

氏名	ふあん よん 樊 涌
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指導教員	東北大学教授 柴田 悦郎
論文審査委員	主査 東北大学教授 柴田 悦郎 東北大学教授 葛西 栄輝 東北大学教授 福山 博之

論文内容要旨

1. Why we do this research?

In the first chapter, a review of current proposals and researches of metals extraction and recovery from copper slag was provided. There are mainly four kinds of methods include mineral processing, hydrometallurgy, pyrometallurgy of reduction and pyrometallurgy of oxidation. Every method has its strong and weak points, so it is not easy to say which one is the best.

Mineral processing method is a traditional method dealing with mineral ores. In general, by using this method, copper slag is regarded as low grade copper or iron ore. Actually, only metallic copper and sulfide minerals can be floated effectively. Since the copper in slag is mainly in the form of oxides, the flotation method is not effective for recovering of them. Moreover, the iron in the copper slag is in the form of iron silicate without phase transformation. So the magnetic separation for iron recovery is not effective as well. (Shen, H., *et al.*, 2003)

Hydrometallurgy method has already been well developed to selectively extract metals such as cobalt, copper, and zinc from copper slag, with the aim of maximizing metal recovery and iron concentration. In fact, iron was regarded as the contaminant in their process which virtually adding the cost burden. What's more, the chemicals used in the

process is hardly say to be safe to the environment. In addition, after the hydrometallurgy processing, the iron is usually reside in the wastes such as ferric hydroxide, which is very difficult to be disposed and reused.

Pyrometallurgy is good option due to the large treatment capacity and fast processing speed. There are two directions in treating of copper slag. One is reduction method by remelt the slag with coal to produce metallic iron (Fe) for magnetic separation. However, the reduction of iron oxides to metallic iron is an endothermic reaction and also uses a lot of carbon as reductant resulting in large energy and coal input. The cost will be high and carbon dioxide cannot be avoided. The other is oxidation method by blowing the oxidizing gas into the slag for magnetite (Fe_3O_4) precipitation for magnetic separation. The oxidation method has energy and cost advantages compared with reduction to metallic iron. However, the reheat of copper slag also require a lot of energy.

Considering the above problems, we proposed a recycling process to directly oxidizing the molten state copper slag for magnetite precipitation in the second chapter. This proposal saves the reheat energy input and cost.

2. How about TTT and CCT oxidation process?

There are two cooling processes adopted into the slag treatment in the copper smelter, one is an air-cooling process and the other is a water quenching process. However, these slag cooling processes does not positively control of microstructure of slag which results the limitation in the downstream utilization. For this purpose, it emphasized the importance of TTT and CCT oxidation process of molten copper slag. With the study of them, the property of the final slag could be estimated by the designed cooling path. Furthermore, it could be possible or easier to recover the heat through a designed cooling path.

The TTT procedures were carried out at different incubation temperatures to study the crystallization behaviors. It can be concluded that although fayalite and magnetite already existed in the original copper slag, their amounts changed with the holding time. In addition, after a certain holding time, hematite was precipitated. From the TTT diagram, it can be clearly understood that magnetite was precipitated before

hematite under isothermal transformation. The initiation time of crystallization increased with decrease in holding temperature. During the CCT treatment under the current experimental, magnetite is directly precipitated from the remelted copper slag instantly contacting with air. Concerned about hematite, it takes relevant short time at tens of seconds in scales for an appearance of peaks in the XRD patterns. Moreover, the hematite peak intensity is increase along with the increase of time duration of oxygen by air.

However, there are some obvious flaws when adopting the TTT and CCT to copper slag in air.

TTT process is actually not widely used because of its complex operations. Moreover, from the study, the initiation time of crystallization decreased with increase in holding temperature which suggesting that higher temperature provide strong reaction driving force for magnetite or hematite precipitation in copper slag. It would take relative longer time for the precipitation of all iron into magnetite or hematite by TTT process compared with molten oxidation. In addition, during the process, hematite was also precipitated. Well actually, the magnetite was preferred because of its intensive ferromagnetism and large crystal size. The hematite appearance would affect the downstream magnetic separation process.

CCT is more famous than TTT process. From the study, it suggested that magnetite is directly precipitated from the remelted copper slag instantly contacting with air, and the lower cooling rate providing more effective magnetite precipitation. However, even at the cooling rate of 1.4 K/s for very long time, it is not sufficient for oxidizing all the iron in copper slag into magnetite or hematite. Moreover, same as TTT process, hematite was also precipitated.

From the above information, the controlled molten oxidation method comes naturally to us.

3. Molten oxidation, what is going on?

In the forth chapter, the simulation of our proposal, i.e., directly blowing oxidizing gas (pure oxygen, air, and 1 vol% oxygen) onto molten slag for magnetite precipitation was implemented. The crystallization behaviors were studied, with the variation of the

magnetite and hematite content during molten oxidation showing a trade-off relationship.

It was concluded that a lower oxygen partial pressure was beneficial to the precipitation of magnetite. In particular, the use of 1 vol% oxygen resulted in a selective oxidation tendency for magnetite precipitation. From this study, it was found that selective precipitation of magnetite from copper slag could be realized by easily controlling the oxygen partial pressure, which set the foundation for the future high efficient magnetic separation of iron-bearing and non-iron-bearing slag constituents for specific purposes. The crystal morphology of the iron oxides and the distribution of impurities were also investigated. It was observed that chromium and zinc exhibited likelihood to be tracked with iron, which emigrated and transformed into precipitated iron oxide during molten oxidation, whereas copper exhibited the reverse behavior. An attempt was also made to describe the reaction mechanism considering the molten oxidation processes based on current knowledge. The ion diffusion, which is assumed to be the mobility of O^{2-} , was relatively weak in the early stage and was enhanced as the oxidation progressed. The gas diffusion was assumed to dominate the “controlling step” during the later stage of the reaction.

4. How to separate the precipitated magnetite out of slag?

The above study was conducted on mill-gram scale experiments using an infrared furnace. Generally, the study on mineral liberation and separation require gram-scale slag sample due to the experimental operation. In the fifth chapter, gram scale slag sample was prepared by an electric furnace. Molten oxidation at 1 vol% oxygen atmosphere was performed for magnetite precipitation. The magnetite precipitated copper slag would be used for mineral liberation and separation. 10 hours of molten oxidation at 1 vol% oxygen atmosphere would lead to approximately 40-50 mass% magnetite content in 100 g copper slag in which the magnetite particle size is larger than approximately 50 μm .

A new specific mineral liberation technology - High-voltage (HV) electrical pulses was implemented for an attempt to the liberation of precipitated magnetite in copper slag, which capable of producing of the high percentage of the monomineral particles at

disintegration of mineral aggregates. (Andres, U., 2010). With the use of laser microscope and its corresponding image software, mineral distribution was complemented and depicted the 100 μm under sieve product has a large percentage of the liberated minerals.

Through 50 μm under sieve crushing product feeding to magnetic separation, iron grade in concentrate would reach to approximately 60 mass% with a recovery of approximately 60 % at magnetic field intensity of 100 mT. There is a trade-off relationship between iron grade and the recovery rate. Higher magnetic intensity would contribute to lower Fe grade in the concentrate, while the improving of recovery rate would result in lower Fe grade in the concentrate. During this whole recycling process, chromium and zinc revealed to be more likely tracking with iron into the concentrate, while copper, arsenic, and lead signified reverse behaviors resided in the tailing.

論文審査結果の要旨及びその担当者

論文提出者氏名	樊 涌 (Fan, Yong)
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論文審査担当者	主査 教授 柴田悦郎 _____ 教授 葛西栄輝 _____ 教授 福山博之 _____

論文審査結果の要旨

本論文は、銅製錬のマット溶錬工程で排出される銅スラグの新たな有効利用として、酸化処理により銅スラグ中から選択的に磁選が可能なマグネタイト粒子を析出させ、それを分離回収することにより、製鉄原料とする技術開発に関するものである。

第一章では、研究の背景を示すとともに銅スラグの有効利用技術に関する国内外の研究例を挙げ、それぞれの特徴ならびに問題点を示している。研究例を「Mineral processing」、「Hydrometallurgy」、「Pyrometallurgy, reduction」、「Pyrometallurgy, oxidation」と技術項目で整理している。

第二章では、第一章での国内外の研究例の検討のもと、本研究で開発を目指す銅スラグの製鉄原料化プロセスの想定フローを示すとともに、状態図ならびに熱力学計算により、本研究で想定した銅スラグの酸化によるマグネタイトの析出分離に関する合理性を検討している。さらに、想定する技術開発を目指した、本研究における具体的な実験手法ならびに検討課題の整理を行っている。

第三章では、銅スラグの空気による酸化処理を各温度での TTT (Time-Temperature-Transformation) ならびに溶融状態からの CCT (Continuous-Cooling-Transformation) プロセスで行うことにより、マグネタイトならびにヘマタイトの析出に関して定量的かつ速度論的な因子も加味しながら検討を行なっている。その結果、先に析出したマグネタイト結晶の転換によりヘマタイト結晶が生成すること、また、溶融状態での酸化が速度論的に最も効率的なことを示している。

第四章では、銅スラグの溶融酸化を、いくつかの酸素濃度のガス (純酸素、空気、1vol% O₂-N₂) を用いて検討している。その結果、純酸素ならびに空気において、先にマグネタイトの析出量が時間と共に増大し、その後ヘマタイトへの転換によりマグネタイト量が減少する共にヘマタイト生成量が増大する挙動が確認された。また、酸素濃度が低い方が、ヘマタイト生成速度が低下し、またマグネタイトの最大析出量が増大する挙動が明らかとなった。熱力学計算よりヘマタイトの生成を抑えることが可能と考えられる 1vol% O₂-N₂ ガスで酸化させたところ、予想通りにマグネタイトのみを析出させることができ、析出したマグネタイトの濃度は 50mass% 以上であった。さらに、詳細な組織観察ならびに化学形態分析によりマグネタイトからヘマタイトへの転換挙動も明らかとしている。

第五章では、マグネタイトの分離回収を目的として、1vol% O₂-N₂ ガスで溶融酸化した銅スラグ試料を、鉱物の単体分離に適した電気パルス破碎装置により破碎し、その後、磁選処理によるマグネタイト回収を試みている。その結果、50 μm 以下の破碎物を 100 mT での磁選に供することにより約 60mass% Fe の品位の回収物を約 60% の収率で回収できることを明らかとしている。また、銅スラグ中の共存元素 (Zn, Cu, Pb, Cr など) の回収物と残渣への分配も調査し、元素ごとの不純物混入傾向も調査している。

第六章では、本研究結果の総括、ならびに研究結果から示唆された今後検討されるべき課題を示している。それをもとに、具体的な実用炉を用いたプロセスイメージも示している。

以上のように本研究は、今後、用途先ならびに処分先がさらに逼迫すると予想される銅スラグの新規的な資源化技術に関して実用技術に向けた基礎的な検討を詳細に行なっており、技術研究としての価値は十分に高いと評価できる。

よって、本論文は博士 (学術) の学位論文として合格と認める。