{-6}		4.17×10^{-5}		
3	(I)	0.0	8.22×10^{-6}		0.00×10^{-5}		
	(II)	4.0	16.74×10^{-6}		8.34×10^{-5}		
4	(I)	0.0	5.35×10^{-6}		0.00×10^{-5}		
	(II)	8.0	11.43×10^{-6}		16.72×10^{-5}		

was to be a constant, because the influence of electric field on the diffusion coefficient was not considered [9], and iii) the mass transfer coefficient of sulfur in molten steel k_3 was also to be a constant because of the external voltage would not alter the mass transfer rate in molten steel [9]. The comparisons between calculated desulfurization kinetic curves by model and experimental data are also given in Fig. 7. Therefore, β_1 of the period (II) of the experiment with external voltage were also obtained, and also shown in Table 3. The obtained values of parameters k_1, k_2 and k_3 are listed in Table 3. The comparison results showed that the present model could describe the desulfurization kinetics of molten steel under conditions of molten slag and applied external voltage.

5. Discussions

(1) Based on Equation (17) and the parameters values of k_1, k_2 and k_3, it can be seen that the value of k_2 was the same order as the value of k_1, the transfer coefficient of sulfur in slag under electromigration conditions was approximately 2.09×10^{-5} $m\cdot s^{-1}\cdot V^{-1}$. The applied external voltage possessed a large transfer coefficient of sulfur in molten slag under electromigration condition. As $k_2=zD_{(S)}FU/RTL$, k_2 could be increased by increasing the applied external voltage U, controlling the distance between the two electrodes or change the thickness of the slag layer, optimizing the composition and properties of molten slag were used to increase the diffusion coefficient of sulfur in molten slag. Generally, the current density was also used as the process parameter, and the current density was closely related to the voltage, so it significantly affected the electrochemical reaction and electromigration process, thereby affecting the efficiency of the desulfurization process.

(2) In the present work, the applied external voltage varied from 0~8V, and assuming that the composition of molten slag did not change significantly. In actual industrial production, the applied external voltage could be higher, for example, the voltage could reach 20-40V or higher in the DC electroslag remelting (ESR) process. The electrolysis might happen in the molten slag, and some oxides could electrolyze to produce cations such as Ca^{2+}, Fe^{2+}, Mg^{2+}, which could diffuse to the slag-steel interface to obtain the electron and dissolved into molten steel. This could reduce the number of electrons that provide the desulfurization reaction, and current efficiency for electrochemical desulfurization under electric field would decrease. The lower efficiency improved by increasing the current density, so that part of the provided electrons might have been consumed for desulfurization process at approximately a constant rate, while excess electrons might have been used for the other reactions, or resistive heating of the slag.

(3) Based on Equation (17), it can also be seen that a low sulfur content in molten steel was beneficial for the sulfur concentration $C_{(S)}^{eq}$ in equilibrium with atmosphere. As for desulfurization processes in direct current reverse polarity (DCRP), the sulfur was transferred from molten steel to molten slag, then some parts dissolved in molten slag reacted with atmospheric oxygen and were removed to the atmosphere as SO_2 gas [22-23]. The decrease of the partial pressure of oxygen at atmosphere and even the vacuum environment influenced remarkably on the transfer of sulfur. Pressurized and vacuum atmospheres played an important role in desulfurization during metallurgical process.

(4) Desulfurization of molten steel during metallurgical process was affected by the thermodynamic and kinetic conditions. The sulfur diffusion in molten steel and molten slag was controlled by mass transfer step during the desulfurization process. Therefore, the desulfurization rate could be enhanced by increasing k_1 and k_3, which could be improved by increasing the stirring intensity of slag-steel reaction system. In actual operation, blowing Ar gas or electromagnetic stirring was used to improve the stirring intensity. In order to understand the transfer behavior of sulfur during metallurgical process, it was necessary to consider the

combined effects of flow, heat transfer, and thermochemical and electrochemical reactions.

(5) It was observed from the present work that it was possible to accelerate the reaction by applying external voltage, and it was very helpful for understanding and controlling electrochemical refining process. Presumably, the effect of external voltage would also depend on several other factors namely temperature, electrode dimensions and the geometry, the slag-metal interface etc. The slag system was very important to the rate of ion transportation, and composition change of slag system had a slight effect on the reaction at the interface between molten slag and molten metal. These have not been studied in the present work. Yet, the promising results obtained in the present work indicated the need for a more investigation for exploration of its potential in many metallurgical processes.

6. Conclusions

(1) The results indicated that sulfur in molten steel could be removed effectively with applied external DC voltage. On application of external voltage to the slag-steel system, not only there was an acceleration in the desulfurization rate, but also lower sulfur content in molten steel.

(2) According to the mechanism analyses of the desulfurization under the applied external DC voltage, the desulfurization kinetics formulae were developed, and the model calculated results were in accordance with the measured values.

(3) From the desulfurization kinetic it can be concluded that the applied external voltage possessed a large transfer coefficient of sulfur in molten slag under electromigration condition. The desulfurization rate could be enhanced by increasing the applied voltage, increasing the current density, decreasing the partial pressure of oxygen at atmosphere, strengthening the stirring intensity of reaction system, and optimizing the composition and properties of molten slag, etc.

Acknowledgments

This work was supported by Project (51704201) sponsored by the National Natural Science Foundation of China; This work was also supported by Open Project of State Key Laboratory of Advanced Special Steel, Shanghai Key Laboratory of Advanced Ferrometallurgy, Shanghai University (SKLASS 2019-10) and the Science and Technology Commission of Shanghai Municipality (No. 19DZ2270200).

Author contributions

Conception and design of study: J.-F. Xu, J.-Y. Zhang. Acquisition of data: X.-Q. Wu, J.-F. Xu. Analysis and/or interpretation of data: X.-Q. Wu, J.-F. Xu, J.-Y. Zhang. Drafting the manuscript: X.-Q. Wu, P.-W. Gu. Critical revision: J.-F. Xu. Funding acquisition: J.-F. Xu, J.-Y. Zhang. All authors have read and agreed to the published version of the manuscript.

Conflict of interests

The Authors declare that they are not aware of any conflict of interests regarding this work.

Data Availability

No additional data.

References

[1] C. B. Shi, Y. Huang, J. X. Zhang, J. Li, X. Zheng, Review on desulfurization in electroslag remelting, International Journal of Minerals, Metallurgy and Materials, 28(1) (2021) 18-29. https://doi.org/10.1007/s12613-020-2075-3

[2] S. J. Tae, H. C. Jin, H. H. Jung, H. P. Joo, Desulfurization behavior of Si-killed 316L stainless steel melt by CaO-SiO2-CaF2-Al2O3-MgO slag, Journal of Materials Research and Technology, 18 (2022) 2250-2260. https://doi.org/10.1016/j.jmrt.2022.03.048

[3] V. V. Visuri, T. Vuolio, T. Haas, T. Fabritius, A review of modeling hot metal desulfurization, Steel Research International, 91(4) (2020) 1900454. https://doi.org/10.1002/srin.201900454

[4] N. Sen, M. Ghosh, U. K. Banerjee, S. Mazumdar, H. S. Ray, Desulphurisation of high sulphur cast iron using an electrochemical technique, Scandinavian Journal of Metallurgy, 28(6) (1999) 249-253.

[5] S. Ramachandran, T. B. King, N. J. Grant, Rate and mechanism of the sulfur transfer reaction, JOM, 8(11) (1956) 1549-1558. https://doi.org/10.1007/BF03377904

[6] M. Grimble, R G Ward, Kinetics of silica reduction by Cabon-saturated iron, Journal of the Iron and Steel Institute, 203(3) (1965) 264-267

[7] A. Nilas, M.G. Frohberg, Untersuchungen zum Schwefelübergang zwischen kohlenstoffhaltigen Eisenschmelzen und flüssigen Schlacken, Archiv für das Eisenhüttenwesen, 41(10) (1970) 951-956. https://doi.org/10.1002/srin.197001682

[8] A. Mclean, I. D. Sommerville, F. L. Kemeny, Enhanced slag-metal reactions, 4th international conference on molten slags and fluxes, Iron and Steel Institute of Japan, Sendai, Japan,1992, p. 268-273.

[9] D. H. Kim, W. Kim, Y. B. Kang, Electrochemical desulfurization of molten steel with molten slag: reaction rate and current efficiency, Journal of The Electrochemical Society, 165(14) (2018) E816-E825. https://doi.org/10.1149/2.0991814jes

[10] P. C. Yan, X. L. Guo, S. G. Huang, J. V. Dyck, M. X.

Guo, B. Blanpain, Desulphurisation of stainless steel by using CaO-Al2O3 based slags during secondary metallurgy, ISIJ International, 53(3) (2013) 459-467. https://doi.org/10.2355/isijinternational.53.459

[11] Y. Li, Z. H. Jiang, M. F. Jiang, J.W. Wang, W. B. Gu, Deoxidation of molten steel with CaO-Al2O3 based refining slag, Journal of Iron and Steel Research, 14(5) (2002) 12-15.

[12] J. F. Xu, J. Y. Zhang, C. Jie, F. Ruan, K. C. Chou, Experimental measurements and modeling of viscosity in the CaO-Al2O3-MgO slag system, Ironmaking and Steelmaking, 38(5) (2011) 329-337. https://doi.org/10.1179/1743281210Y.0000000014

[13] J. F. Xu, J. Y. Zhang, J. C. Li, M. Q. Sheng, T. Zeng, K, Wan, Study on transport of oxygen through CaO-MgO-Al2O3 slag from molten ultra-low carbon steel by chronoamperometry, Journal of Iron and Steel Research International, 19(2012) 1141-1144

[14] G. H. Zhang, K. C. Chou, F. S. Li, Deoxidation of liquid steel with molten slag by using electrochemical method, ISIJ International, 54(12) (2014) 2767-2771. https://doi.org/10.2355/isijinternational.54.2767

[15] J. J. Li, K. Yoshinao, A new design of oxygen sensor for electromotive force measurement and electrochemical deoxidation by using oxygen pump, ISIJ International, 60(6) (2020) 1135-1140. https://doi.org/10.2355/isijinternational.ISIJINT-2019-641

[16] W. D. Judge, J. Paeng, G. Azimi, Electrochemical characteristics of molten iron electrodes in slag and electrochemical properties of their interface, Electrochimica Acta, 389(2021) 138755. https://doi.org/10.1016/j.electacta.2021.138755

[17] C. K. Cooper, D. A. R. Kay, Behaviour of sulphur during ac electroslag remelting, Journal of the Iron and Steel Institute, 208(1970) 856-859.

[18] X. G. Lu, F. S. Li, L. F. Li, K. C. Chou, Electrochemical model of oxygen ion transport in slag, Acta Metallurgica Sinica, 35(7) (1999) 743-747.

[19] K. S. Coley, Progress in the kinetics of slag-metal-gas reactions, past, present and future, Journal of Mining and Metallurgy, Section B: Metallurgy, 49(2) (2013) 191-199. https://doi.org/10.2298/JMMB121220017C

[20] Z. G. Yu, H. Y. Leng, L. J. Wang, K. C. Chou, Evaluation of carbide capacity in CaO-based ternary systems at 1773K for refining process, Journal of Mining and Metallurgy, Section B: Metallurgy, 56(1) (2020) 35-42. https://doi.org/10.2298/JMMB190110054Y

[21] H. B. Yuan, B. Cai, X. C. Song, D. Z. Tang, B. Yang, Insight on the reduction of copper content in slags produced from the Ausmelt Converting Process, J Min Metall BJournal of Mining and Metallurgy, Section B: Metallurgy, 57(2) (2021) 155-162. https://doi.org/10.2298/JMMB201016013Y

[22] M. Kato, K. Hasegawa, S. Nomura, M. Inouye, Transfer of oxygen and sulfur during direct current electroslag remelting, ISIJ International, 23(7) (1983) 618-627.

https://doi.org/ 10.2355/isijinternational1966.23.618

[23] A. Mitchell, IOP Conference Series Materials Science and Engineering, Leoben, Austria, 2016, p. 012001

ODSUMPORAVANJE RASTOPLJENOG ČELIKA POMOĆU RASTOPLJENE ŠLJAKE ELEKTROHEMIJSKOM METODOM

X.-Q. Wu [a], J.-F. Xu [a, b *], P.-W. Gu [a], J.-Y. Zhang [b]

[a] Fakultet za gvožđe i čelik, Univerzitet u Sudžouu, Đangsu, Kina
[b] Glavna laboratorija za modernu metalurgiju i obradu metala u Šangaju, Univerzitet u Šangaju, Šangaj, Kina

Apstrakt

Odsumporavanje tokom metalurškog postupka je po prirodi elektrohemijska reakcija. Odsumporavanje elektrohemijskom metodom je predloženo u ovom radu u prisustvu rastopljene CaO-MgO-Al_2O_3 *šljake koja je prekrivala rastopljeni čelik. Razmatrano je dejstvo primenjenog spoljašnjeg jednosmernog napona koji je varirao od 0 do 8V. Rezultati su pokazali da se sumpor u rastopljenom čeliku može efikasno ukloniti primenom spoljašnjeg napona. Na osnovu analize odsumporavanja pod primenjenim spoljašnjim naponom, razvijene su kinetičke formule i model koji je upotrebljen za izračunavanje rezultata koji su u skladu sa eksperimentalnim vrednostima. Koeficijent prenosa sumpora u rastopljenoj šljaci u uslovima elektromigracije iznosio je približno* $2.09\times10^{-5}\ m\cdot s^{-1}\cdot V^{-1}$. *Odsumporavanje rastopljenog čelika pomoću rastopljene šljake se može unaprediti povećanjem primenjenog napona, smanjenjem parcijalnog pritiska atmosferskog kiseonika, jačanjem inteziteta mešanje reakcionog sistema i optimizacijom sastava i svojstava šljake.*

Ključne reči: *Odsumporavanje; Elektrohemija; Kinetika; Elektromigracija; Koeficijent prenosa mase*