Influence of Electrolyte on an Energy-Saving Copper Recycling Process Using Ammoniacal Alkaline Solutions

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In order to make the energy-saving copper recycling process more economical by reducing the power consumption during copper electrowinning, the influence of the bath composition on the saturated concentration of cuprous ion, the electric conductivity, the cathodic current efficiency and the power consumption were studied in an ammonia-ammonium chloride-cuprous/cupric ion solution. The saturated cuprous ion concentration increased with the ammonia and ammonium chloride concentrations. The electric conductivity of the solution increased in proportion to the ammonium chloride concentration, because ammonium chloride acts as a supporting electrolyte. When the ammonia concentration increased from 3 to 10 kmol·m⁻³ or when the cuprous ion concentration increased from 0.5 to 2 kmol·m⁻³, the cathodic current efficiency decreased by 5–10% at a current density higher than 500 A·m⁻². This result from an increase in the cupric ion concentration formed by the unavoidable oxidation and the disproportionation of cuprous ions. The low current efficiency, however, had little influence on the power consumption compared to the influence of the electric conductivity that was the dominant factor determining the power consumption. Actually, when the concentration of ammonium chloride increased from 2 to 4 kmol·m⁻³, because of its function of increasing the electric conductivity of the solution, the power consumption was reduced by half. Based on this study, a suitable bath composition for the energy-saving copper recycling process was determined to be 3–10 kmol·m⁻³ ammonia, 4–5 kmol·m⁻³ ammonium chloride and 1–2 kmol·m⁻³ cuprous ions. [doi:10.2320/matertrans.47.2871]

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1. Introduction

The development of an economical process for the recycling of metals from waste is necessary to minimize environmental pollution and to effectively utilize the mineral resources. As for copper metal, a pyrometallurgical recycling process using a copper smelting plant along with copper ore has already been commercialized. However, the copper smelting plant requires a large area and generates a huge quantity of sulfur dioxide. The copper smelting plant, therefore, is generally located at a great distance from urban areas that generate copper-containing wastes. On the other hand, a hydrometallurgical process has certain advantages such that it could be economically operated even on a small scale and that the capital cost is lower than that for the conventional smelting process. So far, some efforts have been made to develop hydrometallurgical recycling processes,¹⁻⁴ these processes, however, have a problem in that power consumption during the copper electrowinning is relatively high. Thus, it is necessary to reduce the power consumption during the electrowinning to make the process economical and comparable to the low market price for copper. Based on this background, our research group has been making efforts to develop an energy-saving copper recycling process from electronic waste⁵⁻⁸ that is one of the most complex materials for recycling. This process employs an ammonia (NH₃)-ammonium salt solution containing cuprous ammine complexes (Cu(I)) and cupric ammine complexes (Cu(II)), and consists of three stages of leaching, purification and electrowinning, as described in our previous paper.⁹ In this process, copper metal in the waste is dissolved as Cu(I) into the solution using Cu(II) as the oxidizing reagent in the leaching stage. After purification, the pure Cu(I) solution is introduced into the cathode compartment of the electrolytic cell, and half of the fed Cu(I) is reduced to metallic copper on the cathode. The remaining Cu(I) is transferred to the anode compartment and oxidized to Cu(II) on the anode. In our previous study, ammonium salts such as ammonium sulfate, chloride and nitrate were added to the solution, and the influence of the anionic species on the electrowinning stage was examined.⁵ Among the solutions examined, the NH₃-NH₄Cl solution showed the lowest power consumption during the electrowinning. This is attributed to the low overpotential at the cathode and the high electric conductivity of the solution. Thus, in this study, we focused on the NH₃-NH₄Cl solutions, and the influence of the electrolyte concentrations on our copper recycling process was investigated in order to obtain fundamental information on this system and to optimize the electrolytic conditions for the copper electrowinning. First, saturated concentrations of Cu(I) in the solutions were roughly measured at various NH₃ and NH₄Cl concentrations. Second, the electric conductivity and kinematic viscosity of the solution were measured. Finally, copper electrodeposition was conducted at various concentrations of Cu(I), NH₃ and NH₄Cl in order to measure the current efficiency and to estimate the power consumption during the electrowinning.

2. Experimental

2.1 Saturated concentration of Cu(I)

The solutions were prepared from an ammonium solution, ammonium chloride (NH₃ and NH₄Cl, 25% solution and 99% purity, Wako Pure Chemical Industries) and de-ionized water. The composition of 5 kmol·m⁻³ NH₃ and 4 kmol·m⁻³ NH₄Cl was selected as the basic composition, and the
concentrations of NH$_3$ and NH$_4$Cl were varied in the range of 1–10 kmol m$^{-3}$ and 1–5 kmol m$^{-3}$, respectively, at a fixed concentration of the other variables. Cuprous oxide (Cu$_2$O, 99.9% purity, Kanto Chemical) and copper particles with an average diameter of 1 mm were used as the Cu(I) source and the reducing reagent for Cu(II) formed by the oxidation of Cu(I), respectively. The solution, copper particles and excess Cu$_2$O were placed in a glass bottle, and the bottle was tightly sealed with a cap that had a silicon rubber septum for the purpose of sampling with an injection needle. The amount of added Cu$_2$O was twice as much as that calculated from the expected saturated concentration for each bath composition, which was measured in our preliminary examination. The solution was agitated by a magnetic stirrer for 96 hours and then allowed to stand at rest for 24 hours. The copper concentration in the solution was then measured by ICP-AES (Ultima2, HORIBA). Though the copper particles were added to the solution in order to reduce Cu(II), the solution contained Cu(II) on the order of 0.01 kmol m$^{-3}$ due to the unavoidable oxidation and disproportionation reaction of Cu(I). Thus, the Cu(II) concentration was also measured by a spectrophotometer (UV-2550, SHIMADZU), and the Cu(I) concentration was calculated as the difference between the total copper and Cu(II) concentrations. In order to measure the Cu(II) concentration, the absorption at 630 nm wavelength was employed, because Cu(II) in these solutions has an absorption peak at that wavelength, and there is a linear relationship between the Cu(II) concentration and the absorbance. The solution was introduced into the spectrophotometer without exposure to air via the injection needle, a filter unit and a Teflon tube in order to prevent oxidation by air. The solutions used for the calibration were prepared from the NH$_3$ solution, NH$_4$Cl and cupric oxide (CuO, 95% purity, Wako Pure Chemical Industries). All the operations were conducted at room temperature (288–298 K).

### 2.2 Electric conductivity and kinematic viscosity measurement

The NH$_3$-NH$_4$Cl solution was prepared in the same way as that for the saturated concentration measurements. The solutions containing Cu(I) were prepared from NH$_3$, NH$_4$Cl, Cu$_2$O and de-ionized water. The Cu(I) concentration was varied in the range from 0 to 3 kmol m$^{-3}$ at fixed NH$_3$ and NH$_4$Cl concentrations of 5 and 4 kmol m$^{-3}$, respectively. Since the electric conductivity is sensitive to temperature, the solution prepared in a glass volumetric flask was immersed in a water bath maintained at 298 ± 0.5 K for about 20 hours before the measurement. The electric conductivity and the kinematic viscosity of the solution were then measured by a conductivity meter (CM-60V, TOA Electronics) and an Ubbelohde type viscosimeter, respectively.

### 2.3 Electrodeposition

The electrolytic bath was prepared from Cu$_2$O, NH$_3$ solution, NH$_4$Cl and de-ionized water. The bath composition of 5 kmol m$^{-3}$ NH$_3$, 4 kmol m$^{-3}$ NH$_4$Cl and 1 kmol m$^{-3}$ Cu(I) was selected as the basic composition, and the concentration of each electrolyte was varied with fixed concentrations of the others. Before the electrodeposition, the copper particles were added to the solution in order to reduce Cu(II), and the solution was stirred for 20 hours under continuous introduction of Ar gas deoxidized by a gas-washing bottle filled with a solution containing 2.5 kmol m$^{-3}$ NH$_3$, 2 kmol m$^{-3}$ NH$_4$Cl, 0.2 kmol m$^{-3}$ Cu(I) and the copper particles. The electrolytic cell was a 130 mm × 50 mm × 90 mm rectangular vessel which was divided into two compartments by an anion exchange membrane (ACM, Tokuyama), and the prepared solution and an NH$_3$-NH$_4$Cl solution were introduced into the cathode and anode compartment, respectively. A 10 mm × 20 mm copper plate, a 45 mm × 50 mm platinum plate and an AgCl-Ag electrode immersed in a 3.33 kmol m$^{-3}$ KCl solution were used as the cathode, the anode and the reference electrode, respectively. Electrodeposition was conducted at room temperature, 288–298 K, using an electrochemical measurement system (HZ-3000, Hokuto Denko) for 1000 s under a galvanostatic condition at a current density of 100–2000 A m$^{-2}$. The deoxidized Ar gas was introduced into the electrolytic cell to prevent oxidation during the electrodeposition. The cathodic current efficiency was determined as the ratio of the experimental mass gain of the cathode during the electrodeposition to the theoretical value based on the assumption that metallic copper is deposited from the monovalent state, i.e., Cu(I). The Cu(II) concentration was also measured by the spectrophotometer before the electrodeposition.

### 3. Results and Discussion

#### 3.1 Influence of electrolyte on the saturated concentration of Cu(I)

Since the amount of copper that could be electrowon from the solution is theoretically proportional to the Cu(I) concentration in the solution, the saturated concentration of Cu(I) for each bath composition is an important value for our copper recycling process. Figure 1 shows the saturated concentration of Cu(I) measured at various concentrations of NH$_3$ and NH$_4$Cl. As shown in Fig. 1, the Cu(I) concentration increased with the NH$_3$ and NH$_4$Cl concentrations. This tendency is explained as follows: (a) the pH was in the range of 9–12, and Cu$_2$O dissolves as ammine complexes under this condition,

![Fig. 1 Saturated Cu(I) concentrations at room temperature in the solutions containing (a) various concentrations of NH$_3$ and 4 kmol m$^{-3}$ NH$_4$Cl, and (b) various concentrations of NH$_4$Cl and 5 kmol m$^{-3}$ NH$_3$.](image-url)
Cu₂O + 4NH₃(aq) + H₂O → 2[Cu(NH₃)₂]²⁺ + 2OH⁻  

(1)

(a) although this reaction stops when the hydroxide ion concentration reaches a certain value even if the solution still contains a sufficient amount of ammonia, the formed hydroxide ions are consumed according to the following reaction,

NH₄⁺ + OH⁻ → NH₃(aq) + H₂O    \ pK_b = 4.76  \ (2)

and (c) consequently, the increases in the NH₃ and NH₄Cl concentrations promoted the dissolution of Cu₂O. At this point, it is necessary to determine the minimum requirement for the saturated Cu(I) concentration, which is acceptable for our recycling process. According to the surface roughness measurement of the electrodeposited copper,90 the surface of the copper deposit tended to be rough when the Cu(I) concentration was lower than 1 kmol·m⁻³. Because surface roughening frequently leads to impurity enhancement, a 1 kmol·m⁻³ or higher Cu(I) concentration is required in the cathode compartment in order to obtain a pure and smooth copper deposit. As a result, the Cu(I) concentration in the feed must be 2 kmol·m⁻³ or higher, because the Cu(I) solution is first fed to the cathode compartment in the present process and each half of the fed Cu(I) is consumed, respectively, on the cathode and anode under the ideal conditions. As shown in Fig. 1, the saturated Cu(I) concentration exceeds 2 kmol·m⁻³ when the NH₃ and NH₄Cl concentrations are about 3 kmol·m⁻³. On the other hand, the higher limits are about 10 and 5 kmol·m⁻³ for NH₃ and NH₄Cl, respectively, because of the limitations such as the NH₃ concentration in a commercial reagent and the solubility of NH₄Cl. Thus, the necessary conditions for our recycling process are 3–10 kmol·m⁻³ NH₃ and 3–5 kmol·m⁻³ NH₄Cl at this point. The Cu(II) concentration was on the order of 0.01 kmol·m⁻³ in all cases, which probably did not affect the result of this measurement.

3.2 Influence of electrolyte on the electric conductivity of the solution

The electric conductivity of the solution is also an important value for our copper recycling process, because it determines a part of the power consumption due to the IR drop in the solution. Figure 2 shows the electric conductivity of the solution as a function of the NH₃ and Cu(I) concentrations. The pH values in the solution changed from 8.8 to 10.1, from 10.2 to 9.4 and from 9.6 to 9.8, when the NH₃, NH₄Cl and Cu(I) concentrations increased in the ranges of 1–10, 1–5 and 0–3 kmol·m⁻³, respectively. In these solutions, the electric conduction was quite dependent on the NH₄⁺ and Cl⁻ ions of which the limiting molar conductivities are 7.37 and 7.63 × 10⁻³ S·m²·mol⁻¹, respectively. Actually, the electric conductivity is nearly proportional to the sum of the NH₄⁺ and Cl⁻ concentrations calculated from the pH value, equilibrium of reaction (2) and the concentrations of the added NH₃ and NH₄Cl. As a result, the electric conductivity for each NH₃ concentration is close to that in the simple solution of NH₄Cl,10 which indicates the importance of the added NH₄Cl concentration in determining the electric conductivity. When each of the NH₃ and Cu(I) concentrations increased, the electric conductivity slightly decreased. The influence of the NH₃ concentration came from the change in the kinematic viscosity of the solution, which increased from 9 to 12 × 10⁻⁷ m²·s⁻¹ when the NH₃ concentration was increased from 1 to 10 kmol·m⁻³. According to Walden’s rule, the electric conductivity decreases about 30% with the increasing kinematic viscosity in that range. The results shown in Fig. 2 are in good agreement with this rule. The decrease in the electric conductivity with the increasing Cu(I) concentration is due to the consumption of NH₄⁺ shown in reactions (1) and (2). These results lead to the conclusion that the electric conductivity remarkably increases with the NH₄Cl concentration and slightly decreases with the increasing NH₃ and Cu(I) concentrations.

3.3 Influence of electrolyte on the current efficiency and power consumption

Since cathodic current efficiency directly influences the power consumption, the effect of the NH₃, NH₄Cl and Cu(I) concentrations on the cathodic current efficiency was examined at various current densities. Figure 3 shows the cathodic current efficiency at various concentrations of (a) NH₃, (b) NH₄Cl and (c) Cu(I) as a function of the current density. As shown in Fig. 3(a), the current efficiency decreased at the NH₃ concentration of 10 kmol·m⁻³. This is due to the high Cu(II) concentration in the 10 kmol·m⁻³ NH₃ solution, 0.06 kmol·m⁻³, which is two or three times higher than those of the others. The increase in the Cu(II) concentration caused a decrease in the current efficiency due to current consumption for the reduction from Cu(II) to Cu(I).81 The equilibrium reaction for Cu(II), Cu(I) and Cu is as follows:111

\[
\text{Cu(NH₃)₂}^{2+} + \text{Cu} = 2\text{Cu(NH₃)}_{2}^{+}
\]

(3)

\[
K = \frac{a_{\text{Cu}^{0+}}^2}{a_{\text{Cu}^{1+}}} = 10^{3.4}
\]

(4)

where \(a_i\) denotes the activity of species \(i\). Thus, a high NH₃ concentration seems to have no effect on the Cu(II) concentration in the presence of Cu metal. However, the measured Cu(II) concentrations in the present experiments, which were reproducible and increased with the Cu(I) concentration, were much higher than the values calculated from the equilibrium constant and the Cu(I) concentration.
This might be attributed to unavoidable oxidation by oxygen gas in the air, and the oxidation rate probably determines the Cu(II) concentration along with the equilibrium shown in reaction (3). In the presence of oxygen gas, Cu(II) is formed according to the following reaction:

\[
2\text{Cu(I)} + \text{O}_2 + \text{H}_2\text{O} = 2\text{Cu(II)} + 2\text{OH}^-
\]

This reaction suggests that the production rate of Cu(II) increases with the NH₃ concentration at a particular partial pressure of the oxygen gas. As for the NH₄Cl concentration, a polarization measurement conducted as a preliminary examination showed that the current corresponding to reduction from Cu(I) to copper metal increased with the NH₄Cl concentration. This suggests that NH₄Cl promotes the reduction from Cu(I) to copper metal; however, the increase in the NH₄Cl concentration showed no significant effect on the current efficiency in the present result shown in Fig. 3(b). These two results suggest that the reduction from Cu(II) to Cu(I) was also promoted with the NH₄Cl concentration. Concerning the Cu(I) concentration, it was found that the current efficiency decreased at the higher Cu(I) concentrations, as shown in Fig. 3(c). This is due to the increase in the Cu(II) concentration, which was experimentally confirmed and is explained by reaction (3) and equation (4). When the activity coefficient of each species is constant, equation (4) indicates that the Cu(II) concentration increases with the Cu(I) concentration.

Based on the results mentioned above, the power consumption during the copper electrowinning was calculated using the following equation:

\[
\text{Power consumption (kWh-ton}^{-1} ) = 422 \text{ (kAh-ton}^{-1} ) \times n \times \frac{\text{Cell voltage (V)}}{\text{Current efficiency}}
\]
5 kmol/m^3 NH₃, 4 kmol/m^3 NH₄Cl and 1 kmol/m^3 Cu(I), the IR drop due to the resistance of the solution was 1.7 V at the current density of 500 A/m^2, while the potential difference between the anode and cathode was 0.34 V excluding the IR drop. This process, therefore, has the potential to achieve a further reduction in the power consumption using an effective supporting electrolyte. As shown in Fig. 4(a), a high NH₃ concentration caused a slight increase in the power consumption, which came from the low electric conductivity and the low current efficiency at a high NH₃ consumption, and the low current efficiency at a high NH₃ consumption, which came from the low electric conductivity increasing the electric conductivity of the solution. According to Fig. 4(a), a high NH₃ concentration caused a slight increase in the power consumption, which came from the low electric conductivity and the low current efficiency at a high NH₃ concentration. The increase in the power consumption was lower than 25% even if the NH₃ concentration increased from 3 to 10 kmol/m^3; therefore, one can vary the NH₃ concentration in this range according to the limitations coming from the performance in the leaching and purification stages, or for economic reasons. The NH₄Cl concentration strongly influenced the power consumption, because of its function of increasing the electric conductivity of the solution. According to Fig. 4(b), as the NH₄Cl concentration, 4–5 kmol/m^3, is more suitable than 2 kmol/m^3, because the power consumption at the latter became twice that of the former. As for the Cu(I) concentration, the power consumption slightly increased with the Cu(I) concentration due to the low cathodic current efficiency and the low electric conductivity. Because the power consumption depends quite weakly on the Cu(I) concentration, the Cu(I) concentration could be varied like the NH₃ concentration. The Cu(I) concentration of 0.5 kmol/m^3 is, however, unsuitable to obtain a smooth copper deposit as mentioned before, even though the power consumption at 0.5 kmol/m^3 was the lowest.

Based on these results, the appropriate concentration range for our copper recycling process was determined to be 3–10 kmol/m^3 NH₃, 4–5 kmol/m^3 NH₄Cl and 1–2 kmol/m^3 Cu(I). In this bath composition range, the power consumption was lower than 750 kWh/ton and was mostly about 500 kWh/ton at a current density of 200 A/m^2. This power consumption is much lower than that for the conventional electrowinning process, which requires 2000–2200 kWh/ton at a current density of 200–300 A/m^2.

4. Conclusions

In order to optimize the bath composition for an energy-saving copper recycling process employing the NH₃-NH₄Cl-Cu(I)/(II) solution, the influence of the electrolyte on the saturated Cu(I) concentration, the electric conductivity of the solution, the current efficiency and the power consumption during the electrowinning was examined. A high NH₃ concentration caused an increase in the saturated Cu(I) concentration and slight decreases in the electric conductivity of the solution and the cathodic current efficiency. Although the NH₃ concentration showed a weak negative effect on the power consumption, a 3 kmol/m^3 or higher NH₃ concentration was necessary to obtain a sufficient Cu(I) concentration. Concerning the NH₄Cl concentration, the saturated concentration of Cu(I) and the electric conductivity of the solution increased with the NH₄Cl concentration, and the cathodic current efficiency was not changed with the NH₄Cl concentration. Due to its significant influence on the electric conductivity, the power consumption was remarkably reduced with the NH₄Cl concentration up to 4 kmol/m^3. The Cu(I) concentration showed a weak negative effect on the electric conductivity of the solution and on the cathodic current efficiency. As a result, the power consumption
slightly increased with the Cu(I) concentration. Based on these results, the appropriate concentration range of NH₃, NH₄Cl and Cu(I) was determined to be 3–10, 4–5 and 1–2 kmol·m⁻³, respectively. In this concentration range, the power consumption in the present process became two or more times lower than that in the conventional electro-winning process.

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