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COPPER DEPOSITION ON STAINLESS STEEL SHEETS IN COPPER NITRATE SOLUTION

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Abstract: The aim of this study was to examine factors that influence copper nitrate based electrorefining of copper and to search the best process parameters for high-purity copper deposition on AISI 316L steel blanks. Considering impurities, the most important goal was to minimize sulfur content in a copper cathode. The effect of Cu^{2+} concentration, current density, temperature and pH were studied. The best parameters for the best copper purity were sorted out. The most important factors for quality copper deposition are sufficiently low Cu^{2+} concentration, low current density, right zone and careful control of pH. Active nitrate ion reduction reactions catalyzed by copper ions are suggested to affect detrimentally both copper deposition current efficiency and purity. Furthermore, nitrate ion reactions seem to elevate an electrolyte pH so that the deposition appears to be dark brown copper oxide. The 6N purity for copper was not reached with this cell construction and it fell behind about 7 ppm (99.9993% Cu). Both, sulfur and silver concentration were slightly above 1 - 2 ppm. To minimize the impurities, electrolyte circulation and filtration are needed. Also, either a separate silver cementation cell or cementation membrane is needed.

Keywords: *copper nitrate, electrorefining, high purity copper, hydrometallurgy*

Introduction

Development of copper based applications in the 21st century requires demanding properties from copper, especially in electronics, semiconductor and superconductor industries (Kim et al., 2007; Moreau et al., 2007; Ojebuoboh and Michels, 2004). For example, it is suggested that control of a copper microstructure in interconnects is an important issue for better conductivity performance of devices (Carreau et al., 2007). Furthermore, the purer the copper, the lower the resistivity and the lower annealing temperature can be used for copper (Kato, 1991; Kato, 1995). Pure copper also has less impurities that precipitate in the grain boundaries from which electrons readily scatter and cause an increase in resistivity (Carreau et al., 2007; Feng et al., 2008). Low resistivity also means better energy performance in traditional conductivity

applications. In electrorefining of copper, this requires new techniques and new means to reduce the impurity level in the cathode. Traditionally, in copper sulfate electrolyte, sulfur is one of the main impurity element in cathode, so that over 5.5N-6N purity (over 99.9995 % Cu) cannot be reached. The normal composition of cathode copper from sulfuric acid electrolyte is better than 4N, ~99.998 % Cu. A copper nitrate bath has no sulfur in the electrolyte and nitrogen has lower affinity towards copper than sulfur (Bruning et al., 1985). To minimize sulfur and silver content, the copper nitrate bath has been studied in the past 25 years. Copper nitrate electrolyte has been tested from the copper nitrate solutions regenerated from etching (Kim and Choi, 2003) and has been described in different patents with different cell constructions and circulation, cementation and filtration processes (Masaki and Masaharu, 2005; Ogata et al., 1989; Shindo and Takemoto, 2005). Additionally, a refining and float-zone melting method has been tried out (Bruning et al., 1985). Target purity for copper in these studies is usually set to 6N but measurement and definition of allowed impurity and non-impurity elements and amounts in copper vary with different authors (Kato, 1995; Takahashi and Kano, 2002; Ojebuoboh and Michels, 2004). In some of the studies silver, for example, is not included as the impurity.

In this paper we investigate the best parameters for copper deposition on 316L steel blanks from the copper nitrate bath to obtain high purity copper of 5.5N - 6N quality. We study the effect of Cu^{2+} concentration, current density, temperature and pH on copper purity.

Materials and methods

A copper nitrate electrolyte solution was made out of >98% copper nitrate pentahemihydrate salt $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ (Sigma – Aldrich, 12837), distilled water and nitric acid (Jt – Baker 65 %). A large 140 mm x 100 mm x 5 mm copper anode was made out of copper that had already been refined once in traditional copper sulfate electrorefining. The purity of this anode was 99.998 wt. % Cu (Boliden Harjavalta Oy). Cathode steel blanks were made out of AISI 316L steel and set into a teflon mask, where only one side of the steel plate with area of 62 mm x 49 mm was in contact with the electrolyte. Both, the anode and cathode were polished with 1200 grade sandpaper and rinsed with distilled water before experiments.

The experimental setup

A 3 dm³ electrorefining cell was made out of inert glass and cleaned with nitric acid and distilled water before the experiments. Cathode to anode distance was 50 mm in all tests. This glass cell was immersed in the water bath with temperature control system. For the cell, a cover lid was made with holes for anode, cathode, pH electrode and thermometer (Fig. 1). A regulated power supply Lab 522 Finn Metric Oy and current meter Hewlett Packard 34401A were used in the experiments. The pH-electrode was manufactured by Mettler Toledo (SevenEasy pH). Cathodic polarization

experiments for copper nitrate electrolyte were done in a standard three-electrode cell with the Luggin capillary connected to a saturated Ag/AgCl reference electrode.



Fig. 1. Left: stainless steel blank in teflon mask. Right: cell cover lid attached with two steel blank cathodes

Electrorefining and cathode analysis

After mixing the copper nitrate salt with distilled water and concentrated nitric acid was added (3 cm^3) in 3 dm^3 of electrolyte to adjust the pH level to 1.3 – 1.6 (Mockrin and Hobin, 1977; Bruning et al., 1985; Kim and Choi, 2003). Just before the experiments the anode and cathode were activated with 1200 sandpaper and cleaned with distilled water and dried. Both, the anode and cathode were immediately connected to the power supply and the experiment was started and lasted for 96 hours. The constant current mode was used. During electrorefining pH alteration, the cell voltage and temperature were measured. After the experiment the copper plate was detached from the steel blank under running distilled water to avoid oxidation, and cleaned in an ultrasonic bath. The cathode elements were analyzed with an ICP mass spectrometry. Copper purity was calculated as 100 % minus the impurities analyzed.

Copper and nitrate reactions

Nitrate ion (NO_3^-) reduction reactions have higher standard electrode potential than the copper reduction reaction (Bruning et al., 1985; Shriver and Atkins, 1999). This makes it possible that nitrate ions reduce at the same time with copper(II) ion. This indicates that the current efficiency for copper deposition might suffer. The equilibrium potential is defined by the Nernst equation:

$$E = E^0 - \frac{RT}{zF} \ln(k). \quad (1)$$

Nitrate ion reduction to weak nitrous acid can be written as



For this reaction we obtain a new equilibrium potential E^0 . If NO_3^- activity is one and temperature 25 °C, then

$$\begin{aligned} E^0 &= 0.94 - \frac{RT}{zF} \ln \left(\frac{[\text{HNO}_2]}{[\text{H}^+]^3 [\text{NO}_3^-]} \right) = 0.94 - \frac{0.059}{2} (\log(1) - 3\log[\text{H}^+]) \\ &= (0.94 - 0.09\text{pH})V \end{aligned} \quad (3)$$

Equation 3 shows that if pH is low, the potential for the nitrate ion reduction reaction is higher. Consequently, if the activity coefficient and concentration of nitrate ion is high, the potential is also higher. This suggests that nitrate ion reduction reactions occur before or at the same time with the copper reduction reaction at the cathode:



If the electrolyte pH value increases too high due to the reaction (2) (hydrogen consumption), copper will deposit as porous copper oxide CuO or Cu_2O on the cathode (Fig. 2) Additionally, copper ions are known to have a catalytic effect on nitrate ion reduction reactions, which is again detrimental for the copper refining process (Ohmori et al., 1998; Bouzek et al., 1999; Epron et al., 2003; Filimonov and Shcherbakov, 2004; Kyriacou and Polatides, 2005; Polatides et al., 2005; Vazquez-Arenas et al., 2007). According to Filimonov and Shcherbakov (2004), nitrate ions can also be reduced chemically:



The exact kinetics of the nitrate reduction reactions are still less known and studied but some suggestions for the mechanism have been presented in different acid media (Vazquez-Arenas et al., 2007).

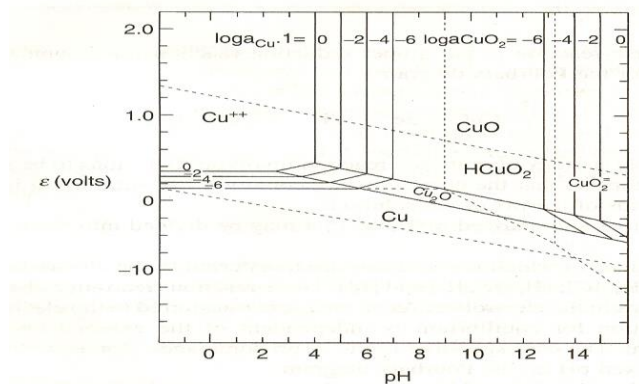


Fig. 2. Pourbaix diagram for copper in water solution at 25°C

Results and discussion

Cathodic polarization experiments

Cathodic polarization experiments were made for copper nitrate electrolyte of 40 and 100 g/dm³ Cu at room temperature. The results are shown in Fig. 3.

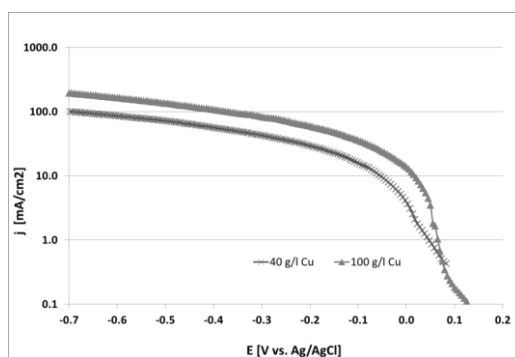


Fig. 3. Cathodic polarization experiment with 40 and 100 g/dm³ Cu concentrations

In the 100 g/dm³ Cu experiment, the polarization effect is smaller than in the 40 g/dm³ Cu test. The limiting current density due to diffusion is higher for the 100 g/dm³ test than for the lower concentration, which correlates with the limiting current theory. With the knowledge of polarization tests, we decided to test three different current densities of 100 A/m² (10 mA/cm²), 200 A/m² and 300 A/m², so that the cell voltage would not increase too high and the process efficiency would still be moderate.

Effect of Cu^{2+} concentration and current density

Three different copper concentrations (40, 100 and 150 g/dm^3) were used in the experiments. Only with the lowest concentration (40 g/dm^3 Cu) we managed to produce pure 99.9993 % (5N) copper and a cathode plate, which was bright copper color and solid (Table 1). In all other experiments, with two highest copper concentrations, the purity remained under 5N and the current efficiency (CE) was poor. In these tests the cathode color was dark, which indicates copper oxide deposition (Figs. 4 - 5). The dark copper oxide cathode plate was very fragile, soft and porous.

Table 1. Results of cathode copper purity analysis

Cu [g/dm^3]	j [A/m^2]	T [$^{\circ}\text{C}$]	E [V]		pH		CE [%]	Cu cal.%	quality / color
			start	final	start	final			
40	100	22	0.35	0.21	1.7	2.2	~90	99.99827	good
40	100	35	0.29	0.20	1.4	2.1	80	99.99934	good
*40	100	35	0.34	0.20	1.5	1.9	~ 90	99.99929	good
40	200	22	0.66	0.29	1.3	2.1	~ 90	99.99904	good
100	300	22	0.60	0.27	1.4	2.2	35	99.99888	bad

*repetition test

It is known that very low and very high concentrations of salts in electrolytes have higher ion activities and mean activity coefficients than the mid-range concentration of salts of 0.1–1 M (Lobo, 1989; Grenthe et al., 2000). Competing nitrate ion reduction reactions with copper ions are harmful for the quality of copper deposition, because they increase the electrolyte pH to the porous copper oxide deposition level, which is seen in the 100 and 150 g/dm^3 Cu concentration experiments (1.57 and 2.36 M) (Figs. 4 - 5). In addition, it is suggested that the copper ions work as catalyzers for the nitrate ion reduction reactions. Good quality deposition of copper was achieved with 40 g/dm^3 Cu if the pH did not increase much above 2 (Fig. 4). It is suggested that the harmful nitrate ion reduction reactions occur slower at the low concentrations and activity levels than at higher concentrations of 100 and 150 g/dm^3 Cu. However, the concentration of 40 g/dm^3 Cu seems to be high enough for copper deposition at the decent current density but low enough for slow copper nitrate reactions or copper reducing reactions to be preferable at the cathode.

The 100 A/m^2 cathodic current density was low enough for a good copper deposit without diffusion problems. The cell voltage remained just at +0.2 – 0.35 V. With 200 A/m^2 current density the cell voltage rose to +0.6 V at the beginning but dropped during copper growth to under 0.3 V (Table 1). Dendrite growth was considerably

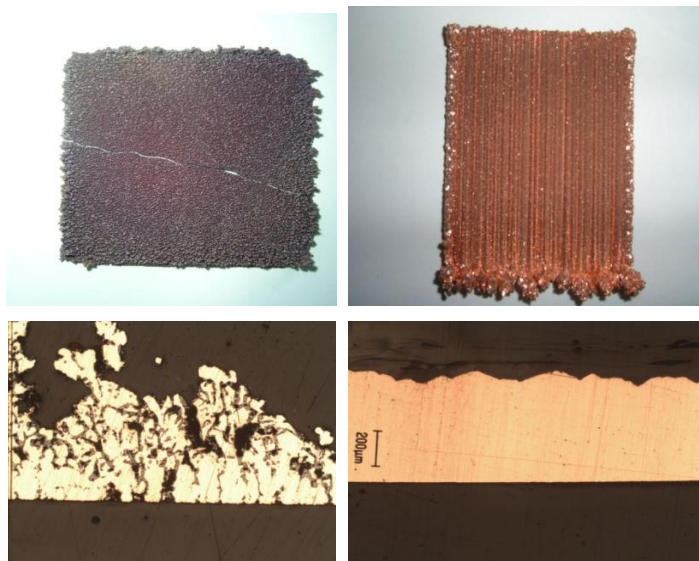


Fig. 4. Left: copper cathode plate ($\text{Cu } 40 \text{ g/dm}^3$) with cross section image.
Right: copper oxide cathode plate ($\text{Cu } 100 \text{ g/dm}^3$) with porous structure

higher with the higher current density. The purity of cathode copper was over 5N with both 100 and 200 A/m^2 experiments. With higher concentrations of copper the higher current density can be used, which is good for the productivity. However the detrimental effect of nitrate ion reduction reactions becomes too high with high concentrations of 100 and $150 \text{ g/dm}^3 \text{ Cu}$ (Fig. 5). A low enough amount of copper in the electrolyte and high current density for higher productivity is a compromise.

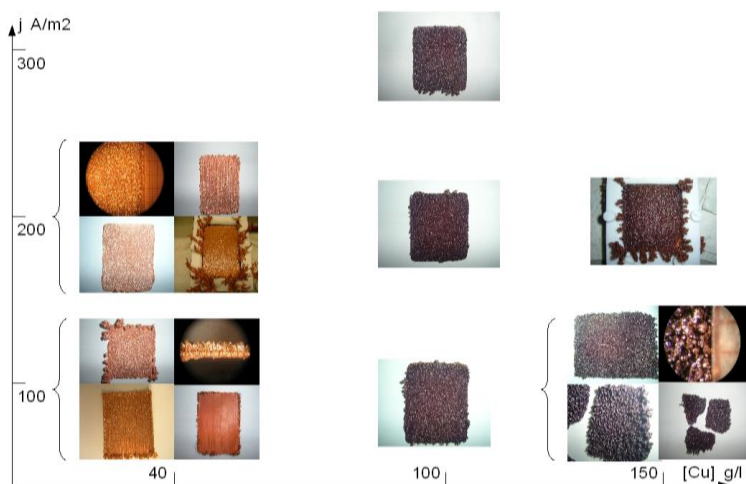


Fig. 5. Current density and copper concentration effect on cathode appearance and quality

Effect of temperature

According to previous studies it seems that copper nitrate based electrorefining works better at relatively low temperatures (Mockrin and Hobin, 1977; Kim and Choi, 2003). At lower temperatures detrimental nitrate reduction reactions might be inhibited significantly. We tested two different temperatures (22 and 35 °C) but no significant differences in the copper quality or purity were noticed (Table 1). At $T = 35$ °C the conductivity of the electrolyte was slightly higher than at 22 °C (74 mS/cm vs. 101 mS/cm) for 40 g/dm³ Cu electrolyte. For 100 g/dm³ Cu electrolyte, the conductivities at the same temperatures were 116 and 132 mS/cm, respectively. In theory, raising temperature to 35 °C should lower the cell voltage slightly but we did not see the major difference in the cell voltage either (Table 1).

Effect of pH

Electrolyte pH is a critical value for the success of refining. The pH tends to increase due to hydrogen ion consumption in nitrate ion reduction reactions or due to hydrogen ion activity drop in reactions with copper and nitrate ions. With high concentrations of copper nitrate salt 100 and 150 g/dm³ Cu, the cathode was covered with dark copper oxide even though pH stayed below 2. This indicates that copper and nitrate ion activities are too high and copper oxide deposits also at lower pH values as can be seen from Table 1. If pH is adjusted too low with nitric acid at the beginning, the nitrate ion reduction potential becomes higher (Eq. 3) and could accelerate the nitrate ion reduction reaction and end with a fast pH increase. Electrolyte pH monitoring and adjustment is needed during a long refining period for better copper deposit. One problem with nitric acid addition is that it increases the NO₃⁻ activity in the solution.

Cathode purity

Over 5.5 N copper purity is not reached with this cell construction. In the cathode, sulfur concentration remained from 0.25 to 1.7 ppm (4 ppm in anode) and silver 1–3 ppm (10 ppm in anode). Iron and nickel remained between 0.2–1 ppm, which is approximately the same amount than in the anode. Silver in the electrolyte varied between 0.02–0.11 mg/dm³. Concentration of 40 g/dm³ Cu, current density 100 A/m², and temperature 35 °C were found to be the best parameters for dense and hard copper deposit (99.9993 %). Although at $T = 22$ °C and $j = 200$ A/m² the result was also 5N (99.9990 %) copper, but with more dendritic growth.

Conclusions

In this work copper nitrate based electrorefining of copper was studied. Monitoring and controlling of pH makes copper electrorefining in copper nitrate electrolyte especially challenging. The pH tends to increase due to the nitrate ion reduction reactions and the pH increase occurs without a clear rate. The pH range of 1.4 - 1.7

should be maintained if possible. In this range, the nitrate reduction reactions are suggested to be inhibited and dense quality copper is able to deposit on the steel plate. To achieve 6N copper with copper nitrate electrolyte more sophisticated cell structure with anode sludge filtration, acid addition and silver cementation processes are needed. For measuring the final purity of copper and how the purity affects properties of copper, it might be reasonable to measure the final product performance i.e. conductivity with the calculated copper purity percent in the future. Lower temperatures (5–15 °C) might be worthwhile to inhibit the nitrate reduction reactions.

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