Dissolution Mechanism of Magnetite into Copper Matte

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（銅溶錬マットへのマグネタイト溶解機構解明）

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要約

Chapter 1: Introduction

While the global consumption of copper is increasing, copper resources are insufficient worldwide. Therefore, it is highly desirable to reduce copper losses in the copper smelting process. Copper loss into slag accounts for 1 mass% of copper production, and copper smelting slag is used only for waste as raw materials for cement or civil engineering materials. In addition, due to the decrease in the grade of copper ore, the amount of slag is increasing every year. Most studies for reducing copper loss assume copper extraction from copper smelting slag, but it is very difficult to apply to the actual industrial process because it requires a large investment in equipment. Therefore, optimizing the actual copper smelting process and suppressing the occurrence of copper loss itself without an additional copper recovery process is the best way to realize the reduction of copper loss. In this study, I focused on the mechanical losses caused by magnetite in the copper smelting process. Since mechanical losses account for 65–80% of the total copper losses, the importance of reduction of the mechanical loss is very high. The stagnation of magnetite at the slag/matte interface can occur in the copper smelting process using a flash furnace. The magnetite inhibits the absorption of the suspended matte in the slag phase into the matte phase, which leads to copper loss. Therefore, the rapid removal of the magnetite by its dissolution into the matte can greatly contribute to reducing copper loss. However, the interfacial phenomena between magnetite and matte are complicated, and the factors that decrease the reaction rate was not clarified. In addition, the reaction rate between matte and magnetite using the matte composition of the actual process has not been evaluated, and the effect of SO_2 gas formation at the interface on the reaction rate has never been studied. Therefore, the effects of the FeS content in matte (range of the industrial matte composition) on the interfacial phenomenon with magnetite are worth studying. Furthermore, another essential research project is to investigate the reaction rate with magnetite using matte with low FeS content, which nobody has clarified. Therefore, this study aims to investigate the effect on the reduction of the dissolution rate by clarifying the interface phenomenon between the magnetite and the matte using the composition of the actual process, and quantitatively evaluating the dissolution rate of the magnetite into the matte. The important results and understandings obtained in this research are concluded by the specific chapters in sequence as follows.

Chapter 2: Clarification of Interfacial Phenomena between Magnetite Thin Film and Matte

In Chapter 2, with the objective to clarify the high-temperature phenomena occurring at the interface between magnetite and matte as a function of the FeS content in matte. The interface was directly observed using a novel in-situ observation system through the magnetite thin film, by utilizing the slight transparency of the magnetite phase under visible light. the reaction rate between magnetite and matte was evaluated based on the time dependence of the decrease in the magnetite thickness, which was analyzed based on the changes in its brightness during the in-situ observations. Finally, using the results of reaction rate evaluation, the effect of gas formation on the dissolution behavior is discussed. The conclusions obtained in this chapter are summarized below: (1) By exploiting the slight transparency of magnetite to visible light, in-situ observations were performed on a magnetite thin film fabricated by sputtering. The morphological changes in the film could be observed clearly, and the decrease in its thickness could be evaluated quantitatively based on the change in the brightness at the interface. (2) During the reaction between FeS and magnetite, no gas was observed at the interface, and the magnetite dissolved immediately into the FeS. (3) The reaction between matte and magnetite was accompanied by the formation of SO_2 gas at the interface regardless of the change in the initial S concentration in the matte, and when the FeS content in the matte increased, the size of the generated gas bubbles decreased. (4) From the dissolution behavior of magnetite in molten matte at 1200 °C, dissolution kinetics was explained in terms of mixed-control by both mass transfer in the solution and chemical reaction by SO_2 gas generation. The calculated overall reaction rate constant K with the FeS content in matte was 5.6×10^{-7} to 1.4×10^{-6} m/s, which was significantly smaller than the reported mass transfer coefficient between FeS and magnetite without the formation of gas bubbles. It is considered that the overall reaction rate is decreased due to the reaction of generating SO_2 gas at the interface between magnetite and matte. Furthermore, as the content of FeS in the matte increased, the rate constant K also increased, the main factor of this is the increase of oxygen solubility.

Chapter 3: Investigation of the Reaction Behavior at the Interface between Bulk Magnetite and Matte

Although the reaction mechanism was clarified due to the use of the magnetite thin film from Chapter 2, the limited oxygen source of the thin film can cause stagnation of the SO_2 gas or difficulty in SO_2 gas separation. Therefore, in Chapter 3, the objective is to evaluate the dissolution rate of magnetite under continuous gas generation conditions at the interface using the bulk phase of magnetite and matte as in the actual industrial process. Furthermore, the gas behavior was evaluated from the reaction between the bulk magnetite and the bulk matte considering the effect of the matte composition and reaction time by ex-situ analysis. The conclusions obtained in this chapter are summarized below: (1) When the initial FeS content in the matte was reduced, the size of the remaining gas in the matte increased. A lot of fine bubbles were observed around the magnetite substrate, but gas bubbles attached to the magnetite interface were not found. When the magnetite is dissolved into the matte, the magnetite surface was not flat, and as the reaction time increases, it became more irregular. (2) From the dissolution behavior of magnetite in molten matte at 1200 °C, dissolution kinetics was explained in terms of mixed-control by both mass transfer of oxygen in the solution and chemical reaction by SO_2 gas generation. The calculated overall reaction rate constant K increased with the FeS content in the matte from 2.5 to 6.3 × 10^{-6} (m/s), which was significantly smaller than the reported mass transfer coefficient between FeS and magnetite without the formation of gas bubbles. It is considered to be the effect of the SO_2 gas generation reaction at the interface between magnetite and matte, and the stagnant gas around the magnetite substrate interferes with the mass transfer of oxygen. (3) The obtained K value for bulk is larger than the K value for the thin film due to the effect of the difference in the manufactured structure of magnetite and convection in matte by temperature difference. It is considered that by using the bulk matte, the convection becomes active, which causes the boundary layer to decrease, and consequently, the mass transfer rate $k(=D/\delta)$ increased.

Chapter 4: Evaluation of Bubble Behavior Considering the Force Balance

The behavior of the gas bubbles stagnant at the interface of the magnetite observed from previous experimental results by considering the force balance was clarified. Furthermore, the critical radius of bubbles with the contact angle between the matte and the magnetite was summarized through calculation so that gas bubbles attached to the interface or stagnant gas bubbles could be easily removed by buoyancy. The conclusions obtained in this chapter are summarized below: (1) At the interface between the sapphire substrate/matte, gas bubbles attached to the interface are difficult to separate from the sapphire substrate due to the high tension on the sapphire substrate. At the interface between the magnetite/matte, the separation of the generated gas bubbles becomes easier because the shape of the magnetite surface is irregularly formed. (2) The smaller the diameter of the stagnant bubble around the magnetite, the greater the contribution of the force due to the surface tension gradient. When the initial FeS content in the matte is decreased, the force due to the surface tension gradient becomes smaller. (3) In order to float the stagnant bubbles, they must be enlarged to a certain bubble diameter. The observed gas bubbles (10–30 μm) in the concentration boundary layer between the magnetite and the matte should be stagnated due to the surface tension gradient around the bubble.

Chapter 5: Conclusions

According to the conclusions summarized in each chapter, the research objectives of investigating the interfacial reaction mechanism of magnetite into matte and quantitatively evaluating the dissolution rate of magnetite on the composition of the matte used in the actual industrial process were achieved. The main factors that reduce the dissolution rate of magnetite are the SO_2 gas generation reaction at the interface and stagnant gases around the magnetite. However, with the matte composition used in the actual industrial process, it would be difficult to remove the stagnated bubbles around the matte-magnetite interface spontaneously, and hence the design of the process to prevent the gas generation at the interface is key to reducing copper loss.

It would be also effective to perform mechanical agitation such as gas injection into the melt to easily remove the stagnant gas bubbles at the matte-magnetite interface.

Key words: Copper smelting, Copper loss, Matte, Magnetite, In-situ observation, Flash furnace