



A study of copper electrowinning parameters using a statistically designed methodology

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Abstract

This study employs a factorial experimental design to relate current efficiency with current density (180 and 300 A m⁻²), copper concentration (25 and 65 g l⁻¹), and temperature (40 and 60 °C). Pure, synthetic electrolyte with a constant acid concentration of 180 g l⁻¹ was used. The designed study produced a linear relationship where the independent variables of current density, copper concentration, temperature and their interactions were found to be statistically significant. It was shown that current efficiency could not solely be used as a predictor of copper cathode quality. The quality of the deposit is difficult to incorporate into a model or relation. It was determined that other measures, such as cathode morphology and crystal structure should be considered. This was done through XRD and SEM analysis.

1. Introduction

During the electrowinning of copper, effort is made to obtain a high current efficiency, as well as to produce a deposit of high quality. Current density is an important parameter in determining current efficiency. The optimum current density level is affected by such factors as electrolyte composition, electrolyte temperature, inter-electrode spacing, addition agents *etc.* The copper electrowinning process variables of current density, copper electrolyte concentration, and electrolyte temperature strongly influence the results and effectiveness of electrowinning in terms of power consumption.

Winand [1] in studying electrocrystallization stated that many factors have an influence on the type of deposit obtained at the cathode of an electrolytic cell. Current density, concentration of the ion-containing metal, temperature of the electrolyte, pH of the electrolyte, agitation within the electrolytic cell, other anions and cations, the presence of inhibitors, and the substrate itself all affect the type and quality of electrodeposited crystals [2–6]. The effects of current density, copper concentration and temperature are evident on the efficiency of the electrowinning process and on the quality of the electrodeposited copper.

Anderson et al. [2] found that it was possible to increase current efficiency in electrowinning copper from acid leach solutions by decreasing temperature, increasing inert salt concentrations, decreasing ferric ion

concentration, increasing applied current density, and decreasing agitation. Positive effects on current efficiency were not necessarily accompanied by good cathode quality. For example, Anderson et al. [2] found that a decrease in temperature raised current efficiency but lowered deposit quality. An increase in current density, while producing an increase in current efficiency, caused deposit quality to suffer. Similarly, Paschen et al. [3], in studying energy conservation and productivity increasing factors for copper electrowinning, found that increasing current density had a positive effect on current efficiency, as did the lowering of electrolyte temperature, but cathode deposit quality suffered.

Krishna and Das [4] examined the effect of electrolyte circulation rate and electrolyte copper concentration on the current efficiency and copper deposit quality in a study aimed at enhancing operating current density in a copper electrowinning cell. They varied the current density from 300 to 450 A m⁻² utilizing copper concentrations of 30, 35 and 40 g l⁻¹. Compact copper deposits were observed at nearly 95% current efficiency when 30 g l⁻¹ of copper was electrolysed at 300 A m⁻². As current density was raised nodular growth resulted with a powdered copper deposit being prevalent. Raising the copper concentration in the electrolyte produced compact deposits. During the formation of these rough cathodes it was noted that the current efficiency fell with increasing current density at constant copper electrolyte

concentrations and fell with decreasing copper concentrations at constant current densities.

Statistical experimental design has been applied in various extractive metallurgical studies including the optimization of conditions for zinc electrowinning and in the optimization of influent factors on the nucleation of copper from solutions containing thiourea. Frazier and Lwin [7] applied Factorial and Box and Wilson experimental designs in an attempt to optimize zinc electrowinning conditions by studying the effects of temperature, current density, and electrode rotation rate on coulombic efficiency. In optimizing the coulombic efficiency, no attempt was made to study the resultant quality of the electrodeposited zinc. Other studies [8–12] have used multivariate statistical techniques to characterize electrolyte performance in zinc electrowinning. For example, Fosnacht and O'Keefe [10] studied impurities and their interactions during zinc electrowinning utilizing a factorial experimental design. The effects of zinc concentration, current density and temperature on current efficiency were observed. Furthermore, X-ray diffraction and scanning electron microscopy were employed to examine crystal structures and morphologies.

Although current efficiency is a widely used measure of tankhouse proficiency in producing electrowon metal, it does not provide a direct measure of metal quality. It is possible to have good current efficiency but have a poor quality cathode product. This is not desirable.

The present study employs a factorial experimental design to relate current efficiency (the dependent variable) with the independent variables of current density, copper concentration, and temperature in an examination of copper electrowinning parameters. Other physical properties of the cathode deposit such as crystal structure and morphology were evaluated using scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (XRD).

2. Experimental details

The electrowinning cells were constructed from 0.25 inch Lexan[®]. They were self-contained, encased in their own outer shell water jacket, enabling temperature control. Each cell held approximately 1.5 litres of electrolyte and allowed for the introduction and recirculation of electrolyte. The cells had three notches, 0.8 cm in length, separated at 2.5 cm, cut into the longitudinal sides to serve as anode and cathode holders and spacers.

Pure electrolyte was utilized throughout the study. Fisher, A.C.S. reagent grade copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) and sulfuric acid (H_2SO_4) were used to formulate the initial starting electrolytes. No other additives or addition agents were employed. Make-up solutions, added to the electrowinning cells during the course of an experiment were made using Fisher A.C.S. reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. These re-

plenishing solutions contained no acid. The anodes and cathodes used during experimentation were cut to laboratory scale from industrial anodes and cathodes. The industrial lead alloy anode, which contained approximately 0.75% silver. The cut dimensions were 10 cm \times 6 cm \times 0.8 cm thick. The anode hanger bar was simply an extension of the anode cut to a length of 15 cm. The cut cathode dimensions measured 11 cm \times 7 cm \times 0.3 cm thick. The cathodes were fitted with edge strips on the sides and bottom to facilitate removal of electrolysed copper. The cathode hanger bar was an extension of the cathode cut to a length of 15 cm.

All copper electrowinning tests were conducted in two laboratory-scale cells. Each cell held two lead alloy anodes and one stainless steel cathode separated at a distance of 2.7 cm by PVC[®] spacers. The cathodes and anodes were wet sanded with 400 grit silicon carbide sandpaper, washed with deionised water, rinsed with a dilute sulfuric acid solution to remove any residual silicon carbide, rinsed with deionized water, and air-dried.

Starting solution electrolytes were freshly prepared for each test to the desired copper concentration. The acid concentration for these starting electrolytes remained constant throughout the course of experimentation at 180 g l⁻¹. Once prepared, the starting electrolytic solutions were preheated to the desired test temperature using an MGW Luada stainless steel water bath and Brinkmann model T-1 immersion heater. The electrolyte was introduced into the cells at temperature. The copper content was determined by atomic absorption spectroscopy and the acid concentration was determined by titration using Fisher 2N A.C.S. reagent grade sodium hydroxide (NaOH). Make-up solution was prepared in a similar manner with identical copper concentrations as the starting electrolytes, however these solutions contained no acid and were not preheated.

Each cell had one Masterflex C/L peristaltic pump dedicated for electrolyte recirculation at 25 ml min⁻¹ and one for make-up electrolyte introduction. The latter pump was adjusted to deliver the quantity of copper electrowon during a test thereby maintaining the copper and acid concentrations within the cell. This calculated flow rate was verified throughout an experiment. Electrolyte overflow was collected per hour and analysed for copper and acid concentration. Electrolyte temperature was monitored and continuously maintained at the desired experimental temperature with an external water bath and immersion heater.

Direct current (d.c.) power was supplied by a laboratory Goodwill GPR-6015HD Super Series Programmable power supply. The two electrowinning cells were connected in series for every test. The voltage was allowed to fluctuate during an experiment and was monitored with an Omega DaqBook 100 data acquisition system. The voltage data was recorded with an AST 486 33SX notebook computer.

Each anode–cathode pair and the circuit were monitored in this manner. The half-cell potential of the anode or the cathode, in one cell, was monitored and

recorded in like fashion by using an electronic bridge reference tube and a saturated calomel electrode (SCE). All copper electrowinning tests were done in duplicates and each test was conducted for six hours.

Upon deposition completion the cathodes were removed, washed with distilled water and allowed to air dry. The cathode copper was analysed for quality of deposit by scanning electron microscopy (SEM), on a Hitachi S-2150 SEM and by X-ray diffraction spectroscopy (XRD) using a Phillips 4000 series XRD with a Phillips 1361 goniometer.

3. Results and discussion

A factorial experimental design was employed to find a relationship between current efficiency (the dependent variable) and current density, electrolyte copper concentration, and temperature (the independent variables). In copper electrowinning, the operating parameters of current density, copper concentration and temperature strongly influence the effectiveness of electrowinning and, conversely, it is these parameters, which may be altered to correct a problem of current efficiency and/or deposit quality. These factors were selected because they are widely considered to be the most important variables in copper electrowinning [8, 11].

Factorial experimental designs allow for the simultaneous study of several treatment factors and also allow for the study of interactions between the factors. Interactions are often the driving force in a process. Without the use of factorial experiments, important interactions may remain undetected. A factorial design dictates that 2^k experiments be performed where k represents the number of factors under study. With three independent variables, requiring an upper and lower value for each variable, the resulting experimental design prescribes that eight experiments be performed. Statistical analysis of these eight experiments should lead to a relationship that relates current efficiency with current density, copper concentration, and temperature while taking into account the interactive effects of these factors. In factorial experimental designs this model is a linear relationship of the form:

$$CE = b_0 + b_1(CD) + b_2(CC) + b_3T + b_4(CD)(CC) + b_5(CD)(T) + b_6(CC)(T) + b_7(CD)(CC)(T) \quad (1)$$

where CE is the current efficiency, CD is the current density, CC is the copper concentration and T is the temperature of the electrolyte. The interactive terms are combinations of the independent variables, for example, $(CD)(CC)$, and the b_i terms represent coefficients.

A two level experimental design was used in this study because it allows for a minimum acceptable number of experiments. A higher design level (e.g., three-level), which would cover a wider range of parameters, would produce additional valuable information about the process. However, it would require a significantly higher number of experiments. From experience, the three-level experimental design is not necessary for the present investigation, which involves synthetic solution. However, it will be considered for the real solution where other important variables such as major impurities, substrate and planting time will be introduced.

Table 1 presents a summary of the experimental results of this study outlining the combinations of independent variables studied and the current efficiencies obtained. The current efficiencies were high and exhibited a narrow range. The use of reagent grade chemicals to make the electrolyte resulted in the absence of impurities such as ferric ions. Fe^{3+} ions, if present, are reduced at the cathode to Fe^{2+} ions. They in turn migrate to the anode and are subsequently oxidized back to Fe^{3+} ions. This reaction sequence continues, consuming current that would otherwise be used to reduce Cu^{2+} to copper metal at the cathode. Furthermore, the experimental plating time was limited to six hours, producing a copper cathode of finite thickness (~ 0.3 mm), eliminating the possibility of shorting and consumption of current. The majority of the current was utilized to electrowin copper with minimal losses.

Although very little variation in current efficiency was realized over the designed experiments, an analysis of variance was performed to determine the significance of any term in Equation 1. Factorial experimental designs are balanced designs, meaning that there are an equal number of observations for each set of conditions. This

Table 1. Experimental design points and corresponding current efficiencies

Sample	Current density /A m ⁻²	Copper concentration /g l ⁻¹	Temperature /°C	Current efficiency (Test 1) /%	Current efficiency (Test 2) /%
1	300	25	60	98.46	98.51
2	300	25	40	96.60	96.51
3	180	25	60	98.11	98.10
4	180	25	40	97.64	97.76
5	300	65	60	98.62	98.69
6	300	65	40	98.84	98.84
7	180	65	60	98.08	98.03
8	180	65	40	98.32	98.48

Table 2. Variance analysis (95% confidence level)

Variables (factors)	Degrees of freedom	F value	P value
Current density (CD)	1	5.39	0.049
Copper concentration (CC)	1	701.44	0.000
Temperature (T)	1	236.80	0.000
(CD) (CC)	1	236.17	0.000
(CD) (T)	1	202.64	0.000
(CC) (T)	1	593.76	0.000
(CD) (CC) (T)	1	135.35	0.000

Table 3. Model coefficients and statistical analysis

Variables (factors)	Coefficients	T value	P value
Constant	105.845	139.00	0.000
Current density (CD)	-0.057448	-18.66	0.000
Copper concentration (CC)	-0.10726	-6.94	0.000
Temperature (T)	-0.13450	-9.01	0.000
(CD) (CC)	0.00090149	14.42	0.000
(CD) (T)	0.00099080	16.41	0.000
(CC) (T)	0.0016306	5.38	0.001
(CD) (CC) (T)	-0.00001426	-11.63	0.000

enables the determination of whether each individual factor, current density, copper concentration, temperature, or their interactive effects, are independently statistically significant.

Utilizing the statistical software package Minitab® yielded the results presented in Table 2. All factors in Equation 1 were determined to be independently statistically significant. The independent variables and their two and three-way interactions returned probability values (*P*-values) less than 0.05. Only current density had a calculated *P*-value close to 0.05 (0.049), indicating that it minimally satisfied this criterion at the 95% confidence interval. Since the main and interactive factors were independently statistically significant the data was analysed to determine the coefficients of the linear relation as defined in Equation 1.

Table 3 lists the coefficients for the relation expressed in Equation 1 as well as the calculated *T* (student's *T* tests) and corresponding *P*-value statistics. Current density, copper concentration, temperature, and their interactive terms were statistically significant. The analysis of variance presented in Table 2 showed that the main and interactive factors were independently statistically significant. The determination of the coefficients, b_i , in Equation 1, and the calculation of their *T*-values tests the significance of the main and interactive factors if the other factors remained in the model. Each of the factors and their two and three-way interactions were found to be of statistical significance at the 95% confidence interval.

Therefore, the experimental design successfully provided a relationship between current efficiency and current density, copper concentration, temperature and their interactive effects. An *R*-squared value of 0.996 indicated a high degree of correlation between the dependent and independent variables. The main and

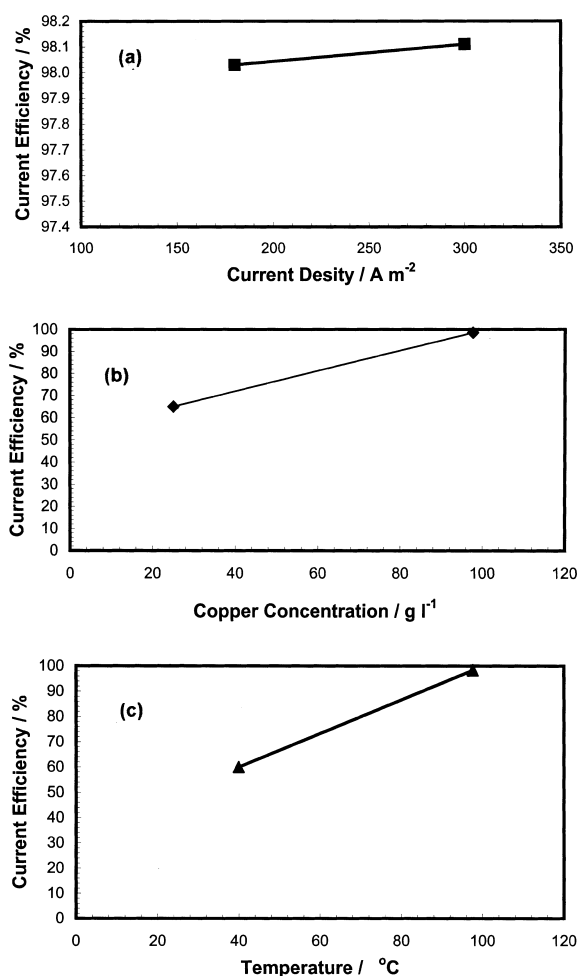


Fig. 1. Main factors effects on current efficiency: (a) current density, (b) copper concentration and (c) temperature.

interactive factor effects on current efficiency are shown in Figures 1 and 2, respectively.

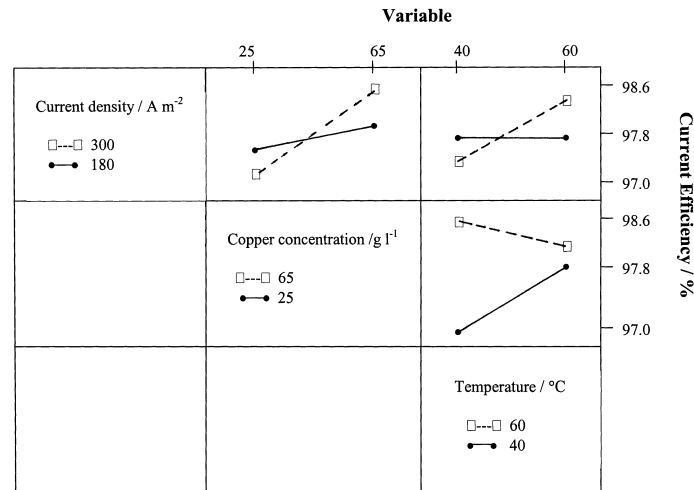


Fig. 2. Interactive factor effects on current efficiency.

The main factors of current density, copper electrolyte concentration, and temperature had positive effects on current efficiency. Increases in each factor increased the current efficiency. Copper concentration and temperature had the largest effect on current efficiency (Figure 1(b) and (c)), while current density had the least effect (Figure 1(a)). Similarly, Figure 2 indicates that the interactive effects on current efficiency were positive with the exception of the copper concentration–temperature interactive factor. At increasing temperatures for electrolyte copper concentrations of 65 g l^{-1} , the copper concentration–temperature interactive factor had a negative effect on current efficiency. Within the scope of the ranges used for the independent variables, higher copper electrolyte concentrations, higher temperatures, and high current densities yielded higher current efficiencies.

It can be concluded that a linear relationship exists between the dependent variable of current efficiency and the independent variables and their two and three-way interactive terms. Furthermore, factorial experimental design can be used to analyse the effects of these parameters on current efficiency in a copper electrowinning process using a pure electrolyte. However, it is expected that the response will be more pronounced when real solutions are employed. This is mainly due to presence of impurities in real electrolytes.

To confirm these findings several copper electrowinning tests were performed at values of current density, copper concentration, and temperature within the ranges of the independent variables as set out by the original factorial design. Table 4 summarizes the obtained re-

sults. There is agreement between the experimental and predicted values of current efficiency. Therefore, the linear relationship can be used to predict current efficiency at independent variable values that fall within the high and low ranges of those initially employed. The electrowinning experiments yielded current efficiencies greater than 96.5%. Typical current efficiencies in most industrial copper electrowinning operations range from 90–95%. This study produced electrowon copper at current efficiencies greater than that obtained commercially. This was expected due to the controlled conditions and the use of pure electrolyte. Although high current efficiencies were obtained the quality of the cathode deposit differed depending on the conditions employed during experimentation. The quality of the electrowon metal varied markedly despite current efficiencies in excess of 96%.

Higher levels of current should lead to a lowering of cathode metal deposit quality as the rate at which copper cations are removed from the vicinity of the electrode exceeds the rate at which copper ions are replaced from the bulk electrolyte [2–4]. Higher copper concentration should alleviate this and allow for compact, good quality copper deposits at higher current densities [2, 4]. Increased temperatures should also enhance mass diffusion rates of Cu^{2+} ions and other electroactive species in solution resulting in a positive effect on the copper cathode quality [2, 3].

The orientation of the grains and the morphology of the cathode produced, as final product is important with regards to downstream physical handling, market

Table 4. Comparison of experimental and predicted current efficiencies

Current density / A m^{-2}	Copper concentration / g l^{-1}	Temperature / $^{\circ}\text{C}$	Experimental current efficiency / %	Predicted current efficiency / %	Difference / %
220	50	50	98.07	98.17	0.10
240	45	50	98.12	98.10	−0.02
240	50	50	98.13	98.20	0.07
260	50	50	98.26	98.23	−0.03

Table 5. Copper powder diffraction pattern (standard sample)

Bragg angle (2θ)	Plane ($h k l$)	Intensities (I/I_1)
43.30	(1 1 1)	100
50.44	(2 0 0)	46
74.12	(2 2 0)	20
89.91	(3 1 1)	17
95.14	(2 2 2)	5

acceptance, and more importantly plant performance [13]. It is essential that electrowinning conditions produce cathodes of good quality at high current efficiencies. The deposits produced in this study were examined

by X-ray diffraction (XRD) to determine the preferred crystal orientation. A standard random copper powder exhibits specific preferences for crystal growth planes. For comparison, Table 5 [14] lists these preferential planes along with their relative intensities. Figure 3(a), (b) and (c) shows the peak height intensities measured from the XRD spectra. Copper forms a face-centred cubic structure that complicates the determination of preferred orientation due to difficulties in differentiating between the parallel and perpendicular planes relative to the stainless steel cathode. However, because the crystal structure of copper is cubic and symmetrical, no differences between vertical and horizontal plane orientations should exist.

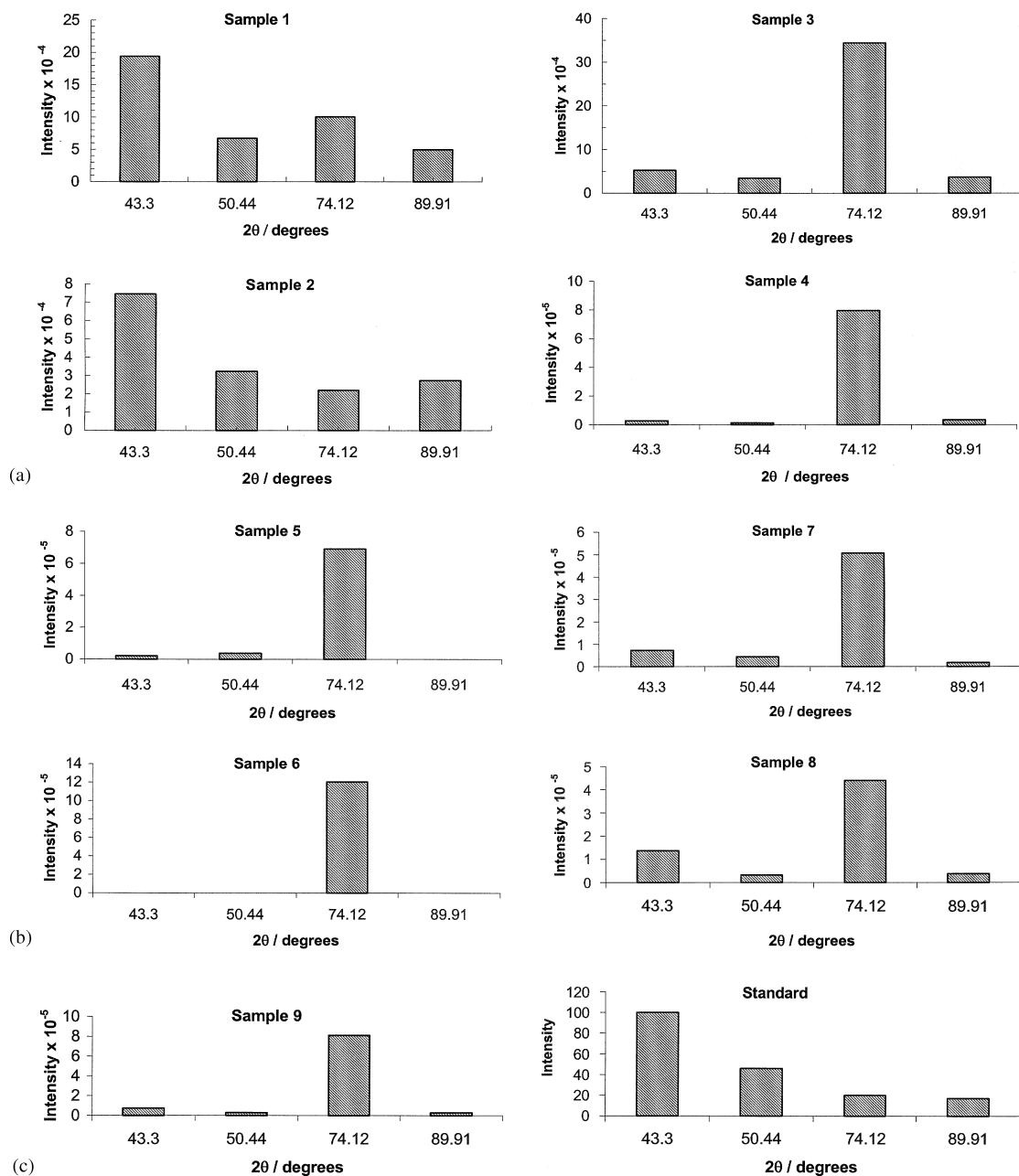


Fig. 3. (a) XRD peak height intensities for samples number 1, 2, 3 and 4; (b) for samples number 5, 6, 7 and 8; (c) for samples number 9 and standard.

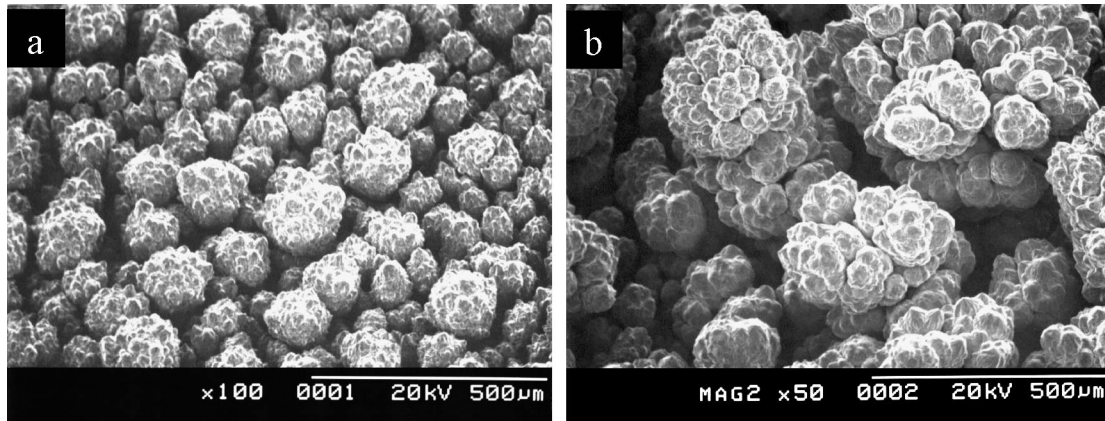


Fig. 4. SEM micrographs for: (a) sample 1 100 \times ($CD = 300 \text{ A m}^{-2}$, $CC = 25 \text{ g l}^{-1}$, $T = 60 \text{ }^\circ\text{C}$) and (b) sample 2 100 \times ($CD = 300 \text{ A m}^{-2}$, $CC = 25 \text{ g l}^{-1}$, $T = 40 \text{ }^\circ\text{C}$).

Only samples 1 and 2 produced relative crystal growth plane intensity patterns similar to the standard. Only these samples exhibited nodular growth. The (1 1 1) plane was preferred in both, however the XRD pattern of sample 2 showed a higher degree of similarity to the standard. Sample 1 exhibited a similar growth pattern but with a larger (2 2 0) crystal growth plane. Samples 3–9 had a dominant polarized (2 2 0) plane. Figure 1(a), (b) and (c) indicate that quality copper deposits are produced when one crystal growth plane is dominant.

A SEM analysis of the samples provided another means of determining the quality of the electrodeposited copper. Figure 4 shows scanning electron micrographs of samples 1 and 2. The deposits are spherically agglomerated copper crystals. Sample 1 deposits are angular and finer than those of sample 2. The agglomerated deposits of sample 1 measure approximately $150 \mu\text{m}$ in diameter. Sample 2 deposits are larger and very spherical. The agglomerated deposits measure approximately $300 \mu\text{m}$ in diameter. Although the

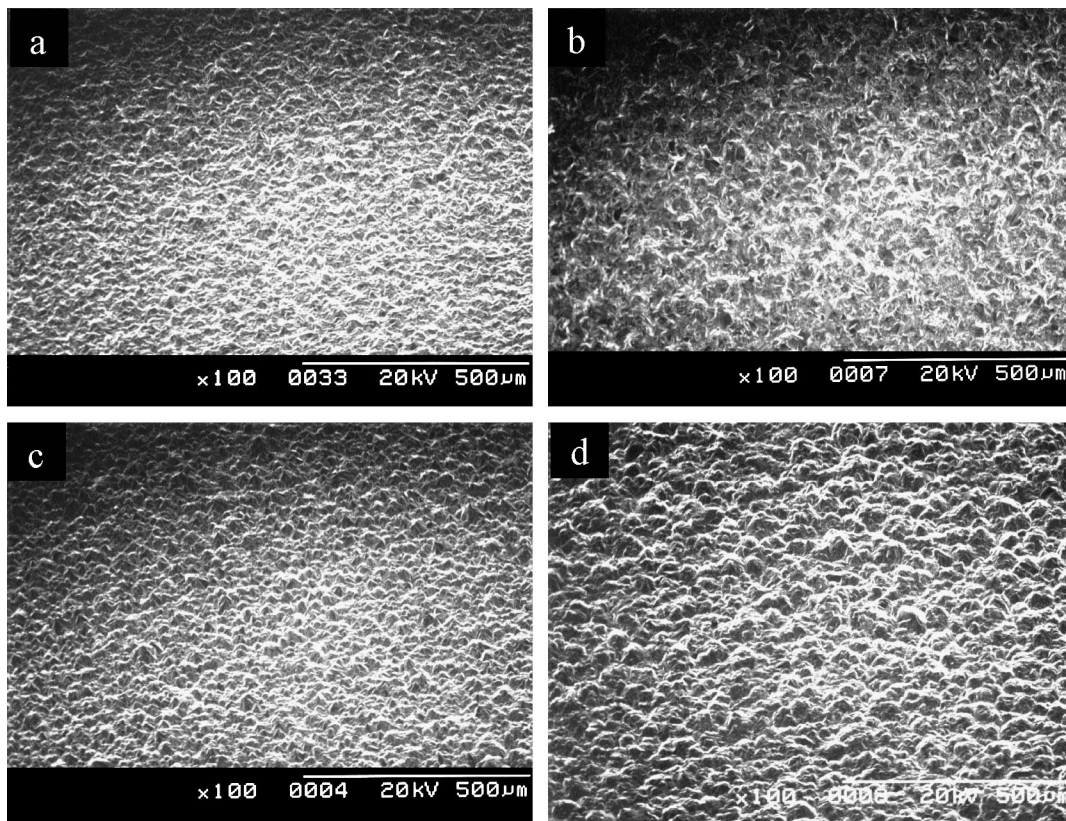


Fig. 5. SEM micrographs of: (a) sample 3 100 \times ($CD = 180 \text{ A m}^{-2}$, $CC = 25 \text{ g l}^{-1}$, $T = 60 \text{ }^\circ\text{C}$), (b) sample 7 100 \times ($CD = 180 \text{ A m}^{-2}$, $CC = 65 \text{ g l}^{-1}$, $T = 60 \text{ }^\circ\text{C}$), (c) sample 4 100 \times ($CD = 180 \text{ A m}^{-2}$, $CC = 25 \text{ g l}^{-1}$, $T = 40 \text{ }^\circ\text{C}$) and (d) sample 8 100 \times ($CD = 180 \text{ A m}^{-2}$, $CC = 65 \text{ g l}^{-1}$, $T = 40 \text{ }^\circ\text{C}$).

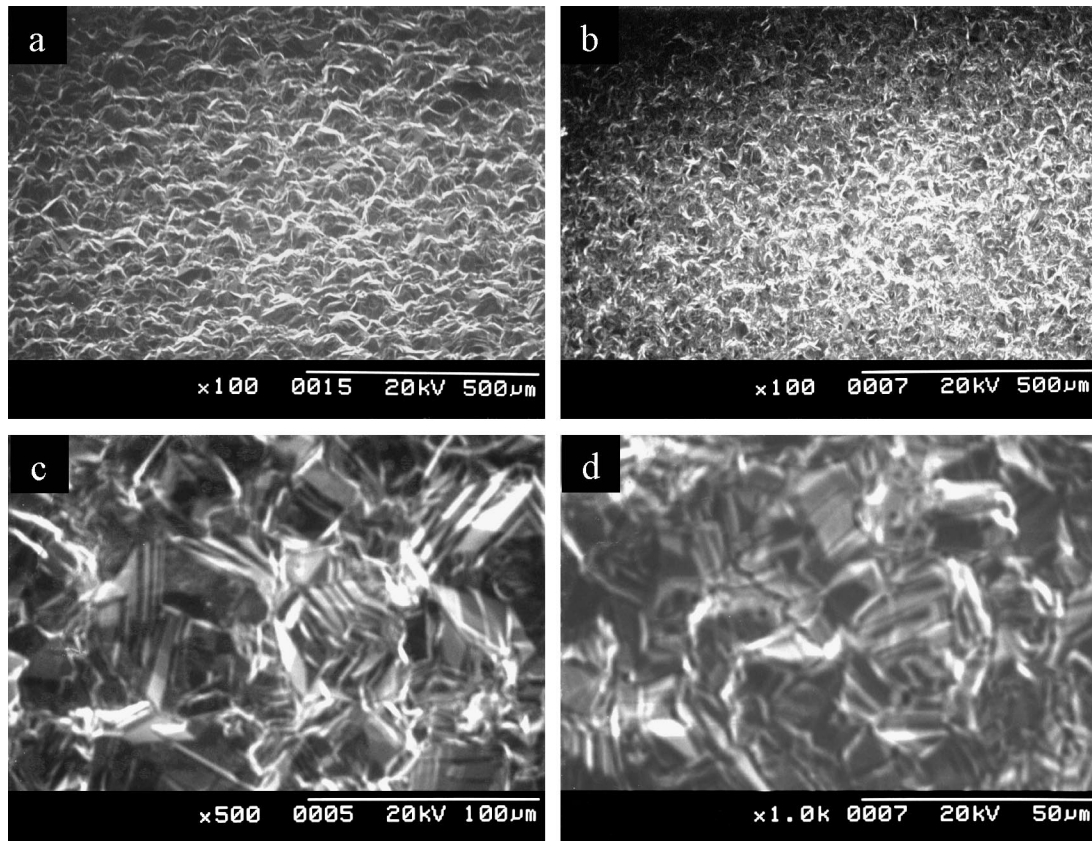


Fig. 6. SEM micrographs of: (a) sample 5 100 \times ($CD = 300 \text{ A m}^{-2}$, $CC = 65 \text{ g l}^{-1}$, $T = 60 \text{ }^\circ\text{C}$), (b) sample 7 100 \times ($CD = 180 \text{ A m}^{-2}$, $CC = 65 \text{ g l}^{-1}$, $T = 60 \text{ }^\circ\text{C}$), (c) sample 5 500 \times and (d) sample 7 1000 \times .

current efficiency achieved for these depositions was in excess of 98 and 96%, for samples 1 and 2, respectively, the quality of the electrodeposited copper was unacceptable. Samples 3–9 exhibited minor differences in crystal size. Figure 5(a)–(d) shows SEM micrographs of samples 3, 7, 4 and 8. These samples were electroplated at a current density of 180 A m^{-2} . The observed differences in preferred crystal growth planes, crystal size and crystal morphology can be attributed to differences in temperature and electrolyte copper concentrations.

The desired morphology of an electrodeposited deposit is one that is ordered, with uniformly sized crystals. Figure 4(a) and (c) have similar crystal deposits. Figure 5(b) and (d) exhibit similar crystal deposits. Samples 3 and 4 have crystals measuring about $30 \mu\text{m}$ in length. Samples 7 and 8 have crystals measuring approximately $60 \mu\text{m}$ in length. These results indicate that temperature had little effect on crystal size and morphology. A comparison of Figure 5(a) with (b) and Figure 5(c) with (d) shows a difference in crystal size when the samples are compared on the basis of electrolyte copper concentration ($30 \mu\text{m}$ versus $60 \mu\text{m}$). Higher levels of copper in the electrolyte produced larger electrodeposited crystals.

A comparison of electrodeposited copper on the basis of current density indicates that a higher current density resulted in larger copper crystal deposits. Comparing Figure 6(a) with (b) supports this conclusion. Figure 6(a)

shows copper crystals that are larger, approximately $100 \mu\text{m}$ in length, than the deposits in Figure 6(b), which are about $60 \mu\text{m}$ in length. Samples 5 and 7 had the greatest degree of ordered crystal deposits. Figure 6(c) and (d) show this well-defined cubic structure polarized along the (2 2 0) plane. However, these samples were not electroplated with the highest current efficiencies.

4. Conclusions

Copper electroplating parameters greatly influence the current efficiency and the cathode quality. The effects of current density, copper concentration, and temperature on current efficiency and copper deposit quality were examined using a pure electrolyte. A factorial experimental design was employed to determine a relationship between the current efficiency and current density, electrolyte copper concentration, and temperature. Furthermore, the electrodeposited samples were analysed by XRD and SEM.

The following conclusions were drawn from this study:

- (i) Factorial experimental design can be used to produce a linear relationship between current efficiency and current density, copper concentration, temperature and their interactions.

- (ii) The independent variables and their two and three-way interactions were statistically independently significant and significant within the relationship.
- (iii) The determined linear relationship can be used to predict current efficiency within the bounds of the independent variables used to determine the relationship.
- (iv) Current efficiency cannot be used as the sole predictor of copper cathode quality.
- (v) The production of electrowon copper must take into account current efficiency and the cathode quality. Therefore, other measures such as cathode deposit morphology and crystal structure are required.
- (vi) The results of this study and the conclusions drawn are based upon experimental work using pure electrolyte. Similar analyses will be performed using an industrial electrolyte.

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