Electrolytic Copper Deposition from Ammoniacal Alkaline Solution Containing Cu(I)

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In order to verify the feasibility of copper electrodeposition from ammoniacal alkaline solutions containing Cu(I), the cathodic polarization characteristics of Cu(I) and the galvanostatic electrodeposition from a Cu(I) solution were investigated. The cathodic polarization curve for the $0.5 \text{ kmol m}^{-3} \text{ Cu}(\text{I})$ -5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂SO₄ solution showed an increase in the electric current corresponding to the deposition of copper at around -0.22 V vs. SHE which is much higher than the potential for hydrogen evolution. The current efficiencies for the copper electrodeposition from the Cu(I) solution nominally without Cu(II) were greater than 95% in the current density range of 200 to 1000 A m⁻². A further increase in the current density resulted in a decreased current efficiency due to the hydrogen evolution. The current efficiency decreased with the increasing Cu(II) concentration and temperature. These results indicate that the present copper electrodeposition method is applicable for the new energy-saving hydrometallurgical recycling process. [doi:10.2320/matertrans.47.2076]

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1. Introduction

We have been studying a novel energy-saving hydrometallurgical process for copper recovery from electronic scraps.¹⁾ This process consists of three stages; leaching, purification, and electrowinning, and is characterized by employing an ammoniacal alkaline solution and electrowinning from Cu(I). In a previous study, we carried out the leaching experiments and reported that the copper in a printed circuit board (PCB) dissolved as Cu(I) in the Cu(I)-Cu(II)-NH₃-(NH₄)₂SO₄ solutions under a nitrogen atmosphere.¹⁾

The electrowinning of copper is also important in order to develop the copper recovery process. There are some complexing agents with copper(I) such as NH₃, CN⁻, Cl⁻ and acetonitrile, where Cu(I) is stable in these solutions. Many researchers studied the copper electrodeposition from a solution containing Cu(I) and NH₃,^{2,3)} acetonitrile,^{4,5)} and Cl⁻.⁶⁻⁹⁾ Schimmel found that the cathode current efficiencies were practically 100% in the 0.25 kmol m^{-3} Cu(I)-1 kmol m⁻³ (NH₄)₂CO₃-2 kmol m⁻³ NH₄Cl solution.²⁾ Sedzimir et al. reported that the anode and cathode current efficiencies at current densities over 100 Am^{-2} in the Cu(I)-NH₃-SO₄²⁻ solution were higher than 95% and practically independent of the electrolysis variables.³⁾ Muir et al. studied the electrorefining and electrowinning of copper from an acidified cuprous sulfate solution containing organic nitrile, such as acetonitrile, and obtained greater than 95% current efficiencies at the cathode.^{4,5)} Andrianne et al. studied the electrowinning from the 0.7 kmol m^{-3} CuCl-4 kmol m⁻³ $NaCl-0.5 \text{ kmol m}^{-3} \text{ HCl solution}^{6)}$ on a laboratory scale. The exchange current density for the reaction: Cu(I) + $e^- = Cu$, measured by Albert *et al.*, was about 2400 A m⁻² in the 0.5 kmol m⁻³ CuCl-4 kmol m⁻³ NaCl-0.5 kmol m⁻³ HCl

solution.7)

In order to develop the copper electrowinning stage in our process, it is necessary to study the behavior of the copper deposition at the cathode and electrolytic oxidation at the anode. In the present study, the polarization characteristics at the cathode and the current efficiencies for the copper electrodeposition from Cu(I)-Cu(II)-NH₃-(NH₄)₂SO₄ solutions were investigated. The effects of the Cu(I) and Cu(II) concentrations, current density, temperature, and pH on the current efficiencies were experimentally examined.

2. Experimental

Figure 1 shows a schematic illustration of the apparatus used for the determination of the cathodic polarization characteristics and current efficiency at a constant current density. The electrolytic cell was rectangular and made of



Fig. 1 Schematic illustration of the experimental apparatus. A: Electrochemical system/potentio-galvano stat, B: Agar salt bridge, C: Reference electrode, D: Cathode, E: Anode, F: Magnetic stirrer, G: Anion exchange membrane, H: Water bath.

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acrylic resin, in which an anion exchange membrane (ACM, Tokuyama Company, Ltd.) was placed between the cathode and anode compartments. The electrolytic cell was immersed in a water bath in order to control the temperature. Copper and platinum plates (each $20 \text{ mm} \times 20 \text{ mm}$) were employed as the cathode and the counter anode, respectively. After a lead wire was fixed on the rear surface of the cathode copper plate by soldering, the rear side of the cathode plate was completely covered with an adhesive tape. This cathode plate was subjected to the measurements after immersing it in ethyl alcohol for 60 seconds, and then in $1 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$ solution for 30 seconds. A Cu(I)-Cu(II)-NH₃-(NH₄)₂SO₄ catholyte solution and 5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂-SO₄ anolyte solution were used. Both solutions were agitated by magnetic stirrers throughout the electrolysis. Nitrogen gas was pumped into the cathode component through a saturator with the 0.5 kmol $m^{-3}~Cu(I)\text{-}5\,kmol\,m^{-3}~NH_3\text{-}1\,kmol\,m^{-3}$ (NH₄)₂SO₄ solution to avoid the oxidation of Cu(I) to Cu(II) by oxygen in the air. The solutions were prepared from cuprous oxide (Cu₂O, 99.9% purity, Kanto Chemical Co., Inc.), cupric sulfate pentahydrate (CuSO₄·5H₂O, 99.5% purity, Wako Pure Chemical Industries, Ltd.), ammonia solution (NH₃ 25%, Wako Pure Chemical Industries, Ltd.), ammonium sulfate ((NH₄)₂SO₄, 99.5% purity, Wako Pure Chemical Industries, Ltd.), and copper particles (Cu, 99.85%) purity, Kanto Chemical Co., Inc.). Deionized water with a specific resistivity of 5×10^4 ohm m after a degassing procedure under vacuum for 20 min in order to remove the dissolved air was used for the preparation of the solutions. When the Cu(I) solutions without Cu(II) were prepared, the copper powder was agitated in these solutions for 4 h. The total copper and Cu(II) concentrations in the solution were measured using an ICP-AES (SPS-4000, Seiko Instruments Inc.) and a UV/VIS spectrometer (UV-2550, Shimadzu Corporation), respectively. The nominal concentration is described because a few percent of Cu(II) is present in the Cu(I) solution as will be described later.

The cathode potential was controlled by an electrochemical system (HZ-3000, Hokuto Denko Corporation). A threeelectrode method was employed for the polarization measurements and the measurements for the cathodic potential during the electrodeposition of copper from the ammoniacal alkaline solution. A Ag-AgCl electrode filled with saturated KCl solution was used as the reference electrode, and an agar salt bridge containing saturated KCl solution was used as the liquid junction between the reference electrode and the cathode compartment.

The copper electrodeposition was conducted under galvanostatic conditions at a current density of $100-1500 \text{ A m}^{-2}$ using a potentio-galvanostat (HA-301, Hokuto Denko Corporation). The current efficiency was determined by the difference in weight during the electrodeposition for 1 h as

Current efficiency/% =
$$\frac{\text{Difference in weight during the electrodeposition/g}}{\text{Theorecical Cu deposition from monovalent state (MIt/F)/g} × 100 (1)$$

where *M*: atomic weight of copper $(g \mod^{-1})$, *I*: current (A), *t*: time (s), and *F*: Faraday constant.

3. Results and Discussion

Figure 2 shows the potential-pH diagram of the Cu-NH₃- H_2O system.¹⁰⁾ This figure is obtained under the conditions that the Cu ion activity is 0.5 and the sum of the concentrations of NH₃ and NH₄⁺ is 7 kmol m⁻³. The dashed lines in this figure show the following reactions:

$$2H^+ + 2e^- = H_2 \tag{2}$$

$$O_2 + 4H^+ + 4e^- = 2H_2O$$
 (3)

In the presence of excess ammonia, Cu(I) and Cu(II) are, respectively, stable as $Cu(NH_3)_2^+$ and $Cu(NH_3)_4^{2+}$ in neutral and alkaline solutions. The redox reaction of Cu(I)/Cu is expressed as follows:

$$Cu(NH_3)_2^+ + e^- = Cu + 2NH_3$$
 (4)

$$E = E_0 - \frac{RT}{F} \ln \frac{a_{\rm NH_3}^2}{a_{\rm Cu(NH_3)}^+}$$
(5)

where the symbols *E*, E_0 , *R*, *T* and *a* are the potential, standard potential, gas constant, temperature, and activity, respectively. The potential of this reaction for the Cu(I) concentration of 0.5 kmol m⁻³, the NH₃ concentration of 7 kmol m⁻³, and pH of 11 is -0.239 V vs. SHE assuming that the activity coefficients are 1. Since the redox potential for hydrogen evolution is less than that of Cu(NH₃)₂⁺/Cu,



Fig. 2 Potential-pH diagram of the Cu-NH₃-H₂O system at 298 K calculated assuming that the activity of copper ion is 0.5 and that the total concentration of the ammonia is $7.0 \, \text{kmol} \, \text{m}^{-3}$.

copper can be electrodeposited without the hydrogen evolution. The hydrogen gas, however, evolves when the cathodic potential becomes lower with the increasing current density.



Fig. 3 Cathodic polarization curves in various Cu(I) solutions. (NH₃: 5 kmol m^{-3} , (NH₄)₂SO₄: 1 kmol m^{-3} , Agitation speed: 200 rpm, Scan rate: 0.01 V s^{-1} , Working electrode: Pt, Temp.: 298 K)

In order to obtain fundamental knowledge on the electrodeposition of copper, the cathodic polarization characteristics of Cu(I) were studied at 298 K. Curves 1 and 2 in Fig. 3 show the results obtained for the 0.5 and $0.1 \text{ kmol m}^{-3} \text{ Cu(I)}$ solutions, respectively. For the sake of comparison, the cathodic polarization curve for a solution without Cu(I) is depicted by Curve 3 in the same figure. All the solutions contained 5 kmol m⁻³ of NH₃ and 1 kmol m⁻³ of (NH₄)₂SO₄ and were agitated by the magnetic stirrer at 200 rpm. In the Cu(I) solutions, the current began to rise at the cathode potential of about -0.22 V vs. SHE, and increased with a reduction in the cathode potential. After the polarization measurement, copper was electrodeposited on the cathode. In the 0.1 kmol m^{-3} Cu(I) solution, the limiting current density in the potential range from -0.6 to -0.9 V vs. SHE was obtained. On the other hand, in the $5 \text{ kmol m}^{-3} \text{ NH}_3$ -1 $kmol m^{-3} (NH_4)_2 SO_4$ solution, the current began to rise at a cathode potential of around -0.9 V vs. SHE. Since the current shown by Curve 3 is believed to correspond to hydrogen evolution, the increase in the current density at the cathode potential of less than -0.9 V vs. SHE depicted for the 0.1 kmol m^{-3} Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ $(NH_4)_2SO_4$ solution was also thought to be caused by the hydrogen evolution. Since the cathode potential for copper deposition is much higher than that for the hydrogen evolution, a high current efficiency for copper deposition is expected in the ammoniacal alkaline solution containing Cu(I).

The electrodeposition of copper was conducted for the solutions of various Cu(I) concentrations at the current densities of 500 Am^{-2} at the agitation speed of 200 rpm. Figure 4 shows the effect of the Cu(I) concentration on the current efficiencies. The current efficiencies increased with the Cu(I) concentration up to 0.4 kmol m^{-3} and gradually decreased thereafter. The maximum current efficiency was 97.5% which was slightly higher than that by Sedzimir *et al.*³⁾ They conducted electrorefining experiments without using



Fig. 4 Effect of the Cu(I) concentration on the current efficiency. (i: 500 Am^{-2} , NH₃: 5 kmol m^{-3} , (NH₄)₂SO₄: 1 kmol m^{-3} , Agitation speed: 200 rpm, Temp.: 298 K)



Fig. 5 Relationship between Cu(I) and Cu(II) concentrations. (NH₃: 5 kmol m⁻³, (NH₄)₂SO₄: 1 kmol m⁻³, Temp.: 298 K)

any membrane between the cathode and the anode. They reported that the current loss was mainly due to the partial dissolution of the copper anode as Cu(II). In the present study, 100% current efficiencies were not obtained in spite of the fact that the anion exchange membrane was used to separate the catholyte and anolyte and that copper powder was added during the solution preparation in order to prevent the generation of Cu(II). The solution was navy blue, indicating that the solution contains Cu(II). Thus, the Cu(II) concentration in the solution containing Cu(I) in equilibrium with metallic copper was measured. Copper powder was added to the solution containing Cu(I), followed by agitation using a magnetic stirrer for 48 h. Figure 5 shows the relationship between the Cu(I) and Cu(II) concentrations,



Fig. 6 Effect of the current density on the current efficiency. (NH₃: 5 kmol m⁻³, (NH₄)₂SO₄: 1 kmol m⁻³, Agitation speed: 200 rpm, Temp.: 298 K)

where the Cu(II) concentration increased with the Cu(I) concentration. The equilibrium equation among Cu, Cu- $(NH_3)_2^+$ and Cu $(NH_3)_4^{2+}$ and equilibrium constant are given as follows.¹⁰⁾

$$Cu(NH_3)_4^{2+} + Cu = 2 Cu(NH_3)_2^+$$
 (6)

$$K = 10^{3.38} \tag{7}$$

For the 0.5 kmol m⁻³ Cu(I) solution, the Cu(II) concentration by eq. (7) is 1.04×10^{-4} kmol m⁻³ assuming that the activity coefficients are 1, which is much lower than the experimental value. One of the reason for the difference between the experiment and equilibrium is possibly large deviation of the activity coefficients from unity in the concentrated electrolyte solutions such as the 0.5 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂SO₄ solution. Sedzimir *et al.* also reported the similar difference.³⁾ Therefore, the decrease in the current efficiency with the increasing Cu(I) concentration was believed to be caused by the reduction of Cu(II) to Cu(I) and/or Cu(II) to Cu with the increase in Cu(II).

Figure 6 depicts the effect of the current densities on the current efficiencies when the total copper concentration was 0.5 kmol m^{-3} . The current efficiencies were greater than 95% at the current densities ranging from 200 to 1000 A m⁻² in the 0.5 kmol m^{-3} Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂-SO₄ solution. The current efficiency was 85% at the current density of 100 A m⁻² due to the reduction of Cu(II) to Cu(I). The current efficiency decreased with the increasing current density when it was greater than 1000 A m⁻². The hydrogen gas evolution at the cathode was observed at the current density of 1500 A m⁻², where the current efficiency was 91%. This means that 9% of the current was consumed for the evolution of hydrogen gas as well as the reduction of Cu(II) to Cu(I) to Cu(I) as previously mentioned.

As a result, the removal of Cu(II) in the solution before the electrowinning is necessary to obtain a high current effi-



Fig. 7 Effect of the temperature on the current efficiency. (i: 500 A m⁻², NH₃: 5 kmol m⁻³, (NH₄)₂SO₄: 1 kmol m⁻³, Agitation speed: 200 rpm)

ciency. During the conventional electrowinning and electrorefining of copper, the adopted current densities are between 100 and 260 A m⁻².^{11,12}) The present result suggests that the electrodeposition of copper at the higher current densities is also possible in the ammoniacal alkaline solution containing Cu(I).

As is clear in Fig. 6, the current efficiencies decreased with the increasing Cu(II) concentration. This is due to the current consumption by the reduction of Cu(II) to Cu(I). The current efficiencies of the electrolysis showed negative values for the 0.3 kmol m⁻³ Cu(I)-0.2 kmol m⁻³ Cu(II) solution at the current density of 100 A m⁻² and the 0 kmol m⁻³ Cu(I)-0.5 kmol m⁻³ Cu(II) at 100 and 200 A m⁻². This indicates that the copper cathode dissolved in spite of the detection of the cathodic current. Actually, according to the observation after the electrolysis, the cathode potentials at which the current efficiencies were negative were in the stable region of Cu(NH₃)₂⁺ in Fig. 2; thus, the negative current efficiency under these conditions are reasonable from a thermodynamic point of view.

A copper plate was obtained in an ammoniacal alkaline solution containing Cu(I) and Cu(II) at the current density of less than 1000 Am^{-2} , while copper powder was stripped from the cathode at the current density of 1500 Am^{-2} due to the hydrogen gas evolution at the cathode.

The effect of temperature on the electrodeposition of copper was examined at 298, 313, 333 and 353 K, using the 0.5 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂-SO₄ solution and the 0.4 kmol m⁻³ Cu(I)-0.1 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂SO₄ solution as catholytes at the current density of 500 A m⁻². These results are shown in Fig. 7. The current efficiencies greater than 95% were obtained for the 0.5 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ Lu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂SO₄ solution, though it slightly decreased with temperature. As previously mentioned, the decrease in the current efficiency was caused by the reduction of Cu(II) to



Fig. 8 Effect of pH value on the current efficiency. (i: $500 \,\text{A}\,\text{m}^{-2}$, C(NH₃) + C(NH₄⁺): 7 kmol m⁻³, Agitation speed: 200 rpm, Temp: 298 K)

Cu(I). The diffusion coefficient of Cu(II) increases with the temperature; thus, the amount of Cu(II) supplied to the cathode surface increased with the temperature. The same relationship between the current efficiency and temperature was observed in the 0.4 kmol m^{-3} Cu(I)-0.1 kmol m⁻³ Cu(I)-5 kmol m⁻³ NH₃-1 kmol m⁻³ (NH₄)₂SO₄ solution.

Figure 8 shows the effect of solution pH on the current efficiency. Electrodeposition experiments were conducted at a constant current density of 500 Am^{-2} using the 0.5 kmol m⁻³ Cu(I) and 0.4 kmol m⁻³ Cu(I)-0.1 kmol m⁻³ Cu(II) solution as the catholyte. The sum of the NH₃ and NH₄⁺ concentrations was maintained at 7 kmol m⁻³, and the pH of each solution was adjusted by the addition of H₂SO₄ solution. As is clear in this figure, there is no significant difference among the current efficiencies at the various pHs employed in this study.

4. Conclusions

In order to verify the feasibility of copper electrodeposition from ammoniacal alkaline solutions containing Cu(I), the cathodic polarization characteristics of Cu(I) and the galvanostatic electrodeposition of Cu(I) were investigated. The cathodic polarization curve for the $0.5 \text{ kmol m}^{-3} \text{ Cu(I)}$ - $5 \text{ kmol m}^{-3} \text{ NH}_3$ -1 kmol m⁻³ (NH₄)₂SO₄ solution showed an increase in the electric current corresponding to the deposition of copper at around -0.22 V vs. SHE which is much higher than the potential for the hydrogen evolution. The limiting current density was observed in the $0.1 \,\mathrm{kmol}\,\mathrm{m}^{-3}$ Cu(I) solution. Although a greater than 95% current efficiency was typically obtained for the Cu(I) solution without Cu(II), the current efficiency did not reach 100%. This would be due to the reduction of Cu(II) which is inevitably present in a few percent in the Cu(I) solution. The current efficiencies were greater than 95% in the current density range of 200 to 1000 A m^{-2} . A further increase in the current density resulted in a decreased current efficiency due to the hydrogen evolution. The current efficiency decreased with the increasing Cu(II) concentration and temperature. Consequently, these results indicate that the present copper electrodeposition method is applicable as a new energysaving hydrometallurgical recycling process.

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