USE OF POLYETHYLENE GLYCOL AS ORGANIC ADDITIVE IN COPPER ELECTRODEPOSITION OVER STAINLESS STEEL CATHODES.

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Abstract— This study comprise a comparative analysis of the effects of polyethylene glycol (PEG) and other additives used in copper electrodeposition processes over 316 L stainless steel permanent cathodes. Both cyclic voltammetry and potentiostatic pulse techniques showed analogous results with regard to the increase in the use of the real organic additive and the persistence of a more constant roughness level at higher electrodeposition times when PEG baths are used instead of baths containing glue. The mechanism taking place in the presence of PEG corresponds to two-dimensional nucleation together with three-dimensional diffusion grain growth. Furthermore, the contribution of the hydrogen evolution reaction (HER) was observed at t > 15 seconds when additives of PEG + thiourea were used, while the same contribution was observed from the beginning of the reaction in the case of solutions without PEG.

Keywords— Polyethylene glycol, copper electrowinning, organic additives, permanent cathodes.

I. INTRODUCTION

Several different additive formulations have been tested for use in industrial copper electrocrystallization processes, replacing copper mother cathodes with permanent stainless steel cathodes.

In this study, based on previously analyzed results by using this polymer on different substrates, such as silicon (Muñoz et al., 2006), polyethylene glycol (PEG) was chosen as an additive to improve the quality of the resulting electrodeposits. Various studies (Hill and Rogers, 1978; Healy et al., 1992; Stoychev and Tsvetanov, 1996; Stoychev, 1998) have reported the action of PEG on copper reduction and deposition; these studies prove that the chloride ion greatly influences the formation of bonds between the copper-polymer complex and the cathode surface and also that the polymer inhibits copper deposition in the absence of Cl (Bražinskiene et al., 2005; Tan et al., 2007).

When the PEG polymer chain is on the surface of the metal, the electron clouds present make the PEG adopt a structural form with its hydrophobic part oriented towards the liquid bulk, thus increasing the overpotential for the hydrogen evolution reaction (HER); this improves efficiency, and contributes to nucleation and growth processes. Furthermore, Kondo et al. (2003) observed that these high molecular weight molecules are usually adsorbed on the edges, thus controlling dendrite formation.

An optimization criterion for the different organic additives was defined for this comparative study. This criterion was related to the additive quantity used in the electrolytic bath that was determined using cyclic voltammetry (CV) and potentiostatic nucleation pulse (PP) techniques, both individually and with mixtures of the additives. Finally, the results were submitted to deposit morphology analysis using Atomic Force Microscopy (AFM).

II. MATERIALS AND METHODS

The electrolytic solutions were prepared using the following analytical grade reagents: H2SO4 (160 g l⁻¹) and CuSO4·5H2O (40 g l⁻¹ copper) (Aldrich), PEG (PEG 3000, Merck), thiourea (Fluka >99% purity) bone glue, and Avitone (Avitone-A, DuPont U.S.A).

The deposit tests were carried out using two different cell types:

- A Jar test cell: a three-electrode electrolytic cell (80 cm²) with controlled temperature inert gas injection (argon) and a working electrode area of 0.196 cm², which is used for electrochemical analysis.
- A bench scale cell: a 250 ml parallel plate cell with a 16 cm² electrode area; the current density applied was 300 Am⁻², this cell was used for AFM analysis.

In both cases and before each test, the steel cathodes underwent a polishing and cleaning process. All experiments were carried out in a thermostated mode (60°C), without stirring.

A Potentiostat/Galvanostat, (EG&G Princeton Applied Research 273-A) was used for the cyclic voltammetry and i/t transient measurements, with an Hg/HgSO4 reference electrode saturated with K2SO4 (ESHg) and a copper wire counter electrode.

Sodium Chloride was added in all tests to reproduce more realistic conditions for the processes. The AFM images and average porosities were obtained using a Digital Instrument Nanoscope IIIa series, used in tapping mode at a scan rate of 0.02 μm s⁻¹.

Calculations

An efficiency factor was defined (Eq. 1) for the evaluation of the optimal additive concentrations in a range of interest to industry. This factor (% Ef-CV) corresponds to the ratio between the oxidation charge (QA) and the...
total reduction charge ($Q_C$). Furthermore, the $Q_d$ was obtained from the integration of the voltammetric curve in the -0.4 and 0 V (vs ESHg) range; this value increases with the increments in additive concentration. The $Q_C$ was estimated from the combination of all the areas in the 1 to -0.4 V (vs ESHg) range and involves a constant value and another that decreases as the additive concentration increases.

$$\%E_f - CV = \frac{Q_d}{Q_C} \times 100$$ (1)

The nucleation and growth processes were studied through the analysis of the current-time transients, which were obtained using potentiostatic techniques that are well described in literature (Milchev and Heerman, 2003). This method consists of the application of a potential pulse to the cathode/electrolyte interface at a potential value where electrocrystallization occurs; the transient ($i$/$t$) is then monitored after the pulse.

The value of electrodeposition potential was chosen from the resulting voltammetric curves. This value is located between the -0.6 V and -0.7 V. As described by Palomar-Pardave et al. (2005), the contribution of the electrical double layer charge may be obtained from the total current. In these cases, the nucleation and growth mechanism is generally three-dimensional (3D) and controlled through diffusion (Palomar-Pardave et al., 2005; Hills et al., 1983; Scharifker, 1983). In addition, the current contribution associated to two-dimensional (2D) growth in terraces can also be distinguished.

The models that were evaluated for the description and calculation of these deposition currents consider hemispherical nucleation and growth under diffusion control (Del Valle et al., 2002). Therefore, the efficiency factor for this case was estimated using Eq. 2:

$$\%E_f (PP) = \frac{Q_{d}^{2D} + Q_{NP}^{2D}}{Q_T} \times 100$$ (2)

where

$$Q_T = \int_0^\infty i(t)dt = Q_d^{2D} + Q_{NP}^{2D} + Q_{HER}$$ (3)

$$Q_{d}^{2D} + Q_{NP}^{2D} = \int_0^\infty i_{d}^{2D}dt + \int_0^\infty i_{NP}^{2D}dt$$ (4)

$$Q_{HER} = \int_0^\infty i_{HER}$$ (5)

Equation 6 describes the $i$/$t$ transient and involves three main terms: the growth current associated with 3D diffusion, the 2D growth and the hydrogen evolution current (Hills et al., 1983, del Valle et al., 2002):

$$Q_{d}^{2D} + Q_{NP}^{2D} = \int_0^\infty i_{d}^{2D}dt + \int_0^\infty i_{NP}^{2D}dt + i(t)_{HER}$$ (6)

The first two terms on the right of Eq. 6 correspond to progressive nucleation (NP) and growth components (the instantaneous nucleation component in the total charge was negligible); the analytical expressions described in the literature (Thirk and Harrison, 1972) are as follows:

$$i(t)_{d}^{2D} = \frac{2\pi n F K c^2 \rho}{\rho_0^2 M^2} \left[ \exp \left( -\frac{\pi M^2 N_{d}^{2} K_{d}^{2}}{\rho^2} t^3 \right) \right]$$ (7)

$$i(t)_{NP}^{2D} = \frac{nF D C}{\pi^2 t} \left[ 1 - \exp \left( -\frac{D_{NP} C}{2} t^2 \right) \right]$$ (8)

where the value of $k$ is estimated as follows:

$$k = \frac{9}{3} \left( \frac{8\pi C^* M}{\rho} \right)^{1/2}$$ (9)

The third term in Eq. 6 was estimated using the expression described by Palomar-Pardave et al. (2005).

$$i(t)_{HER} = \frac{A}{1 - \exp \left( -B \frac{t}{\tau} \right)}$$ (10)

where

$$A = (n_{HER} F K_{HER} C^*) \left( \frac{2C^* M}{\pi D} \right)^{1/2}$$ (11)

$$B = \frac{N_{d} D}{\pi} \left( \frac{8\pi C^* M}{\rho} \right)^{1/2}$$ (12)

The images obtained via the AFM technique correspond to copper deposits on the stainless steel cathodes, which were obtained under the previously described operative conditions, using the optimum values for the estimated additive concentrations. A deposition potential of -0.63 V (vs ESHg) was selected from the voltammetry tests (only one value was used due to the comparative purpose of this study).

The root-mean-squared average roughness ($R_{rms}$) of a representative number of samples taken from the total area of deposited copper was calculated using expression 13:

$$R_{rms} = \left[ \frac{1}{n-1} \sum (Z_i - Z_{av})^2 \right]^{1/2}$$ (13)

A statistical procedure of taking a limited number of singular target points on the deposit was used to obtain a representative sample for the total deposit area.

III. RESULTS AND DISCUSSION

A. Cyclic Voltammetry

The voltammograms for the solutions containing copper with the different additives are shown in Figs. 1 to 4. The cathodic peaks move towards more negative potentials, a phenomenon which is related to an increase in the HER overpotential; on the other hand, the anodic peaks move towards more positive potentials, which shows that the deposited copper electro-dissolution needs more energy when organic additives are used.

The effect of thiourea is shown in Fig. 1. During the negative direction potential scan, with and without additives, a complex cathodic process is observed, which is characterized by one contribution when thiourea is present (current peak C1') or two contributions when thiourea is absent (current peaks C1 and C2). The C1 (-0.68 V) and C1' (-0.84 V) peaks are related to the copper reduction with and without thiourea. The HER contribution is represented by the C2 peak (-0.88 V).
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Fig. 1. First cycle of the CV with initial potential: open circuit; sense: from cathodic to anodic; scan rate: 50 mV s⁻¹; temperature: 60 °C; Electrolyte: 100 g l⁻¹ CuSO₄ + 160 g l⁻¹ H₂SO₄ in distilled water. Continuous curve: 5 mg l⁻¹ of Thiourea; Dotted curve: without additives. Insert graph: efficiency factor relative to additive concentration.

Fig. 2. First cycle of the CV with initial potential: open circuit; sense: from cathodic to anodic; scan rate: 50 mV s⁻¹; temperature: 60 °C; Electrolyte: 100 g l⁻¹ CuSO₄ + 160 g l⁻¹ H₂SO₄ in distilled water. Continuous curve: 35 mg l⁻¹ of Glue; Dotted curve: without additives. Insert graph: efficiency factor relative to additive concentration.

The differences between the copper electrodeposition without (A1) and with (A1') thiourea may be attributed to the charge associated to organic oxidation (Lukomska et al., 2001; Reents et al., 1998; Brown and Hope, 1996; Chia and Su, 1987; De Maere and Winand, 1995; Winand et al., 1982; Krzewska et al., 1984). The efficiency factor reaches an 81% maximum that corresponds to 5 mg l⁻¹ of thiourea (insert in Fig. 1). After this value a decrease in this factor is observed, as when the concentration is increased, the polymerization of this additive that blocks the areas for copper nucleation is favored.

The presence of glue (Fig. 2) causes a displacement of the cathode peak, from -0.68 V in the absence of the additive (contribution C1) to -0.85 V (contribution C1').

The insert in Fig. 2 shows a maximum of 65% that corresponds to a glue concentration of 30 mg l⁻¹. An increase past this level of concentration causes the additive to tend to be absorbed onto the electrode surface, thus blocking sites for copper deposition (Blechta et al., 1993; Saban et al., 1992).

The effect observed in the C1' peak was not evident for the Avitone additive (Fig. 3), where an optimum concentration of 40% was observed due to the low direct influence of this additive in electrocrystallisation processes. This fact has been discussed in the literature (Scholen and Ekler, 1953), where it has been stated that the main Avitone effect is to act as a flocculant for the anode slime. However, Avitone also has the ability to change the electrical double layer conditions, thus favoring the action of other additives.

No displacement was observed in the copper electrodeposition potential due to the presence of PEG (Figure 4). In fact, this cathodic process starts at the same potential (b1) in the presence and absence of the additive.

Similar tests to those shown in Figs. 1 to 4 were carried out for different additive mixtures, of which the mixture of 5 mg l⁻¹ of thiourea + 25 mg l⁻¹ of PEG showed the best efficiency factor (95%, figures not shown).

Fig. 3. First cycle of CV with initial potential: open circuit, sense: from cathodic to anodic; scan rate: 50 mV s⁻¹; temperature: 60 °C; Electrolyte: 100 g l⁻¹ CuSO₄ + 160 g l⁻¹ H₂SO₄ in distilled water. Continuous curve: 25 mg l⁻¹ of Avitone; Dotted curve: without additives. Insert graph: efficiency factor relative to additive concentration.

Fig. 4. First cycle of CV with initial potential: open circuit, sense: from cathodic to anodic; scan rate: 50 mV s⁻¹; temperature: 60 °C; Electrolyte: 100 g l⁻¹ CuSO₄ + 160 g l⁻¹ H₂SO₄ in distilled water. Continuous curve: 25 mg l⁻¹ of PEG; Dotted curve: without additives. Insert graph: efficiency factor with regard to additive concentration.
Fig. 5. Experimental $i/t$ transients (symbols curve (o)) for copper electrodeposition over 316L stainless steel, in 100 g l$^{-1}$ CuSO$_4$ + 160 g l$^{-1}$ H$_2$SO$_4$, for ED = -0.63 V in the presence of the different organic additives (added separately) (a) Thiourea, (b) Glue, (c) Avitone, (d) PEG and components of the total current obtained from Eq. 6: progressive three-dimensional growth (continuous curve); HER contribution (dotted curve) and progressive two-dimensional contribution (point-line curve).

B. Potentiostatic pulses

The $i/t$ current transients showed the charging process of the electrical double layer, which was characterized by high current values with time close to zero that later fell rapidly to a constant value. This indicates that the formation and growth of copper nuclei on the steel surface is controlled by diffusion.

The experimental $i/t$ transient for an ED of $-0.63$ V is shown in Fig. 5. This initial electrode potential was selected from the cyclic voltammetry tests, like those shown in Figs. 1-4, since this is the lower potential at which the electrocrystallisation currents become evident. This experimental curve was adjusted to the model shown in Eq. 6 and the model constants were estimated. The contributions of each component of the total charge were then calculated and are shown in the same graph.

The most important contribution is that of the current associated to the process controlled by the diffusion. The comparison of the cases presented in Fig. 5 shows there is a two-dimensional contribution only for the PEG additive. Furthermore, the charge of the HER contribution is observed for thiourea and PEG after 15 seconds, while for glue and Avitone it is observed at the beginning of the reaction, competing with the Cu$^{2+}$ reduction. This, therefore, shows that only the first two additives are absorbed in the surface to block the active areas for hydrogen evolution.

The efficiency factors estimated with Eq. 2 and the comparison made between these values and those obtained with Eq. 1 are shown in Table 1. This Table shows that the resulting values are analogous.

Similar experiments were carried out for additive mixtures; the results are shown in Table 2.

The additive mixtures show results which are similar to those obtained individually. The main differences involve a decrease of the current value at $t = 0$, and a marked increase of the 2D progressive charge, which was more evident when using the thiourea – PEG – Avitone – chloride mixture than with a thiourea – glue - Avitone – chloride mixture.

C. AFM Measurements

The roughness values in relation to electrolysis time for the different additive-containing electrolytes are shown in Fig. 6. It can be observed that without the organic additive, the deposit reaches a significant roughness level after a very short time (650 nm after 180 s). Similar behavior is observed while using the Avitone.

In the case of glue, the deposits obtained after 180 s show lower roughness than that observed with thiourea and PEG. However, after this initial period, the roughness largely exceeds the levels of thiourea and PEG, which maintain a much lower variation.

The roughness obtained during the long electrolysis tests (after 5 hours) are shown in Fig. 7. Average roughness, which was slightly higher than 400 nm, was obtained with the thiourea and PEG additives. In contrast to glue, which is decomposed through acid hydrolysis, the leveling properties of the PEG and thiourea...
Fig. 7. Average roughness found in copper deposits over stainless steel 316L cathodes (1 cm diameter disc) from an aqueous electrolyte composed of 100 g l−1 CuSO4 + 160 g l−1 H2SO4, (60ºC) after 5 hours of electrolytic deposition, in the presence of different additives.

Fig. 8. Average roughness found in copper deposits over stainless steel 316L cathodes (1 cm diameter disc) from an aqueous electrolyte composed of 100 g l−1 CuSO4 + 160 g l−1 H2SO4, (60ºC) measured consecutively every two hours (total time 8 hours) during electrolytic deposition, in the presence of a mixture of additives a) Thiourea-Glue-Avitone-Sodium chloride and b) Thiourea-PEG-Avitone-Sodium chloride.

Two electrolysis solutions were prepared to compare the effect of the PEG and glue in the mixture:

- a) thiourea / glue / Avitone / chloride,
- b) thiourea / PEG / Avitone / chloride.

The mixture concentrations were chosen according to the optimum concentrations obtained in the tests done for each additive. Copper deposit tests were carried out with each mixture under the same operative conditions; roughness levels were measured every two hours until the maximum limit of the AFM technique (1300 nm) was reached. The results are shown in Fig. 8.

It may be observed that the properties of the (a) mixture are progressively lost during the electrolysis period; in contrast, the deposit quality remains the same using the (b) mixture, at least in the 8-hour interval that the PEG degradation was not verified.

IV. CONCLUSIONS
A comparative study of the effect of the organic additives generally used in copper electrowinning and PEG was carried out. The PEG additive has an influence on the processes of nucleation and growth, thus maintaining a longer regulating effect on the deposit morphology than is observed using the glue additive. The strong increase in roughness observed during electrolysis in the solution containing glue is related to low stability in the acid electrolyte. The optimum concentration for each additive was determined through cyclic voltammetry and potentiostatic pulses; both methods gave analogous results.

The adjustment made to the experimental current transient curves of the suggested model have enabled evaluation of the different deposition charge components, thus proving the depressant action on the HER that is observed from the beginning of the process in the presence of PEG; this effect is not observed when using glue.

The marked effect on the HER depression, and also the notable increase in the period over which the roughness level of the deposit is maintained, clearly show the advantages of replacing the glue additive with PEG in the process of copper electrodeposition on stainless steel permanent cathodes.

List of symbols

- A0 crystal nuclei formation rate
- \( C^\infty \) copper ion concentration in the bulk of the solution
- \( D \) diffusion coefficient
- \( \rho \) density of film deposit
- \( E_D \) starting value of applied electrode potential
- \( %\text{Eff} \) efficiency factor of additive use
- \( F \) Faraday constant
- \( h \) height of first crystal nucleation layer
- \( i \) electric current
- \( k_{\text{HER}} \) reaction rate constant of hydrogen evolution
- \( K_{2D} \) incorporation rate of molecules/atoms at growth center
- \( n' \) total number of sites scanned (AFM scan)
- \( n \) number of electrons involved in the electrochemical reaction
- \( n_{\text{HER}} \) number of electrons associated with the hydrogen evolution reaction
- \( N_{2D} \) number of two-dimensional nuclei formed
- \( N_0 \) total number of active sites for nucleation on the electrode surface
- \( M \) molar mass
- \( Q_A \) anodic charge determined by voltammetry
- \( Q_C \) cathodic charge determined by voltammetry
- \( Q_{\text{HER}} \) charge associated with hydrogen evolution reaction
- \( Q_{\text{NP}} \) 2D progressive nucleation charge
- \( Q_{3D} \) 3D progressive nucleation charge
\( Q_t \) total charge
\( R_{\text{rms}} \) root-mean-squared average roughness
\( t \) time
\( Z_{\text{av}} \) average height of the surface (AFM scan)
\( Z_{\text{rms}} \) time of each scanned site (AFM scan)

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