

Assessment of activated polyacrylamide and guar as organic additives in copper electrodeposition

C.P. Fabian^{a,b,*}, M.J. Ridd^b, M.E. Sheehan^a

^a Department of Chemical Engineering, School of Engineering, James Cook University, Townsville, QLD., 4811 Australia

^b Department of Chemistry, School of Pharmacy and Molecular Sciences, James Cook University, Townsville, QLD., 4811 Australia

Received 3 August 2006; received in revised form 7 November 2006; accepted 8 November 2006

Available online 19 December 2006

Abstract

The effect of current density, temperature, diffusion layer thickness (δ), deposition time, Guarfloc66 (Guar) and activated polyacrylamide (APAM) on the topography (surface roughness) of electrodeposited copper was studied. The level of these variables approximates current commercial copper electrowinning (EW) and electrorefining (ER) operating conditions. The effect of Guar and APAM on surface roughness and number of Peaks-per-Centimeter was assessed both in combination and alone using a rotating cylinder electrode (RCE) for up to 6-hour EW time. Observed effects on surface roughness indicate that a more uniform surface and lower roughness/smooth copper deposits were obtained using the additive APAM rather than Guar. Regression models indicate APAM has a significant effect on reducing surface roughness at 65 °C.

Bench-scale *continuous* electrowinning tests were carried out at 50 °C for 44.6 h using parallel plate electrodes into which APAM and Guar were dosed continuously and independently. These tests also indicated that APAM produces smoother deposits than Guar. The cross sections of the copper deposits from these tests showed that APAM exhibits a *slightly columnar* copper deposit and Guar produced a *porous* copper deposit. The copper deposit produced with additive APAM was brighter and produced greater amounts of both smaller and larger crystallite sizes than those obtained with Guar. This infers that APAM favours higher nucleation rates and greater 3D crystallite growth and coalescence than Guar.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Copper; Electrodeposition; Electrowinning; Electrorefining; Polyacrylamide; Rotating cylinder electrode; Guar; Surface roughness; Statistical analysis

1. Introduction

In the copper deposition industry in general, organic additives and chloride ions need to be dosed to produce smooth deposits, free of voids or porosity. It is also

known that organic additives significantly influence the current–potential relationship due to their competition for surface coverage with the components of the electrolyte system including chloride ions. Therefore these organic additives must be carefully selected according to their role at the metal/electrolyte interface to control the nucleation and growth during the deposition process. Table 1 summarizes the industry-standard additives used in copper EW, ER and in the damascene process for micro-electronics industry. Table 1 shows the typical concentration of these organic additives in

* Corresponding author. Department of Chemical Engineering, School of Engineering, James Cook University, Townsville, QLD., 4811 Australia. Tel.: +61 2 9717 7067; fax: +61 2 9543 7179.

E-mail addresses: cfabian2@bigpond.net.au, ces.fabian@ansto.gov.au (C.P. Fabian).

the electrolyte bath and their respective roles. An electrode is polarized when, under constant experimental conditions, the potential in the presence of an additive, e.g., animal glue, PEG, is more negative than the potential without the additive. An electrode is depolarized when the potential in the presence of an additive, e.g., chloride ions, is less negative. The polarizer/inhibitor/leveller controls the vertical growth to produce smooth deposits by conferring preferential adsorption on the peaks or active sites. The grain refiner/accelerator may predominantly control the nucleation process or promote the formation of new nuclei to possibly form new crystallites at the recesses (Vereecken et al., 2005). This synergistic process between the inhibitor and grain refiner is aimed at improving the overall quality of the copper deposit: purity, smoothness and plant productivity i.e., elimination/reduction of short-circuits caused by dendrites.

The first step of metal deposition is the formation of nuclei of the depositing metal on a foreign substrate and on a substrate of the same metal. The structure of the first monolayer(s), has an impact on the deposition of further layers and therefore on the morphology of the deposited metal. The competition between nucleation and growth determines the smoothness of the deposit: the higher the nucleation rate; the finer the crystal size (Budevski et al., 1996). Moreover, the forms of the growing crystals determine their physical appearance and structure. A higher crystal size growth rate, normal to the substrate, leads to a more fibrous/columnar structure. A brightening effect can be achieved when large developed crystal faces grow parallel to the substrate (Budevski et al., 1996).

It has been shown elsewhere (Fabian, 2005; Fabian et al., 2006b) that a rotating cylinder electrode (RCE) may be applied as a novel method of determining the effect of the preparation media of polyacrylamide (PAM) on the surface roughness of electrodeposited copper. It has been shown that when a high molecular weight PAM (MW 15 million Dalton) is prepared in 16-fold diluted copper electrolyte at 50 °C for 2 h and dosed into an EW cell, the electrodeposited copper had a significantly lower

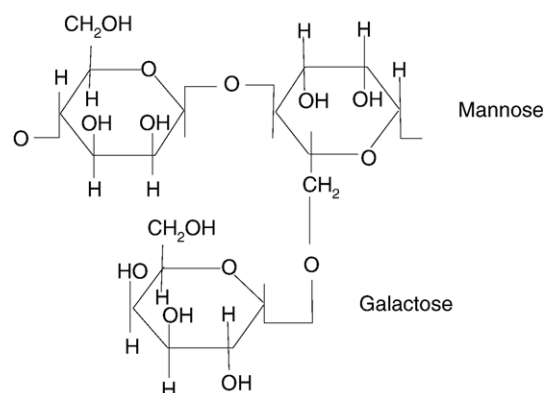


Fig. 1. The chemical structure of Guar based on Mark et al. (1969).

mean surface roughness than was the case when polyacrylamide was prepared in water or full-strength electrolyte or alkaline solution. The hydrolysis of PAM in pH 2 solutions is reported to produce a block copolymer (Halverson et al., 1985; Panzer and Halverson, 1988; Panzer et al., 1984). The PAM hydrolysed in 16-fold diluted copper electrolyte (pH 1.5) was named ‘activated polyacrylamide’ (APAM). It has been also shown that APAM also produced deposits exhibiting a lower surface roughness than polyacrylic acid (Fabian, 2005).

Guar is a naturally occurring galacto-mannan polymer, a polysaccharide, used as flocculant and coagulant with typical molecular weights ranging from 200,000 to 500,000 Da. Guar is a linear D-mannose sugar with a D-galactose sugar chain on every other mannose as shown below, Fig. 1 (Mark et al., 1969). Guar is the industry-standard organic additive used in copper EW as a weak levelling agent for about 40 years to produce bright copper deposits (Langner et al., 1989; Stantke, 1999).

Pye and Schurz (1957) patented the electrowinning of zinc and copper in the presence of polyacrylamide. They reported that acrylamide polymer can be dissolved in water or electrolyte. Vereecken and Winand (1976) compared the influence of non-ionic and cationic

Table 1
Industry-standard additives used in copper electrometallurgy

Role of the additive	Electrorefining		Electrowinning		Micro-electronics, PCB and IC	
	Additive	mg/L	Additive	mg/L	Additive	mg/L
Leveller	Glue	1	Nil	Nil	PEG* and JGB	100–300 and 1
Brightener**			Guar	0.25–5		
Grain refiner***	Thiourea	2	Nil	Nil	SPS/MPSA	1/1
Depolarizer	Cl [−]	50–60	Cl [−]	20–25	Cl [−]	40–60

*PEG, polyethylene glycol; SPS, bis(3-sulfo-propyl) disulfide; JGB, Janus Green B (safranin dye); MPSA, 3-mercapto-1-propanesulfinate. **Guar is also known as weak polarizer in the industry. ***Grain refiner or accelerator.

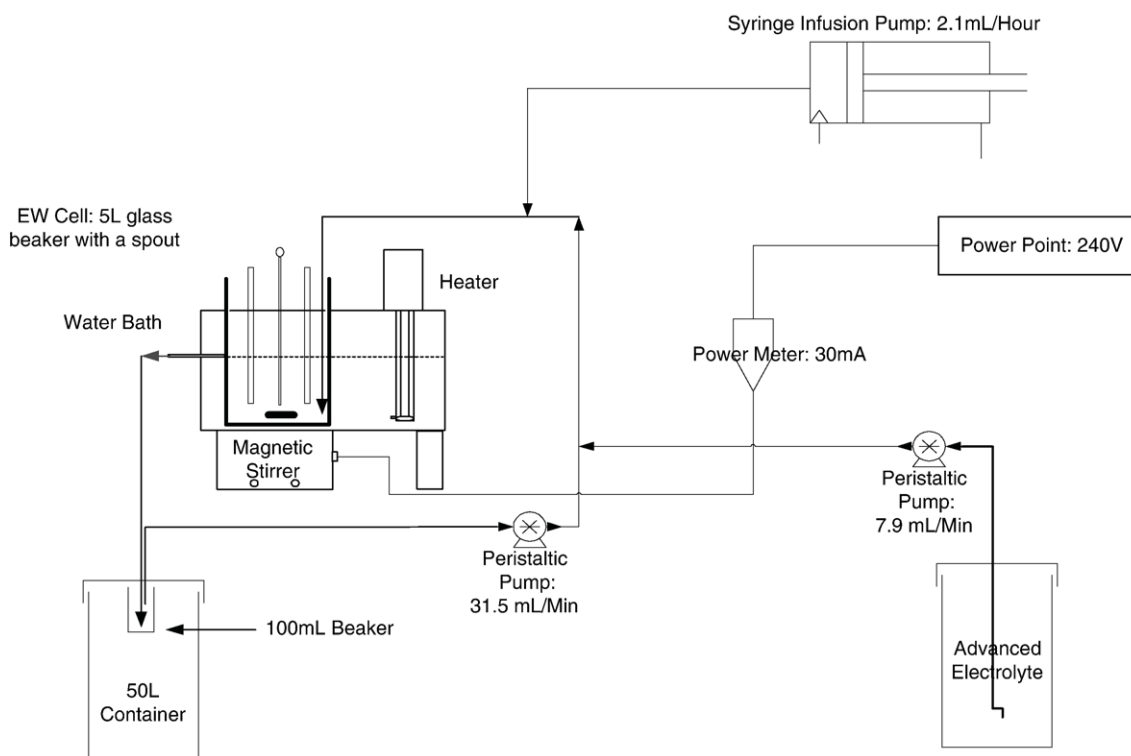


Fig. 3. Bench scale process.

convection and decrease the diffusion layer thickness, δ . In the experimental work described in this publication, the following studies were conducted to evaluate APAM against the industry standard Guar. (i) A fractional factorial experimental design was devised to evaluate whether APAM or Guar act independently or perform the same role. (ii) As APAM and Guar were found to have different roles, APAM and Guar were directly and separately compared in a Guar or APAM 2^2 experimental design at 6-hour EW time. (iii) As these tests indicated that APAM produces smoother copper deposits than Guar, APAM and Guar were further compared in *continuous* bench scale tests using parallel plate electrodes and commercial copper EW conditions.

2. Experimental

The testwork described below was designed to evaluate the effectiveness of APAM and Guar to control dendrite formation using the rotating cylinder electrode (RCE) and parallel plate electrodes (PPE) described by Fabian (2005) and Fabian et al. (2006b). The construction and characterization of the RCE is described

elsewhere (Fabian, 2005; Fabian et al., 2006b). The RCE was used to conduct experimental design testwork at batch scale.

The electrolyte was prepared using AR grade copper sulfate and sulfuric acid and its composition throughout the testwork was as follows: Cu^{2+} = 36 g/L, H_2SO_4 = 160 g/L and chloride ions = 25 mg/L. 15 million Dalton polyacrylamide, Magnafloc® 800 HP, CIBA was prepared in 16-fold diluted electrolyte at 50 °C for 2 h under stirring conditions (Fabian et al., 2006b). Guarfloc®66 (Guar) from Cognis Corporation Mining Chemicals was prepared in water at 25 °C. The Guar concentration in the EW system used at the Mt. Gordon Operation in Australia was approximately 0.52 mg/L electrolyte or 175 g Guar/tonne copper cathode. This concentration was used as the low level factor in the experimental design and the high level was set at 1.0 mg/L electrolyte.

2.1. Experimental using an RCE

Table 2 shows two 2^{5-2} fractional factorial experimental designs. The factors at low level are common for both designs. The factors at high level differ in temperature only. The values of the diffusion layer

thickness, δ were derived using the equation developed by Arvia and Carrozza (1962) and Fick (Newman and Thomas-Alyea, 2004), respectively, using Mathcad 12 (MathSoft Engineering and Education, 2004) and Fluent® as described in Fabian et al. (2006a). The low and high temperature levels of 45 °C and 65 °C were chosen to evaluate the behaviour of APAM at electrolyte temperatures similar to commercial copper EW and ER conditions, respectively. The organic additives, once dosed to the electrolyte, were subjected to 15 min mixing at 40 rpm and 5 min at 10 or 25 rpm before the application of the desired current to the electrolytic cell. Therefore the total residence time of the organic additives in the electrolyte was 20 min in addition to the EW times at 45 °C, 50 °C or 65 °C $\pm$ 0.5 °C.

The surface roughness was measured using a Mahr Perthometer M1 (Mahr, 2002) as described elsewhere (Fabian, 2005; Fabian et al., 2006b, Ilgar and O'Keefe, 1997). The surface roughness evaluation includes analysis of variance (ANOVA) and statistical inference procedures using Design-Expert® software (Stat-Ease, 2003; Fabian, 2005; Fabian et al., 2006b, Ilgar and O'Keefe, 1997; Barkey et al., 1989). The adequacy of the models was checked using residual analysis as described by Montgomery (2001) and Stat-Ease (2003).

The cross-section of the copper deposits was prepared for SEM examination. The samples were embedded in an epoxy resin and the cross-section cut with 600 grit silicon carbide powder. It was then sequentially polished with 3, 1 and 0.25 μ m diamond paste. It was finally etched with a solution of 5 g of ferric chloride and 5 mL hydrochloric acid in 90 mL ethanol for 20–25 s. XRD data were collected from the copper deposits produced using a Siemens/Bruker General Area Detector Diffraction Solution, GADDS diffractometer and interpreted using the Scherrer equation (Fabian et al., 2003; Mathe et al., 2005).

Guar was dosed *twice* and APAM was dosed *once* during this testwork unless otherwise stated. The first dose was added at the beginning and the second at approximately half EW time depending on the current density. The total electrowinning time was 4 h 21 min at a current density of 320 A/m² and 4 h 58 min at 280 A/m². The number of Coulombs applied was 500 C/cm².

2.2. Experimental using parallel plate electrodes

The comparison between Guar and APAM was also carried out using parallel plate electrodes at current-industry standard copper electrowinning operating conditions — except for current density which was

increased to 340 A/m² from the industry standard of 280–300 A/m². (Robinson et al., 2003). Simultaneously, Guar and APAM concentrations were also increased from about 175 g/tonne copper cathode or 0.25–0.50 mg/L in the electrolyte (as was dosed at Mt. Gordon) to 200 g/tonne or 0.68 mg/L.

A 316L 2B finish stainless steel cathode with a surface roughness of $0.25 \pm 0.05 \mu$ m and a lead–alloy anode procured from Mt. Gordon Operations were cut to prepare the electrodes for this testwork. Current industry-standard ABS edge strips were inserted on the stainless steel and the corners were joined at 45° with Araldite K138 and hardener K138 Part B — an acid resistant and thermally stable epoxy resin. The stainless steel substrates were thoroughly washed with acetone and water, soaked in an electrolyte solution for 24 h and washed again with distilled water. The distance between the electrodes was 40 mm, which is similar to the industry standard in copper EW. Fig. 2 shows the EW cell design in detail and Fig. 3 shows the overall bench scale design.

Table 3 shows the details of the operating conditions for the bench scale experiments. The net electrolyte volume in the EW cell was 3.9 L (without electrodes) and the flow rates of the re-circulating and advanced electrolyte were maintained constant at 31.5 and 7.9 mL/min, respectively. Eighty percent of the total electrolyte flow rate was re-circulated to the EW cell using a Watson Marlow 505S peristaltic pump to simulate the commercial operation at Mt. Gordon. This recirculation maintains the activity of Guar or APAM constant in the EW cell and also possibly

Table 3
Bench scale experimental conditions

Current density, A/m ²	340
Voltage drop, V	2.15
EW time, h	44.6
Deposition area (85.5 × 103.5 mm), cm ²	88.5
Average copper concentration, g/L	35 ± 1
Sulfuric acid concentration, g/L	160
Chloride ions concentration mg/L	25
Electrolyte net volume, L	3.9
Electrolyte temperature, °C	50.5 ± 0.5
Guar or APAM, g/tonne copper cathode	200
Guar or APAM concentration in electrolyte, mg/L	0.68
Advanced electrolyte, mL/min	31.5
Recirculating electrolyte, mL/min	7.9
Syringe pump-dosing Guar or APAM, mL/h	2.1
Power to stir solution, (30 mA), Watts	7–8
Copper concentration in advanced electrolyte, g/L	50
Sulfuric concentration in advanced electrolyte, g/L	142
Chloride concentration in advanced electrolyte, mg/L	30

controls their ageing processes. The organic additives were dosed constantly at 2.1 mL/h using a syringe infusion pump. The concentration of the organic additive in the aliquot was 0.68 mg/mL. The electrolyte in the EW cell was stirred with minimum agitation using a magnetic stirrer to improve the diffusion of the organic additive. The electrolyte temperature was kept at 50.5 ± 0.5 °C in a water bath.

3. Results and discussion

3.1. 2^{5-2} Experimental design results at 45 °C–55 °C

Table 4 presents the results indicating the effect of temperature (*A*), current density (*B*), Guar concentration (*C*), APAM concentration (*D*) and diffusion layer thickness (*E*) on surface roughness. The regression model obtained from this testwork is shown in Eq. (1). An *F*-value of 9.41 implies that the model is significant. There is only a 0.01% chance that the model *F*-value this large could occur due to noise. If the “Prob>*F*-value” (α) is very small (less than 0.05), then the terms in the model have a significant effect on the response (Montgomery, 2001; Stat-Ease, 2003).

$$\begin{aligned} \text{Surface Roughness}(\mu\text{m}) = & +6.26 + 0.05*A + 0.27*B \\ & -0.053*C - 0.056*D \\ & + 0.25*E - 0.62*B*C \\ & - 0.38*B*E \end{aligned} \quad (1)$$

It can be seen that the surface roughness is strongly influenced by the current density *B*, ($\alpha=0.0180$) and diffusion layer thickness *E*, ($\alpha=0.0247$) as depicted in

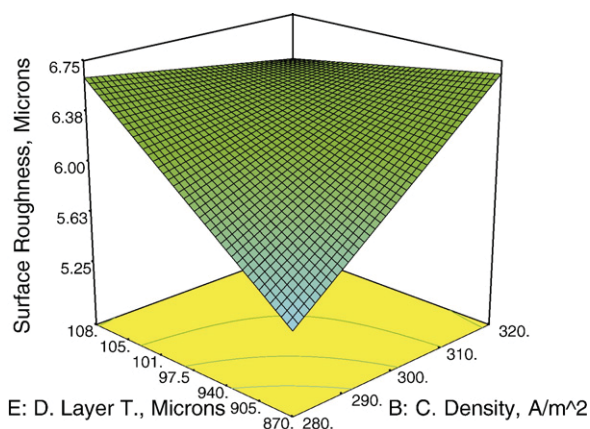


Fig. 4. The significant effect of diffusion layer thickness (*E*) and current density (*B*) on surface roughness in the temperature range of 45 °C–55 °C. The other variables are fixed at their centre point: *A*: temperature, 50 °C; Guar, 0.75 mg/L and *D*: APAM, 0.75 mg/L.

Fig. 4. Fig. 4 clearly indicates that at high rotational speed of the cylinder and low current density the smoothest surface roughness is achieved. In addition, it is also evident that the terms involving *B***C* (current density*Guar, $\alpha<0.0001$), depicted in Fig. 5, significantly affect surface roughness. It can be seen that increasing the Guar concentration increases surface roughness at current densities lower than about 300 A/m², a surprising result for an organic additive dosed to control dendrite formation. Moreover, it indicates that the surface roughness increases more steeply with an increase in the current density than with an increase in Guar concentration.

The effect of APAM was insignificant in this temperature range possibly due to the kinetics of its ageing in the electrolyte. The rationale for this conclusion is as follows. Cyclic voltammetry results

Table 4
 2^{5-2} Fractional factorial experimental results—temperature levels 45 °C–55 °C

Run	<i>A</i> Temperature	<i>B</i> Current density	<i>C</i> Guar	<i>D=A*B#</i> APAM	<i>E=A*C#</i> Diffusion layer thickness	Mean surface roughness	S.D.
Standard	°C	mA/cm ²	mg/L	mg/L	μm	Ra, μm	
1	45	28	0.50	1.00	108	5.95	0.47
2	55	28	0.50	0.50	87	4.90	0.42
3	45	32	0.50	0.50	108	7.08	1.38
4	55	32	0.50	1.00	87	7.33	1.09
5	45	28	1.00	1.00	87	5.83	0.72
6	55	28	1.00	0.50	108	7.31	1.08
7	45	32	1.00	0.50	87	5.99	0.66
8	55	32	1.00	1.00	108	5.71	0.68
CP	50	30	0.75	0.75	97.50	7.04	0.93

#Level of factors *D* and *E* were determined by the levels of *A***B* and *A***C*, respectively.

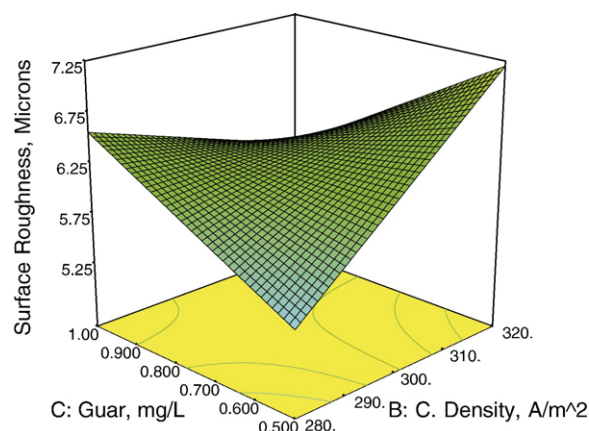


Fig. 5. The significant effect of current density (B) and Guar (C) on surface roughness in the temperature range of 45 °C–55 °C. The other variables are fixed at their centre point: A : temperature, 50 °C; D : APAM, 0.75 mg/L and E : diffusion layer thickness, 97.5 μm .

(Fabian, 2005) indicate that at 45 °C, a maximum polarization of APAM was obtained at about 3-hour residence time in the electrolyte whilst at 65 °C it was obtained at about 1-hour residence time. It is therefore inferred that the first 3 h of the EW tests at 45 °C–55 °C took place under sub-optimal adsorption/polarization conditions of APAM.

3.2. 2^{5-2} Experimental design results at 45 °C–65 °C

Table 5 presents the results indicating the effect of temperature (A), current density (B), Guar concentration (C), APAM concentration (D) and diffusion layer thickness (E) on surface roughness. The EW tests at this temperature range were also carried out for 4.35 and 4.97 h (14,000 C) as in the previous testwork. The model obtained from this testwork is shown in Eq. (2). An

F -value of 2.06 implies that the model is significant and that there is a 6.3% chance that the model F -value this large could occur due to noise.

$$\begin{aligned} \text{Surface Roughness}(\mu\text{m}) = & +6.16 - 0.051*A - 0.089*B \\ & - 0.075*C - 0.41*D \\ & + 0.23*E - 0.17*B*C \end{aligned} \quad (2)$$

It can be seen from this model that APAM (D , $\alpha=0.0041$) has the most significant effect on reducing surface roughness. Diffusion layer thickness (E , $\alpha=0.1004$) has the next largest effect and an increase in E increases surface roughness as expected (Ilgar and O'Keefe, 1997). The aliased effect of current density (B) and Guar (C) are insignificant ($B*C$, $\alpha=0.2185$). Current density B ($\alpha=0.5192$), Guar C , ($\alpha=0.5855$) and temperature A , ($\alpha=0.7129$) are also insignificant. The regression analysis (Montgomery, 2001) indicates again that APAM and Guar are also not aliased and therefore confirms that APAM acts independently of Guar to reduce surface roughness. Therefore the effect of Guar and APAM on surface roughness was investigated separately, as described in the following Sections.

3.3. Effect of Guar or APAM over 6-hour EW at 50 °C

This test was conducted to continue evaluating the effectiveness of Guar or APAM, either alone or in combination, on surface roughness and on the number of Peaks-per Centimetre (PPC) over 6 h of EW. PPC is defined as the number of roughness profile elements per centimetre which consecutively intersect at a specified upper profile section level and a lower profile section (Mahr, 2002). A surface profile can have the

Table 5
 2^{5-2} Fractional factorial experimental results—temperature levels 45 °C–65 °C

Run	A Temperature °C	B Current density mA/cm ²	C Guar mg/L	$D=A*B$ PAM mg/L	$E=A*C$ Diffusion layer thickness μm	Mean surface roughness Ra, μm	S.D.
1	45	28	0.50	1.00	110	5.95	0.47
2	65	28	0.50	0.50	87	6.36	0.64
3	45	32	0.50	0.50	110	7.08	1.38
4	65	32	0.50	1.00	87	5.56	0.67
5	45	28	1.00	1.00	87	5.83	0.72
6	65	28	1.00	0.50	110	6.86	2.28
7	45	32	1.00	0.50	87	5.99	0.66
8	65	32	1.00	1.00	110	5.66	0.69

Table 6
6-hour EW time at 50 °C: Guar-or-APAM

Run	Factors, mg/L		Surface roughness, μm		No. PPC		Dendrites
	$B = \text{APAM}$	$A = \text{Guar}$	Mean	S.D.	Mean	S.D.	Small needles
1	0	0	7.68	2.16	65.13	13.95	Numerous
2	0	1	6.48	0.70	87.63	8.35	Numerous nascent
3	1	0	6.42	0.27	82.75	8.24	None
4	1	1	6.71	0.36	83.38	7.46	None

same surface roughness with a different number of PPC. Guar was dosed twice and APAM once. The electrolyte temperature, current density and δ were 50 °C, 300 A/m² and 109 μm (10 rpm), respectively. The experimental design and results are shown in Table 6. Eq. (3) shows the surface roughness model for this testwork where A is Guar concentration and B is APAM concentration.

$$\text{Surface Roughness}(\mu\text{m}) = 6.45 + 0.144*A - 0.627*B \quad (3)$$

The Model F -value of 2.58 for surface roughness implies the model shown in Eq. (3) is significant with a 9.37% chance that a “Model F -Value” this large could occur due to noise. APAM (B , $\alpha=0.0388$) has a significant effect on reducing surface roughness and Guar (A , $\alpha=0.623$) has an insignificant effect on increasing surface roughness as shown in Fig. 6.

The number of PPC reported in Table 6 was also analysed to confirm the surface roughness results described above. The model for the PPC is presented in

Eq. (4) and depicted in Fig. 7. The Model F -value of 8.85 for the number of PPC implies the model is significant with only a 0.11% chance that a “Model F -Value” this large could occur due to noise.

$$\begin{aligned} \text{Number of Peaks – per – Centimetre} = & 85.2 + 0.313*A \\ & + 8.81*B \end{aligned} \quad (4)$$

It is concluded from these results that APAM significantly reduced surface roughness and increased the number of PPC. In contrast, Guar increased the surface roughness and decreased the number of PPC similar to the copper deposit produced without additives. Table 6 shows results and visual observations from the testwork. It can be seen that qualitatively, the formation of dendrites is reduced in the presence of APAM.

3.4. Effect of Guar or APAM in continuous bench scale tests

Bench scale testwork was aimed at verifying the effectiveness of Guar and APAM in controlling dendrite growth in a continuous copper EW system using *parallel plate* electrodes. The surface roughness of the copper deposits was unable to be measured since it surpassed the specifications of the M1 Perthometer (10 nm–100 μm). Photographs of the electrowon copper deposits in the presence of Guar and APAM are shown in Figs. 8 and 9, respectively. It can be seen that the physical appearance of copper deposit obtained with Guar was rougher than that obtained with APAM. Both sides of the deposit produced with Guar have a needle-like, granular appearance throughout the plate. In contrast, the deposit produced with APAM is smoother, brighter and more compact than the copper deposit produced with Guar. Moreover, the copper deposits obtained with Guar possess three areas where copper deposition has not taken place. This is described as “lacy” copper

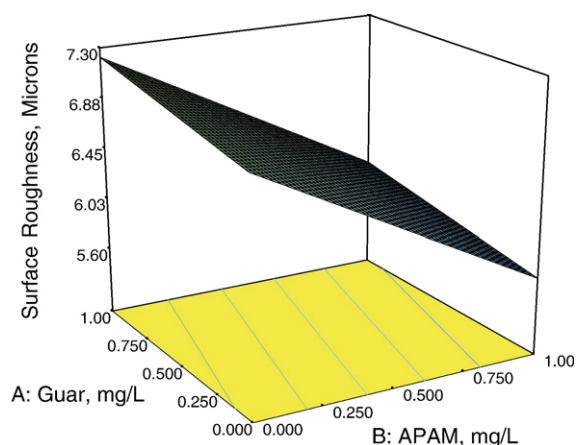


Fig. 6. The significant effect of APAM on surface roughness after 6-hour EW.

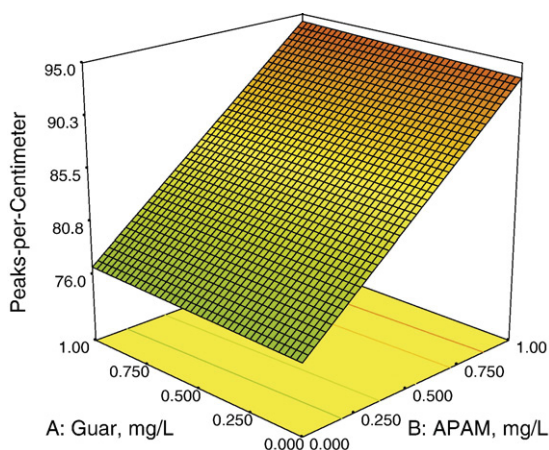


Fig. 7. The significant effect of APAM on Peaks-per-Centimetre after 6-hour EW.

deposit and was also reported by Sun and O’Keefe (1992) in the absence of additives. This kind of deposit is often found at commercial scale electro-winning operations but not at ER operations where animal glue and thiourea are used as organic additives. The brightening effect of the copper deposit in the presence of APAM was probably achieved through large crystal faces that are parallel to the substrate.

Figs. 10 and 11 are SEM micrographs of the cross-sectioned copper cathodes obtained from this testwork. It can be seen in Fig. 10 that the cross section of the copper cathode obtained with APAM exhibits colum-

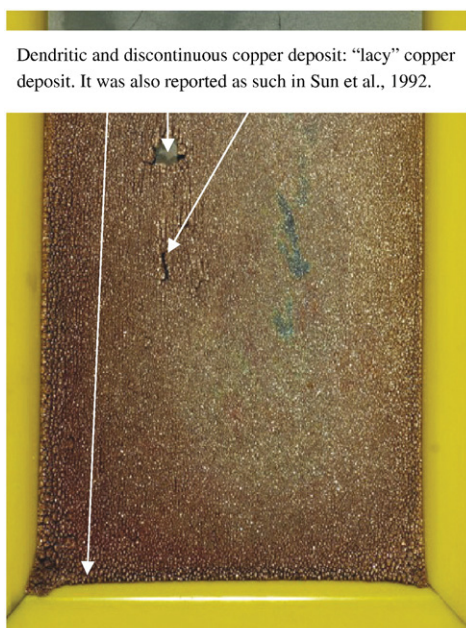


Fig. 8. Copper deposit obtained with Guar at 340 A/m² and 44 h and 35 min.



Fig. 9. Copper deposit obtained with APAM at 340 A/m² and 44 h and 35 min.

nar growth. It has been reported that this type of growth may be improved into an equiaxial microstructure by adding a sulfur bearing organic additive into the electrolyte bath (Plieth, 1992). In contrast, in the presence of Guar, the microstructure of the copper deposit is porous (Fig. 11).

Crystallite size was also determined using an XRD technique, General Area Diffraction Detector Solution (GADDS), according to the technique described elsewhere (Fabian et al., 2003). The crystallite size was determined to assess whether the presence of APAM or Guar results in higher nucleation rates during EW under otherwise constant conditions. These tests may also be important to determine coalescence of small crystallite sizes to form larger crystal sizes according to the mechanism of 3D crystallite size growth.

Table 7 shows the Kruskal–Wallis test results for APAM and Guar crystallite size obtained from the bench scale testwork using parallel plate electrode. The median crystallite size with APAM (405 Å) is slightly smaller than with Guar (427 Å). Therefore APAM appears to favour a higher nucleation rate than Guar. The other important results are the 41% crystallite size greater than 1800 Å: for APAM and 24% for Guar. The inferred crystallite size decreases as the full width at half-maximum (FWHM) of the copper deposit sample increases (Klug and Alexander, 1974). If the FWHM of

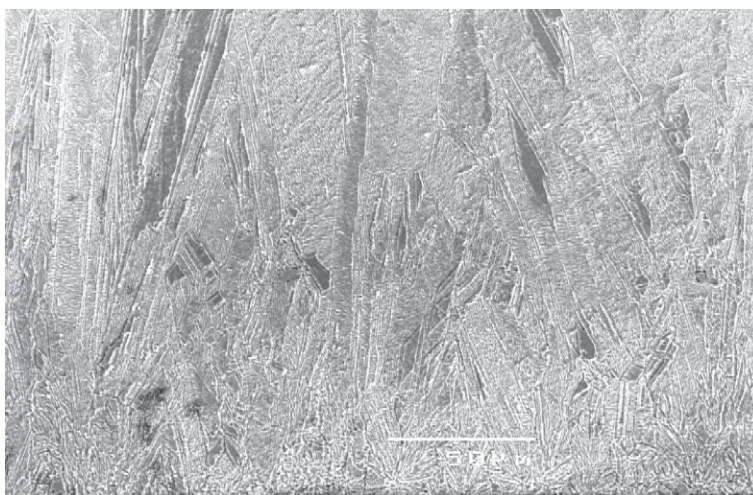


Fig. 10. SEM micrographs of copper deposit obtained using 0.68 mg/L APAM (200 g/tonne Copper Cathode) at 340 A/m² current density. Note the slightly fibrous or columnar structure.

the sample is smaller than that of the LaB₆ standard, the crystallite size is not processed and is reported as greater than 1800 Å. These calculations therefore appear to indicate that nucleation rates, 3D crystallite growth, and coalescence is higher with APAM than with Guar.

Bench-scale continuous electrowinning tests using parallel plate electrodes where APAM and Guar were dosed continuously and independently also indicated that APAM produces smoother deposits than Guar. The overall results suggest that APAM is more specifically adsorbed than Guar at the metal electrode/electrolyte

interface where high electrical fields are convergent. This behaviour can therefore inhibit the formation of protrusions/dendrites. The covalent bonding that polyacrylamide block polymer confers at the metal/electrolyte interface (Halverson et al., 1985; Panzer and Halverson, 1988; Panzer et al., 1984) probably plays an important role for APAM to be more specifically adsorbed than Guar.

The adsorption properties for Guar were not found in the literature. The difference on inhibition (polarization) and adsorption produced by Guar and APAM has been studied by us using Cyclic Voltammetry and

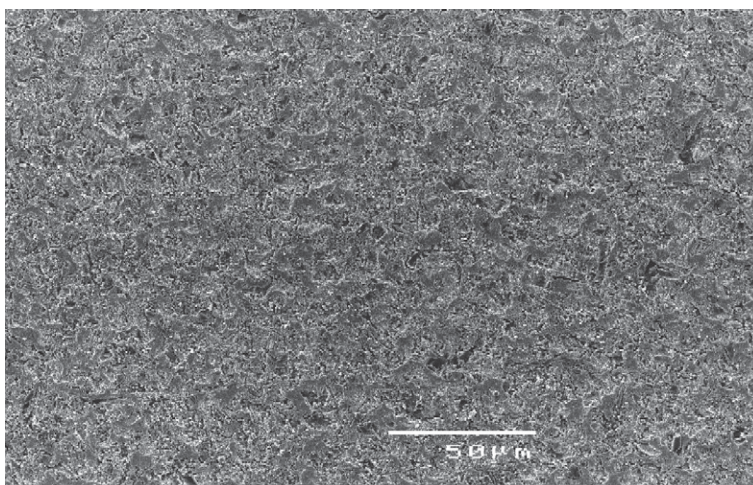


Fig. 11. SEM micrographs of copper deposit obtained using 0.68 mg/L Guar (200 g/tonne Copper Cathode) at 340 A/m² current density. Note a porous copper cathode.

Table 7
Kruskal–Wallis test results for APAM and Guar crystallite size

Test no.	APAM	Guar
Electrowinning Time, h	44.60	44.60
FWHM number of readings, N	338	440
Crystallite size data processed, N	198	335
Crystallites size >1800 Å, %	41	24
Kruskal–Wallis crystallite size mean rank	220	295
Asymptotic significance	0.000	
Median crystallite size, Å	405	427

Electrochemical Impedance Spectroscopy (Fabian, 2005) and will be discussed in subsequent papers.

4. Conclusions

It was found that when 14,000 C were applied in the fractional factorial experimental design that the effect of APAM was significant in reducing surface roughness at 65 °C but insignificant at 45 °C. This difference is attributed to stronger adsorption and enhanced polarization of APAM at 65 °C. The regression models from this experimental design indicated that APAM and Guar are not aliased and that APAM acts truly independently of Guar. It was also found that current density and Guar were aliased but decreases in significance with increasing temperature consistent with the faster degradation of Guar. Therefore, the role of Guar and APAM was concluded to be independent. In the 6-hour EW tests, APAM significantly reduced surface roughness and increased the number of Peaks-per-Centimetre.

Bench-scale continuous electrowinning tests where APAM and Guar were dosed continuously and independently indicated that APAM produces smoother deposits than Guar. SEM examination of cross sections of the copper deposits showed that Guar produced porous deposits and APAM produced slightly columnar deposits. Furthermore, the copper deposit with APAM is brighter and has greater amounts of both smaller and larger crystallite sizes than those with Guar. We infer that presence of APAM favours higher nucleation rates and greater 3D crystallite growth and coalescence than Guar and that APAM can produce purer copper deposits since voids and porosity can be reduced by smaller crystallites.

The overall results of this work indicate that APAM produces smoother, brighter and more compact copper electrodeposits than Guar. Therefore APAM can be viewed as a potential new levelling and brightening agent for copper electrometallurgy.

Acknowledgments

We wish to thank Mount Gordon Operations of Western Metals Copper Ltd. and to the Australian Research Council for funding this study.

References

- Arvia, A.J., Carrozza, J.S.W., 1962. Mass transfer in the electrolysis of $\text{CuSO}_4\text{--H}_2\text{SO}_4$ in aqueous solutions under limiting current and forced convection employing a cylindrical cell with rotating electrodes. *Electrochimica Acta* 7, 65–78.
- Barkey, D., Muller, R., Tobias, C., 1989. Roughness development in metal electrodeposition I. Experimental results. *Journal of the Electrochemical Society* 138 (8), 2199–2207.
- Budevski, E., Staikov, G., Lorenz, W., 1996. *Electrochemical Phase Formation and Growth — an Introduction to the Initial Stages of Metal Deposition*. VCH, New York.
- Fabian, C., 2005. Copper electrodeposition in the presence of guar or activated polyacrylamide. PhD Thesis, James Cook University, Australia.
- Fabian, C., Ridd, M., Ness, S., Lancaster, T., Griffin, G., 2003. Determination of crystallite size and surface roughness of copper deposits for electrowinning in the presence of an organic additive. In: Young, C.A., Anderson, C.G., Dreisinger, D.B., Harris, B., James, A. (Eds.), *Hydrometallurgy. The Minerals Metals and Materials Society (TMS), Warrendale*, pp. 1233–1245.
- Fabian, C., Mandin, P., Ridd, M.J., Sheehan, M., 2006a. Hydrodynamic modelling of copper electrodeposition at a vertical rotating cylinder electrode. In: Woods, R., Doyle, F.M., Kelsall, G.H. (Eds.), *Electrochemistry in Mineral and Metal Processing VII. The Electrochemical Society Inc., Denver, CO*, pp. 303–315.
- Fabian, C., Ridd, M.J., Sheehan, M.E., 2006b. Rotating cylinder electrode study of the effect of activated polyacrylamide on surface roughness of electrodeposited copper. *Hydrometallurgy* 84 (3–4), 256–263.
- Halverson, F., Lancaster, J., O'Connor, M., 1985. Sequence distribution of carboxyl groups in hydrolyzed polyacrylamide. *Macromolecules* 18 (6), 1139–1144.
- Ilgar, E., O'Keefe, T., 1997. Surface roughening of electrowon copper in the presence of chloride ions. In: Dreisinger, D. (Ed.), *Aqueous Electrotechnologies: Progress in Theory and Practice. The Minerals Metals and Materials Society (TMS), Warrendale*, pp. 51–62.
- Klug, H., Alexander, L., 1974. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. John Wiley & Sons, Sydney.
- Langner, B.E., Stantke, P., Reinking, E.F., 1989. Method of Measuring the Effective Inhibitor Concentration During a Deposition Process of Metal from Aqueous Electrolytes and Test Apparatus Therefore. *Norddeutsche Affinerie Aktiengesellschaft, Hamburg, DE*, p. 11.
- Mahr, 2002. M1 Mahr Perthometer Operating Manual.
- Mark, H., Gaylord, N., Bikales, N., 1969. *Encyclopedia of Polymer Science and Technology*, vol. 11. Wiley-Interscience, New York, pp. 401–420.
- Mathe, M.K., Cox, S.M., Venkatasamy, V., Happek, U., Stickney, J.L., 2005. Formation of HgSe thin films using electrochemical atomic layer epitaxy. *Journal of the Electrochemical Society* 152 (11), C751–C755.
- MathSoft Engineering and Education, I, 2004. Mathcad.
- Montgomery, D.C., 2001. *Design and Analysis of Experiments*. John Wiley & Sons.

- Newman, J., Thomas-Alyea, K.E., 2004. *Electrochemical Systems*. John Wiley & Sons, Inc., Hoboken, New Jersey.
- Panzer, H., Halverson, F., 1988. Blockiness in hydrolyzed polyacrylamide. In: Moudgil, B., Scheiner, B. (Eds.), *Flocculation Dewatering*, Proc. Eng. Found. Conf., Florida. Eng. Found., New York, N.Y., pp. 239–249.
- Panzer, H., Halverson, F., Lancaster, J., 1984. Carboxyl sequence distribution in hydrolyzed polyacrylamide. *Polymeric Materials Science and Engineering* 51, 268–271.
- Plieth, W., 1992. Additives in the electrocrystallization process. *Electrochimica Acta* 37 (12), 2115–2121.
- Pye, D., Schurz, G., 1957. Electrowinning of metals, U.S. Patent 2,798,040. The Dow Chemical Company.
- Robinson, T., Davenport, W.G., Quinn, J., Karkas, G., 2003. Electrolytic copper refining — 2003 world tankhouse operating data. In: Dutrizac, J.E., Clement, C.G. (Eds.), *Proc. Copper 2003–Cobre 2003*, Santiago, Chile. Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 3–66.
- Stantke, P., 1999. Guar concentration measurement with the Collamat system. In: Dutrizac, J., Ji, J., Ramachandran, V. (Eds.), *Proc. Copper 99–Cobre 99*, vol. 3. Minerals, Metals and Materials Society, Warrendale, PA, pp. 643–651.
- Stat-Ease, S.M.E., 2003. *Design-Expert Software*. John Wiley & Sons, Inc.
- Sun, M., O’Keefe, T., 1992. The effect of additives on the nucleation and growth onto stainless steel cathodes. *Metallurgical Transactions. B, Process Metallurgy* 23B, 591–599.
- Vereecken, J., Winand, R., 1976. Influence of polyacrylamides on the quality of copper deposits from acidic copper sulphate solutions. *Surface Technology* 4, 227–235.
- Vereecken, P.M., Binstead, R.A., Deligianni, H., Andricacos, P.C., 2005. The chemistry of additives in damascene copper plating. *IBM Journal of Research and Development* 49 (1), 3–19.