Behaviors of the Molten Copper Slags in the Vertical Electric Field

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The behaviors of molten copper slag under the vertical electric field were investigated in this paper. The presence of the electric field could accelerate the migration of copper drops from anode region to the cathode. Electrolysis reaction of molten copper slag was occurred at the interface of electrode and the molten slags. The copper slag cleaning process would be promoted in the electric field due to the electrocapillary and a certain degree of electrolysis. The Physical and chemical processes of copper slag cleaning under the vertical electric field was also summarized in the article.

KEY WORDS: electric potential gradient; electrolysis; electrocapillary phenomenon; copper slag cleaning.

1. Introduction

The main losses form of copper element are physically entrapped or chemically dissolved in the copper slags. The traditional slag cleaning method is electric furnace process including two steps, intensive slag reduction and quiet sedimentation. Although the process is suitable for the various copper slags, it is also with the higher energy consumption.

Ionic structures of the molten copper slags indicated the possibilities of utilization of the electrocapillary phenomenon in accelerating the settling of copper drops from the slag, and the slag electrolysis in reduction of magnetite and precipitation the dissolved copper. Vertical electric field could lead to a steep electric potential gradient along the molten slag height and accelerate the migration of copper drops from anode region to the cathode.

This paper with the objective to determine the settling behaviors of copper for the intensive copper slags under a vertical electric field was therefore initiated. A second purpose was to investigate the copper sedimentation process to get a better understanding of the physical and chemical phenomena occurring in the molten slags.

2. Experimental Materials and Procedure

The materials are the copper slags from a factory of China. The main phases of slag are fayalite and magnetite. The main existing form of copper in the slag was primarily the pure copper metal, a spot of cuprous oxides and matte were also included in the sample. The obtained properties and chemical composition of slags were presented in Table 1.

A schematic of the experimental apparatus is given in Fig. 1. An alumina crucible with 35 mm diameter was placed in the constant temperature zone of the vertical alumina reaction tube by using MoSi2 bar as the heating elements. The temperature was measured by two Pt-Pt/Rh thermocouples. The reaction tube was closed from both two ends by water-cooled caps. High-purity Argon as the shielding gas was added during the whole experimental process.

During the experiments, 50 grams of copper slag and 20 grams of pure copper as the cathode were added to an alumina crucible. At the top of slag, a layer of intensive graphite was as the anode. Two molybdenum rods with the alumina shielded which were connected to a DC power supply equipped immersed into the electrode as shown in Fig.

Table 1. Chemical composition of slags (Mass%).

| Chemical composition | FeO | Fe₂O₃ | SiO₂ | Al₂O₃ | CaO | Cu | Others |
|---------------------|-----|-------|------|-------|-----|----|--------|
| Weight percent (wt pct) | 41.03 | 11.11 | 36.94 | 1.78 | 0.2 | 5.11 | 3.83 |

Fig. 1. Experimental set-up for slag cleaning under the electric field.

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It should be reached to the experimental temperature at a larger heating rate as soon as possible after being 1100°C. The slag was separated from the crucible, weighted and analyzed for chemical composition and phase by X-ray Fluorescence (XRF), X-ray Diffraction (XRD) and was also examined microscopically by Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS).

3. Results and Discussion

3.1. Copper Content in the Slag
The effects of the Electric potential gradient (EPG) on copper contents in the slag during the cleaning process under a vertical electric field at 1230°C (1503 K) were shown in the Fig. 2. As shown in Fig. 2, the copper contents in the slag were almost not changed with the passage of time in natural settling process. With the added of electric field, the copper contents were decreased significantly. Higher the EPG was, lower the copper contents in the slag were. But the sedimentation of copper phase was not evident when the EPG was up to 1.5 V/cm after 30 minutes. The reason was probably that the migration of copper droplets in electric field was related with the diameter of the droplets [10]. The action of electric field mainly celebrated the concentration of the small copper partials. When the diameter of the partials was bigger than a limited degree, the principle force of the copper sedimentation was gravity, not the electric field.

3.2. Slag Phases
The existence of electric field on the molten slags could not only celebrate the congregation and migration of copper drops in the molten slag by electrocapillarity, but could affect the slag composition through electrolysis action. The influences of electrolysis on the slag composition under various EPG were shown in Fig. 3.

From Fig. 3, the peaks of Magnetite were gradually disappeared along with the increase of EPG, which were replaced by some dispersed fayalite peaks with lower intensity. In addition, a new Cristobalite peak was appeared at the 2-theta of about 58. The results indicated that the compositions of slag were changed gradually. The SEM and EDS analyses of the slag with the various electric field indicated that the copper content could be decreased significantly and the compositions of the slag were very different. They were exhibited in the following Fig. 4. The experimental temperature was 1503 K and the settling time under the electric field was 30 min. As shown in the pictures, the original slag contained much more Fe₂O₃ and the particle which included copper element was bigger. With the increasing of EPG, Fe₂O₃ was more and more scarce and the particulates including copper element became smaller and less until disappeared. But the free phase of SiO₂ was emerging in a higher EPG. These results further illustrated that the electrolytic actions was occurred in the molten slag under the electric field.

The increasing of EPG could promote the congregation and sedimentation of the copper particles and the reduction of Cu₂O and Fe₂O₃. Utilization of the electrolytic action in copper recovery from metallurgical slags can be particularly beneficial for the treatment of slags with high cuprous oxide contents. On the other hand, the Al₂O₃ phase was increasing as the EPG increased (Fig. 4(d)). The electrolytic corrosion of the crucible was more and more seriously with the higher EPG.
3.3. Copper Cathode

The ions in the molten slags could be congregated nearby the electrodes. Oxidation or reduction reactions were occurred in the surface of the electrodes. A. Warczok et al. proved the existence of the electrode reaction in the molten copper slags under a vertical electric field. The liquid copper was as the cathode, and a 4 mm diameter platinum rod as the anode. The model of the electrolysis process of fayalite based copper slag was presented in Fig. 5. The results were in agreement with the current work.

At the interface between the molten slags and liquid copper cathode, the Fe³⁺, Fe²⁺ and Cu⁺ could be reduced as follows:

\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \]  \hspace{1cm} (1)
\[ \text{Fe}^{2+} + e^- \rightarrow \text{Fe}^0 \]  \hspace{1cm} (2)
\[ \text{Cu}^+ + e^- \rightarrow \text{Cu}^0 \]  \hspace{1cm} (3)

The follow reactions would be in progress under the condition in excess amount of Fe³⁺ in the molten slag.

\[ 2\text{Fe}^{1+} + \text{Fe}^0 \rightarrow 3\text{Fe}^{2+} \] \hspace{1cm} (4)

The settling of copper droplet and electrolysis of the molten slags contained FeO led to an increase in the mass of copper cathode due to precipitated metallic iron and copper droplets. Figure 6 shows that the cathode mass gain increased with increasing the potential gradient up to about 1.5 grams at the potential gradient of 1.5 V/cm. At the same time, the iron content of the copper cathode increased also up to about 1%. This could indicate that a second iron-rich metallic phase was formed at the cathode.

On the other hand, the microanalysis was carried out for the surface of slag nearby the copper cathode with various EPG at 1503 K. The results were showed in Fig. 7. There were more and more copper matte based particles in the sur-

![Fig. 5.](image)

**Fig. 5.** Mechanisms of electrolysis of liquid fayalite slags containing cuprous oxide.\(^6\)

![Fig. 6.](image)

**Fig. 6.** Mass gain of copper cathode and iron content in copper as a function of potential gradient (1503 K, 30 min).

![Fig. 7.](image)

**Fig. 7.** SEM and EDS analyses of the copper slag surface nearby the cathode (a: EPG is 0 V/cm, b: EPG is 1.0 V/cm, c: EPG is 1.5 V/cm).
face of the slag with the increasing of EPG. These demonstrate that the vertical electric field could accelerate the settling speed of the copper and matte in the molten slags. Through the EDS analysis of the typical particles, the [O] contents in these particles were decreased under the electric field. The deoxidation process occurred at the interface of the copper cathode and molten slags. There were slightly differences of [O] content in the slag when the EPG was higher than 1.0 V/cm.

3.4. Graphite Layer Anode
In this experiment, the anode was used the graphite layer on the top of molten slag. The main anode reactions at the interface were showed as follows:

\[
\text{[O]}^2- - 2e \rightleftharpoons 1/2 \text{O}_2 \tag{5}
\]

\[
\text{C} + 2\text{[O]} \rightleftharpoons \text{CO}_2 \tag{6}
\]

\[
\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO} \tag{7}
\]

After these reactions reached equilibrium, the outlet gas did not contain the [O] in theory. Figure 8 illustrates the [O] contents in the outlet gas before and after applying an electric field for the various EPG. The picture investigated that the electric field could make the O\(^2-\) congregated at the anode, and reacted with graphite when the O\(^2-\) concentration reached a certain value. That is to say, the primary product is carbon monoxide rather than Fe\(_3\)O\(_4\) \(^[6]\) at the anode. The higher the EPG, the faster the deoxidation rate.

3.5. Interface Tension and Electrocapillary Motion
When a liquid metallic or matte is placed in an electrolyte, an electric double layer was formed at the metallic or matte-electrolyte interface. The external electric fields could affect the charge of this double layer. Regrouping of ions takes place in the diffusion layer, and it could create a gradient of the electric charge density along the drop surface, so, an interfacial tension gradient was developed. The fluid would flow from low interfacial tension regions towards the high one. Therefore, the liquid around the drops started to circulate, as shown in Fig. 9. This is the electrocapillary phenomenon. It was considered as the primary driving force to accelerate the settlement of copper drops in the molten slag under the electric field.

The electrocapillary motion was determined by the slag-metal interface under the electric field. The Girifalco-Good relation could estimate the slag-metal interface tension as the following Eq. (8),

\[
\gamma_{s-m} = \gamma_s - 2\Phi (\gamma_m \cdot \gamma_s)^{1/2} \tag{8}
\]

\(\gamma_{s-m}\) - slag-metal interface tension (N·m\(^{-1}\))
\(\gamma_s\) - molten slag surface tension (N·m\(^{-1}\))
\(\gamma_m\) - liquid metal surface tension (N·m\(^{-1}\))
\(\Phi\) - relation coefficient

K. C. Mills\(^{11}\) studied that the liquid metal surface tension was about 3 times higher than the molten slag at the same system.

\[
\gamma_m \approx 4\gamma_s \tag{9}
\]

In the molten copper slags, the copper droplet was micro and the diameters were usually about a few microns, the droplet could be completely wetted by the molten slags. Based on this hypothesis, the Eq. (10) was true.\(^{12}\)

\[
\Phi = 1 \tag{10}
\]

Consequently, Eq. (8) could be described as:

\[
\gamma_{s-m} = \gamma_s \tag{11}
\]

Therefore, the slag-metal interface tension could be replaced by the surface tension of the bulk molten slags. The molten slags surface tension in the electric field was measured through the cylinder contact method in this study. The schematic of the experimental unit was illustrated in Fig. 10.
The surface tension constant was determined using deionized water as a standard before each measurement.

The surface tension as the function of the potential gradients at 1,523 K was displayed in Fig. 11. From the picture, the fitting curve of the experimental points basically met the parabola equation. The potential gradient value was about 1.2 V·cm⁻¹ when the slag surface tension reached the maximum. According to the Lippmann’s equation, 10) the corresponding electrode potential of the maximum value of slag-metal interface tension was the zero charge potential. At the maximum of electrocapillary curve the surface charge density was zero and a droplet does not migrate because there was no tension gradient at the metal-slag interface. On the other hand, the interface tension gradient reached the maximum when the electrode potential approached close to the zero charge potential infinitely.

On fundamental grounds, 7) the slope of the electrocapillary curve at the ordinate must satisfy certain physical requirement. The droplet migration direction could change via the slope of the arms of the electrocapillary curve as shown in Fig. 12. For this experiment, the electrocapillary curve was with the first case, which was to say, the copper droplet migrated to the cathode.

4. Conclusions

The following conclusions could be drawn regarding the behavior of molten copper slag under the electric field:

(1) The settlement of copper drops in the molten slags could be affected significantly by an electric field. The settling rate under an electric field was much higher than the natural settling only under the gravity.

(2) Electrolysis reaction of molten copper slag was occurred on the interface of electrode and slag. The deoxidation process were occurred at the interface of the copper cathode and the molten slags, and a second iron-rich metallic phase was formed at the cathode. At the interface of graphite layer anode and molten slag, there would be CO and CO₂ gas evolution under the electric fields.

(3) The electrocapillary curve was also studied using the classical empirical formula and experiments. The migration direction of copper droplet could be judged by the curve shapes.

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