Iron Removal from Copper-based Alloy Scraps through Oxidation Slagging Process

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A process of removing iron from copper-based alloy scraps using oxidation slagging method is researched, in which the iron is oxidized to FeO and then reacted with SiO₂ forming Fe₂SiO₄ and enter into the slag phase. The addition of SiO₂ could restrict the Fe₃O₄ generation through the transformation of FeO to 2FeO·SiO₂ in a certain O₂ pressure, which is favorable to decreasing the melt viscosity and increasing the separation efficiency of Cu and Fe. Under optimized conditions of O₂ flow rate of 40 ml/min, temperature of 1 673 K, oxygenation time of 8 min, and SiO₂ amount of 2.17 mass%, Fe content in the metal phase is decreased to 0.0030 mass% with Cu loss rate being of 1.14%.

KEY WORDS: copper-based alloy scraps; iron remove; oxidation slagging; SiO₂; waste utilization.

1. Introduction

With the shortage of primary copper resources, an increasing emphasis has been placed on the copper recovery from secondary sources, such as electroplating sludge, copper based alloy scraps, and anode slime, *etc.*^{1–4)} Specially, there is a gaining considerable interest to recover copper from copper based alloy scraps due to its large amount, economic point and increased requirement of environmental protection.^{5,6)}

Different Cu content in copper scraps corresponds to a different treatment process. The treatment of copper alloy scraps could be classified into two methods: pyrometallurgical and hydrometallurgical processes.^{5–24)} As for the purple copper scraps, the vertical furnace and reflector furnace are generally used to produce anode copper directly. For the copper scraps alloyed with other metals, a two-stage treatment process, containing smelting in blast furnace or blowing by the converter and then refining into the anode copper by reflector furnace, is generally used to recover copper from them. Most of copper alloy scraps have been recycled using pyrometallurgical process at present, but the recovery of Re, Ag, Co and other associated precious metal cannot be realized effectively.^{2,8–14)} In addition to the commonly used pyrometallurgical process, several hydrometallurgical methods have also been developed.^{5–7,15–25)} Hydrometallurgical treatment of these materials, containing leaching, extraction and electrowinning, is proposed as an alternative low-cost and environmental friendly technology.^{15,16)} However, it has

drawbacks such as complex process flows, high consumption of chemical reagents, and secondary environmental pollution.¹⁷⁾ Direct recovery of valuable metals from copper based alloy scraps is a comprising process with regard to the economy and environment, and several related processes have been developed for recovering metals using anodic dissolution.^{16,18,19)} In Chile, anode support system has been used in industrial electro-refining of copper scraps and blister copper granules, which claims an energy saving as high as 50%.^{20–24)} A simultaneous electroleaching-deposition process was also used to recover copper from printed circuit boards powder concentrates and achieved good experimental results.²⁵⁾ However, when the Fe²⁺ concentration is 1–2 g/L, 6–9 g/L and 10 g/L in the electrolyte, the current efficiency is only 94%, 79% and 71% respectively, and further the high Fe²⁺ concentration increases the acid consumption obviously.^{25,26)} This Fe should be removed first before the hydrometallurgy treatment.

A method of fire refining-electrolysis complex process was proposed and this paper mainly investigated effects of processing parameters on the iron removal from a copper scrap using oxidative slagging method during the fire refining stage. The parameters including O₂ flow rate, slagging temperature, oxygenation time and SiO₂ addition amount were studied systematically.

2. Experimental

2.1. Materials

Table 1 gives chemical composition of the homogenized sample of copper-based alloy scraps (**Fig. 1**) by elemental analysis method and ICP-AES. It shows that the major ele-

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Table 1. Chemical composition of the copper-based alloy scrap (mass%).

Element	Cu	Fe	Ni	Zn	Others
Content	96.97	3.01	0.002	0.0009	0.0171

Fig. 1. The scrap appearance. (Online version in color.)

ments presented are copper (96.97 mass%) and iron (3.01 mass%). “Others” at a little content is mainly composed of “Si”, “Ag”, and “O” *etc.* Powdered SiO₂ with >99% purity used was purchased from Aladdin Industrial Corporation in Shanghai, China, and oxygen (purity of 99.9%) was procured from local suppliers.

2.2. Experimental Procedures

The reaction system was set up in a tube furnace (TCW-32B, Shanghai Instrument Co. Ltd., China) as shown in **Fig. 2**, and the roasting temperature was measured by a Pt-Rh thermocouple and controlled by a KSY Intelligent Temperature Controller (accuracy ± 1 K). The SiO₂ addition amount was calculated based on the quality ratio of SiO₂ to the scrap in all the tests. The scrap was first crushed and sieved to yield a particle size below 741 μm and mixed thoroughly with a given amount of SiO₂. Then the mixture was placed in a corundum crucible, and then located in the corundum tube which was fastened in the vertical furnace under Ar atmosphere. The sample was raised from room temperature with a heating rate of 10 K/min and then retained at a proper temperature for a stated time. When the scrap was melted completely, the O₂ was injected into the melt through a corundum nozzle. The O₂ flow rate was controlled by a flow meter. After a required time, the sample was cooled in Ar atmosphere, taken out when the temperature reached at room temperature, and prepared for analysis.

2.3. Characterization

Chemical composition and mineralogy of the samples were characterized by chemical analysis, ICP-AES, and EPMA. Especially, the “O” content in the sample was detected by XRF analysis (MINIPAL4, PANalytical, Netherlands). Phase compositions of all the samples were detected by XRD with Cu Kα radiation (the scanning rate was per 8 deg of 1 minute, and 2θ was 25 to 50 deg). The thermodynamic data of species were given by FactSage 7.0 thermochemical software. The mathematical expression of

Fig. 2. Experimental apparatus. 1: Flowmeter, 2: Si-Mo heating component, 3: Corundum nozzle, 4: Corundum crucible, 5: Intelligent temperature controller.

Cu loss rate was defined as Eq. (1).

$$R = \left(1 - \frac{M_D \times W_{S2}}{M_O \times W_{S1}} \right) \times 100 \text{ pct} \quad \text{..... (1)}$$

Where R stands for the Cu loss rate, M_O stands for mass of the scrap used, W_{S1} stands for copper content in the original scrap, M_D stands for mass of the metal phase after treated, and W_{S2} stands for copper content in the metal phase after treated.

3. Thermodynamic Analysis

The FactSage 7.0 was used to calculate equilibrium phases in products in Gibbs free energy minimization under isothermal, isobaric and fixed mole conditions. Required data for computation were provided by FactPS database of the programme.

The calculations were performed for the mixture of 0.909 mole Cu and 0.032 mole Fe with variable amounts of O₂ at temperature of 1 573 K. The phases of FeO, Fe₃O₄, Fe₂O₃, Cu₂O and CuO are assumed to be present in the products. Results of their equilibrium are present in Fig. 3. When O₂ amount is less than 0.018 mole, **Fig. 3** shows that the Fe is preferentially oxidized to FeO (Eq. (2)) and Fe₂O₃ (Eqs. (2)–(4)),²⁷⁾ and the Cu stays in the form of metallic state. With O₂ amount ranges from 0.018 to 0.022 mole, the Cu₂O and Fe₃O₄ appear, and their amounts increase. Simultaneously, the Fe₂O₃ amount decreases, which implies that Eq. (5) happens in this stage. Increasing O₂ amount further to 0.03 mole, the FeO, Fe₂O₃ and Cu₂O amounts increase while Fe₃O₄ decreases, indicating that the Cu can be directly oxidized to Cu₂O through Eq. (6) except for Eqs. (5) and (6) plays a major role at a higher O₂ pressure.

The Fe₃O₄ increases the melt viscosity, which goes against

the separation of Cu and Fe oxides. In case of this, the SiO_2 was added to decrease the Fe_3O_4 formation in a certain O_2 pressure. FactPS and FToxid databases of the Factsage 7.0 were used to calculate the phase changes of Fe–O thermodynamic system with the addition of SiO_2 at 1 atm pressure of shielding gas, and the results are shown in **Figs. 4** and **5**. Compared them, it can be seen that some part of thermodynamically stable region of Fe_3O_4 (gray area in Fig. 4) has transformed to Fe_2SiO_4 (red region in Fig. 5) with the

Fig. 3. Equilibrium phase changes in products with O₂ amount at 1573 K.

Fig. 4. Phase diagram of Fe–O₂. (Online version in color.)

Fig. 5. Phase diagram of Fe–O₂–SiO₂. (Online version in color.)

addition of SiO_2 . In Fig. 5, the red and yellow areas are both thermodynamically stable regions of Fe_2SiO_4 . Specifically, the red area shows that after the SiO_2 addition, part of thermodynamically stable region of Fe_3O_4 has transformed to Fe_2SiO_4 and SiO_2 stable region, and the yellow area means part of Fe stable region has transformed to that of Fe_2SiO_4 and SiO_2 .

4. Results and Discussion

4.1. Effects of O₂ Flow Rate

Under slagging temperature of 1523 K, oxygenation time of 10 min, and SiO₂ amount of 2.17 mass%, five O₂ flow rates of 25, 40, 55, 70, and 85 ml/min were chosen for studying the effects on iron remove and copper loss from the scrap.

Figure 6 shows that the Fe content in the metal phase (**Fig. 7**) after treatment decreases from 1.30 to 0.0039 mass% with O₂ flow rate from 25 to 85 ml/min, while the copper loss rate increases from 1.32 to 5.72%. **Figure 8** shows that the main Fe phase is 2FeO·SiO₂ in the slag phase with O₂ flow rate of 40 ml/min, and the Cu exits in the form of Cu₂O and CuFe₂O₄. Increasing O₂ flow rate to 55 ml/min,

Fig. 6. Effects of O₂ flow rate on the iron remove and copper loss from scraps. (Online version in color.)

Fig. 7. Sample appearance after scrap treatment under slagging temperature of 1 523 K, oxygenation time of 10 min, SiO₂ amount of 2.17 mass%, and O₂ flow rate of 25 ml/min. (Online version in color.)

Fig. 8. XRD patterns of the slag at O_2 flow rate of 40 ml/min, 55 ml/min and 80 ml/min.

Fig. 10. XRD patterns of the slag at slagging temperature of 1 473 K, 1 573 K and 1 673 K.

Fig. 9. EPMA analysis of the slag at different O_2 flow rates (a, 55 ml/min; b, 85 ml/min). (Online version in color.)

massive Fe_3O_4 (Fig. 8) are generated through Eq. (5), which causes an increase of the molten slag viscosity during the slagging stage. As a result, the Cu entrainment loss in the form of Cu phase seen from Fig. 8 increases and the copper loss rate increases in Fig. 6. The Fe_3O_4 amount decreases accompanied with the appearance of Fe_2O_3 with the O_2 flow rate from 55 to 85 ml/min, which accords well with that in Fig. 1. It implies that some Cu has been oxidized directly by O_2 and lost in the slag deduced from Fig. 1. Compared Figs. 9(a) with 9(b), the Cu_2O amount increases at O_2 flow rate of 85 ml/min, and it causes Cu loss rate increase as shown in Fig. 6. For the purpose of increasing iron remove and reducing copper loss, the O_2 flow rate is determined as 40 ml/min.

4.2. Effects of Slagging Temperature

With O_2 flow rate of 40 ml/min and SiO_2 amount of 2.17 mass%, effects of slagging temperature on the iron remove were tested. The increase of slagging temperature decreases the melt viscosity. Besides, the Fe_3O_4 formation could be restricted at a higher temperature through the transformation of FeO to Fe_2SiO_4 deduced from Fig. 5, also resulting in a decrease of the melt viscosity. Figure 10 shows that increasing slagging temperature from 1 473 to 1 673 K, the Fe_2SiO_4

intensity increases obviously accompanied with the decrease of Fe_3O_4 intensity. As a result, the Cu entrainment loss decreases with temperature (Fig. 11) and the copper loss rate decreases from 3.02 to 1.31% (Fig. 12). In addition, the iron content in the metal phase after treatment is decreased from 0.0043 to 0.0033 mass% due to a higher oxidation and slagging rate at a higher temperature. Increasing temperature to 1 703 K, more Cu is oxidized to copper oxides and lost in the slag, causing the copper loss rate and iron content in the metal phase after treatment both increase as shown in Fig. 12. For increasing the separation efficiency of Cu and Fe, the appropriate slagging temperature is 1 673 K.

4.3. Effects of Oxygenation Time

Under the conditions of O_2 flow rate of 40 ml/min, SiO_2 addition amount of 2.17 mass% and slagging temperature of 1 673 K, the equilibrium phase changes in products with oxygenation time is calculated using FactSage 7.0, and the result is shown in Fig. 13. Figure 13 shows that increasing oxygenation time to 8 min, the Fe amount decreases accompanied with Fe_2SiO_4 amount increasing, and then Fe_3O_4 and Fe_2O_3 phases appear with oxygenation time over 8 min and 11 min respectively. Meanwhile, the $CuFe_2O_4$

Fig. 11. EPMA analysis of the slag at slagging temperature of 1 473 K and 1 673 K. (Online version in color.)

Fig. 12. Effects of slagging temperature on the iron remove and copper loss from scraps. (Online version in color.)

Fig. 14. Effects of oxygenation time on the iron remove and copper loss from scraps. (Online version in color.)

Fig. 13. Equilibrium phase changes in products with oxygenation time at 1 673 K.

Fig. 15. XRD patterns of the slag at the oxygenation time of 8 min and 10 min. (Online version in color.)

formed between CuO and Fe_2O_3 appears at oxygenation time of 12.9 min and Cu_2O appears at oxygenation time of 17.3 min, and both of them increase with oxygenation time. The appropriate oxygenation time is 8 min from the view of thermodynamic.

The experimental results in Fig. 14 shows that the Fe

content in the metal phase after treatment decreases from 0.092 mass% to 0.003 mass% with oxygenation time from 6 to 8 min, and the Cu loss rate is low to 1.14% and changes little in this time range. Increasing oxygenation time over 8 min, the Fe_3O_4 appears (Fig. 15) causing the melting

slag viscosity increase, as a result of which the copper loss rate increases in Fig. 14. For the purpose of increasing the Fe removal rate and decreasing the copper loss, the oxygenation time is determined as 8 min, which accords well with the result of thermodynamics equilibrium calculation in Fig. 13.

4.4. Effects of SiO₂ Addition Amount

In a certain range, the addition of SiO₂ promotes the Fe to be oxidized to FeO through the formation of 2FeO·SiO₂ and restricts the generation of Fe₃O₄ deduced from Figs. 4, 5 and 13. That increases the iron remove from the scrap. **Figure 16** shows that with the increase of SiO₂ amount from 1.5 to 2.17 mass%, the Fe content in the metal phase after treatment decreases from 0.0063 to 0.003 mass% accompanied with a slight decrease of Cu loss rate. When the SiO₂ amount exceeds 2.17 mass%, the number of SiO₂ solid particle in the melt during the slagging process increases (**Fig. 17**), as a result of which the melt viscosity increases and it hinders the Fe oxidation through decreasing the O₂ mass transfer rate. As a result, the Cu loss rate and

Fe content in the metal phase after treatment both increase as shown in Fig. 16. The appropriate SiO₂ addition amount is 2.17 mass%.

Fig. 16. Effects of SiO₂ addition amount on the iron remove and copper loss from scraps. (Online version in color.)

Fig. 17. Mineral phase distribution of the slag with SiO₂ addition amount of 3.6 mass%. (Online version in color.)

Based on the discussion above, it can be concluded that removing iron from the copper based alloy scraps through oxidation slagging process is viable. Under conditions of O_2 flow rate of 40 ml/min, slagging temperature of 1 673 K, oxygenation time of 8 min and SiO_2 addition amount of 2.17 mass%, the Fe content in the metal phase is decreased to 0.003 mass% accompanied with a Cu loss rate low to 1.14%. The iron content in the metal phase fulfills the requirement of iron content in the anode copper.^{28,29)}

5. Conclusions

The effective remove of iron from copper-based alloy scraps through oxidation slagging process is practicable. The factors, including O_2 flow rate, slagging temperature, oxygenation time, and SiO_2 addition amount, play important roles in the process of iron remove.

At a low O_2 amount, the Cu is oxidized to Cu_2O mainly by Fe_2O_3 , and it can also be directly oxidized by O_2 at a higher O_2 amount and plays a major role compared to the oxidation of Fe_2O_3 from the point of view of thermodynamics. As a result, the Cu loss rate increases with O_2 flow rate and oxygenation time. The addition of SiO_2 restricts the Fe_3O_4 generation through the transformation of FeO to $2FeO \cdot SiO_2$ in a certain O_2 pressure, which is favorable to decreasing the melt viscosity and increasing the separation efficiency of Cu and Fe. Under optimized conditions of O_2 flow rate of 40 ml/min, temperature of 1 673 K, slagging oxygenation time of 8 min, and SiO_2 amount of 2.17 mass%, Fe content in the metal phase is decreased to 0.0030 mass% with Cu loss rate being of 1.14%.

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