



Galvanostatic and microscopic studies of nodulation during copper electrolysis

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Abstract

The galvanostatic technique on a laboratory scale has been shown to be a useful tool in detecting the presence of nodules on the cathode during copper electrodeposition by using the value of the starting electrolytic potential and by the presence of a cathodic polarization peak on the potential–time curve. Studying the morphology of the deposit with a scanning electron microscope at various magnifications confirmed the galvanostatic results. It is postulated that inappropriate concentrations and/or ratios of the additives (thiourea, gelatin and chloride ions) are associated with a certain current density that generates intergranular microcracks due to adsorption of the additives and leads to the formation of nodules at the macroscale.

1. Introduction

This paper deals with the cathodic deposit type obtained in copper electrodeposition. The deposit is considered to be poor quality when it is rough and nodular. Nodules often cause short circuits with a reduction in current efficiency and may cause entrapment of anode slimes reducing cathode purity. Improved control of the nodule phenomenon is currently a major preoccupation for many copper refineries [1].

The objective of this work was to provide new information about copper electrodeposition and especially nodule growth, deposit morphology. The structure of the deposit, copper crystalline shape, is also discussed. Of particular interest is the combination of scanning electronic microscope SEM studies of the deposit with electrochemical galvanostatic polarization, cathodic potential curves.

Organic additives are widely used in the copper refining industry to promote smooth deposits. The combination of these additives affects the electrocrystallization of copper, influences the cathodic polarization and controls the grain structure. The use of higher current densities requires an adjustment to the concentration of the additives to avoid cathode nodulation [2–6].

2. Experimental conditions

Copper deposition was carried out at 65 °C (a constant temperature was maintained by using a thermostat bath

controlled by a thermostat ± 0.5 °C) on a circular pre-treated stainless steel cathode type 316 (surface 1.27 cm²) in 700 ml of synthetic additive-free electrolyte containing [H₂SO₄] = 160 g l⁻¹, [Cu²⁺] = 42 g l⁻¹, [Ni²⁺] = 18 g l⁻¹ at constant direct current. The electrolytic bath contained additives (thiourea noted TU, gelatin G, chloride Cl⁻), which were introduced into the synthetic electrolyte once, at the beginning of each experiment. The distance between the cathode and the anode was 2.5 cm. The anode was made of platinum (area 1.3 cm²). Before each experiment, the cathode was ground with SiC abrasive paper down to 600 grit and washed with distilled water and alcohol.

We used different current densities, $j = 300, 340, 500$ or 750 A m⁻² and four kinds of additive mixtures (thiourea, gelatin and chloride): industrial standard solution (4–11.5–40), solution A (4–2–40), solution B (4–6–40) and solution C (12–11.5–40). The industrial standard solution was calculated from one 24 h period addition and without considering the degradation of the additives, the diluting effect of the additives tank and the circulating solution.

Other parameters such as the polarization delay, stirring, cathode temperature and deposition time were also studied.

Experiments were conducted with immediate polarization. In certain cases, polarization occurred after delaying the immersion of the electrode. This delay corresponds to the period of time when the mixed potential goes to more noble values and becomes stable after 200–300 s. In these cases, the term ‘delayed

polarization' will be used. The latter procedure is usually used by industry.

Experiments were conducted without stirring. However, to test the influence of this parameter, the solution was stirred (moderately ~ 60 rpm and strongly ~ 90 rpm) in certain experiments using a magnetic stirrer, in these instances 'stirring' is mentioned.

The working electrode (cathode) was at ambient temperature when it was introduced into the electrolyte at 65°C . In certain experiments, the working electrode was preheated to 65°C before being introduced into the electrolytic bath. The term 'preheated' electrode is then mentioned.

A one hour of deposition period was chosen. However, this was reduced in some experiments to study the beginning of electrolysis. In these cases, the deposition period is specified.

Industrial standard solution at a current density $j = 500 \text{ A m}^{-2}$ with immediate polarization without stirring and with a preheated electrode was chosen as a reference.

All potentials were measured using the silver chloride reference electrode with a saturated KCl double junction (KCl/AgCl, Ag), which is 0.202 V vs SHE. The potential of this reference electrode can change a little in a very acidic copper sulfate solution at 65°C due to contamination of the double junction by copper ions. The potential measurements are therefore within $\pm 10 \text{ mV}$. At least three tests (cathodic potential versus time) were made in each condition. The electrolyte volume per unit cathode surface was 5510 l m^{-2} .

A computer controlled potentiostat/galvanostat (EG&E Princeton Applied Research 273) was used. The software Softcorr M432 was used for acquisition and analysis of polarization data. A scanning electron

microscope SEM (Jeol T 20) was used for microstructural analysis.

3. Results and discussion

3.1. Potential variation and deposit properties for 1 h polarizations

3.1.1. Influence of current density

The influence of current density ($j = 300, 340, 500, 750 \text{ A m}^{-2}$) on the cathodic potential and electrolytic deposit (morphology and structure) was studied in an additive-free and industrial standard solution (thiourea: 4, gelatin: 11.5 and chloride: 40 mg l^{-1}). Immediate polarization lasting one hour without stirring and preheated electrode was conducted. The results are summarized in Table 1.

For both solutions, an increase in current density gave an increase in cathodic polarization (Figure 1). Polarization was much more significant for the industrial standard solution than for the additive-free solution (about -100 mV). With the industrial standard solution the E/t curve at 340 A m^{-2} showed one cathodic peak which appeared around 200 s after a rapid shift of about -100 mV on the cathodic curves (Figure 1(a) and Table 1). The E/t curves at 500 A m^{-2} (reference) and 750 A m^{-2} showed two cathodic peaks which appeared after 230 and 600 s on the cathodic curves (Figure 1(a) and Table 1). Each peak corresponds to a rapid shift of about -25 mV . The starting cathodic potential at the beginning of the galvanostatic studies becomes lower than 100 mV vs SHE under the conditions described above (Figure 1(b)). The cathodic peak or an increase in polarization means that the deposition of copper is more

Table 1. Cathodic peak associated with the structure and morphology of the deposit

Experimental conditions		Results						
$j/\text{A m}^{-2}$	Industrial standard solution	Cathodic potential peaks*/s		Electrolytic deposit				
				(Structure)		(Morphology)		
				Columnar	Pyramidal	Smooth	Rough (FI [†])	Nodules
300	•	–	–	+	–	+	–	–
340	•	–	–	+	–	+	–	–
500	•	–	–	+	–	+	–	–
750	•	40	–	+	–	–	+	–
300	×	–	–	+	–	+	–	–
340	×	180	–	–	+	–	–	+
500[‡]	×	230	600	–	+	–	–	+
750	×	290	700	–	+	–	–	+

* Observation time for formation of peaks.

[†] Isolated crystals, which are oriented by the field.

[‡] Bold type (reference).

× experiment undertaken.

• experiment not undertaken.

+ observed.

– not observed.

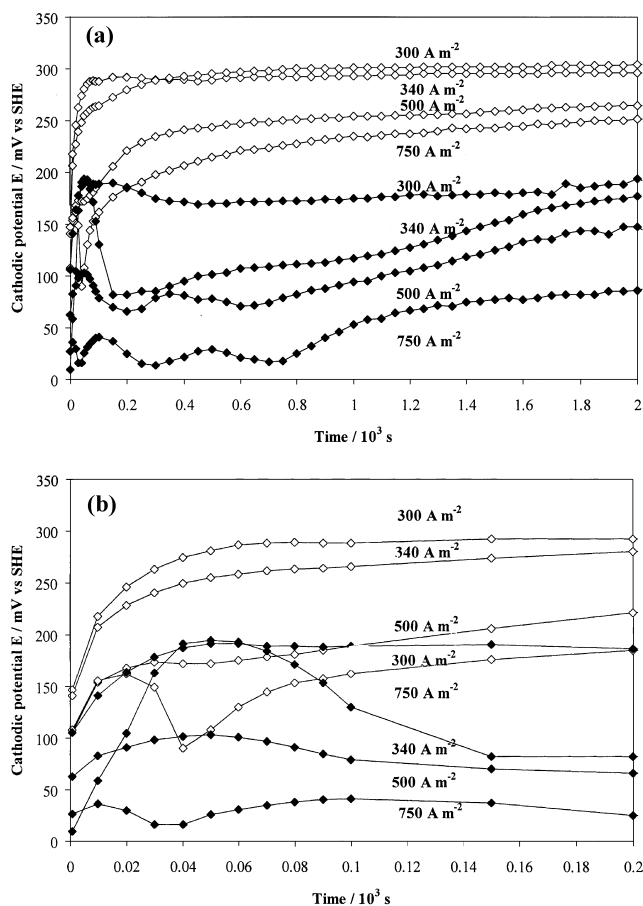


Fig. 1. (a) Influence of the current density on cathodic polarization curves with additive-free (\diamond) and industrial standard (\blacklozenge) solutions with immediate polarization, without stirring and with a preheated electrode for 1 h of deposition. (b) Magnification of Figure 1(a) for the first 200 s.

difficult, this part will be discussed in point 4.2. This leads to the formation of nodules on the cathode (Figure 2). Nodules always have a regular spherical shape. They are composed of copper crystals, which have the same crystalline structure as those seen in the rest of the matrix.

Nodules are primarily situated on the periphery of the cathode and their number and size increase with current density. The crystalline copper structure is pyramidal. These square base pyramids represent the shape of the perfect copper crystal [7]. The crystals become sharper and smaller than those of the reference solution as the current density decreases (Figure 2). Crystallization with pyramidal shape shows that the preferential growth direction of copper is the $\langle 100 \rangle$ direction [8]. The morphology of the deposit is smooth and the structure of the grain is fine. Without additives and even for rough deposits, $\langle 110 \rangle$ is the direction of growth [9].

The deposit is free of nodules when the initial potential of electrolysis stays higher than 100 mV vs SHE. At these potentials, copper grows in a columnar structure (copper crystals seem to grow in a more disorganized way around the perpendicular axis to the cathode) (Figure 3). The additive-free solution at

750 A m^{-2} gives a rough deposit (Figure 3(b)). It is generated by the rough edges of prismatic shape crystals, also called FI structure (isolated crystals which are oriented by the field [10]). There is a cathodic peak at 40 s on the polarization curve (Figure 1).

3.1.2. Influence of polarization delay, stirring and preheated electrode

The influence of delayed polarization on cathodic potential (cathodic peaks) and electrolytic deposit (nodulation phenomenon) was studied at 500 and 750 A m^{-2} in an additive-free and industrial standard solution (thiourea: 4, gelatin: 11.5, and chloride: 40 mg l^{-1}). Experiments lasting one hour without stirring and with a preheated electrode were conducted. The influence of stirring and a preheated electrode on cathodic potential and electrolytic deposit was studied at 500 A m^{-2} in an industrial standard solution. Immediate polarization lasting one hour was conducted. Table 2 summarizes the results.

With the additive-free solution, at 750 A m^{-2} , delayed cathodic polarization eliminates the peak observed under the same conditions at 40 s with immediate polarization but did not eliminate the rough deposit on the cathode surface. Delayed polarization brings the curve to a lower cathodic polarization level at the beginning of the electrolysis. At about 500 s, the two curves converge (Figure 4).

Using the industrial standard solution at 500 A m^{-2} , delayed polarization as well as stirring (changes in polarization delay and in electrolyte stirring compared with the reference), can eliminate both the cathodic peaks observed at 230 s and 600 s on the polarization curves and the nodules at the cathode. These two parameters bring the curve to a higher starting potential ($>100 \text{ mV}$) at beginning of electrolysis (until 2000 s) (Figures 4 and 5). On the other hand, heating the cathode at 500 A m^{-2} (changes in the temperature of the electrode compared with the reference) as well as delayed polarization at 750 A m^{-2} with the industrial standard solution only eliminates the second cathodic peak (Figures 4 and 5). The starting electrolysis potential remains lower than 100 mV vs SHE. These conditions did not completely avoid nodulation but resulted in a reduction of nodule density.

In the industrial standard solution, it seems possible to associate the first cathodic peak around 230 s with the appearance of nodules at the cathode. The second cathodic peak as well as the cathodic peak observed at 40 s in the additive-free solution with 750 A m^{-2} cannot be related to the morphology of the deposit (nodular or rough). These peaks, which increase with current density, can normally be attributed to the diffusion phenomenon.

Nodules only form in a matrix made of a pyramidal structure. However, a pyramidal structure does not necessarily indicate the presence of nodules. Pyramids formed in the stirred solution, compared with the reference solution, are sharper but the mass of the

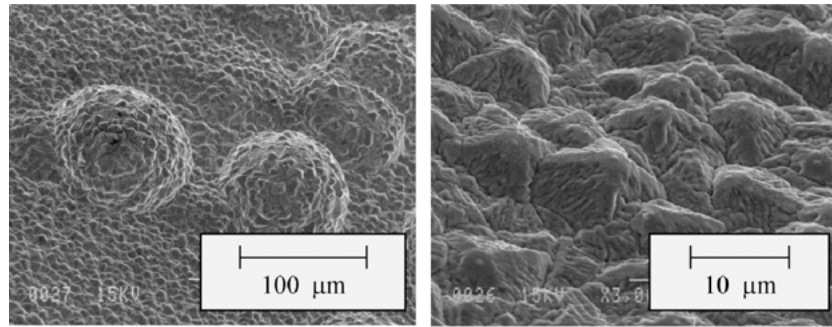
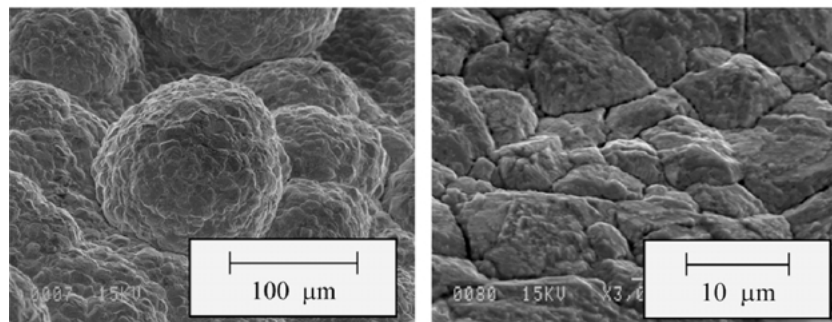
(a) $CD = 340 \text{ A m}^{-2}$ (b) $CD = 500 \text{ A m}^{-2}$

Fig. 2. SEM micrographs of cathodes produced at two current densities in industrial standard solution (4–11.5–40) with immediate polarization, without stirring and with a preheated electrode for 1 h of deposition: nodular morphology deposit and pyramidal crystalline structure.

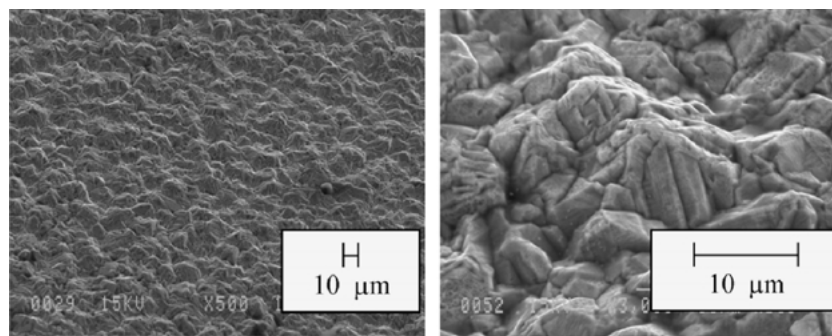
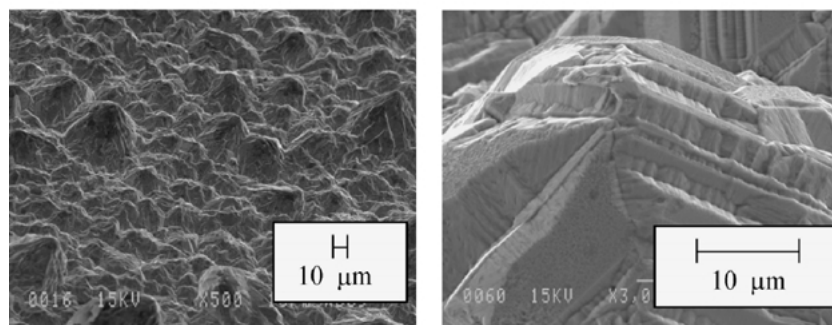
(a) $CD = 500 \text{ A m}^{-2}$ (b) $CD = 750 \text{ A m}^{-2}$ (rough deposit – FI structure)

Fig. 3. SEM micrographs of cathodes produced at two current densities in additive-free solution with immediate polarization, without stirring and with a preheated electrode for 1 h of deposition: no nodular morphology deposit and columnar crystalline structure.

Table 2. Influence of delayed polarization (DP), stirring (S) and preheating electrode (PE) on nodulation and crystalline copper structure shape

Experimental conditions					Results			
$j/A\ m^{-2}$	Industrial standard solution	Variable parameters			Cathodic potential peaks [*] /s	Electrolytic deposit		
		DP	S	PE		(Structures) Pyramidal	(Morphology)	
							FI [†]	Nodules
500	×	×	●	●	—	+	—	—
500	×	●	×	●	—	+	—	—
500	×	●	●	×	1	+	—	+
750	×	×	●	●	1	+	—	+
750	●	×	●	●	—	—	+	—

* Number of peaks.

† Isolated crystals, which are oriented by the field.

× experiment undertaken.

● experiment not undertaken.

+ observed.

— not observed.

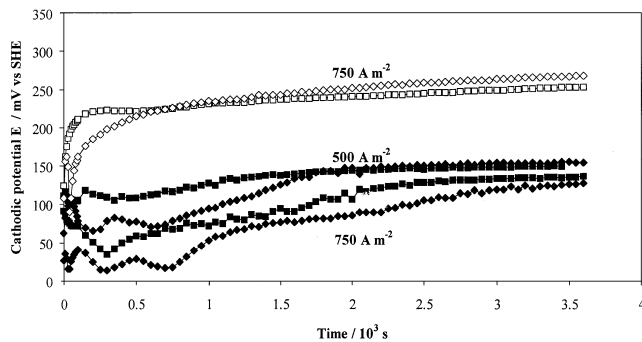


Fig. 4. Influence of immediate polarization IP and delayed polarization DP at $750\ A\ m^{-2}$ with additives-free solution (\diamond for IP and \square for DP) and at 500 and $750\ A\ m^{-2}$ with industrial standard solution (\blacklozenge for IP and \blacksquare for DP), without stirring and with a preheated electrode for 1 h of deposition.

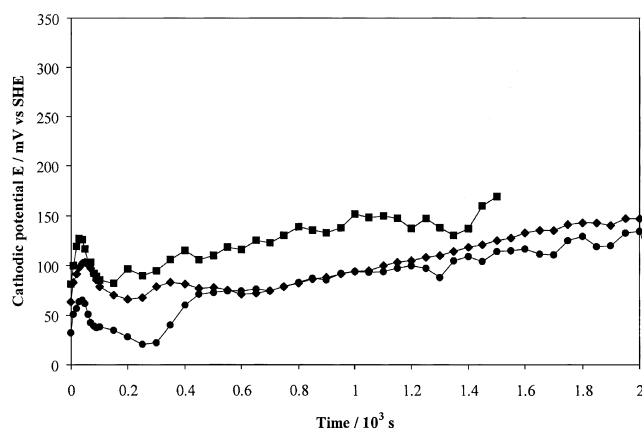


Fig. 5. Influence of stirring (\blacksquare) and the temperature of the cathode (\bullet) with industrial standard solution, 4–11.5–40, (\blacklozenge) at $500\ A\ m^{-2}$ with immediate polarization for 1 h of deposition.

copper deposit is reduced in half. Pyramids formed with delayed polarization, compared with the reference solution, are sharper and bigger. Pyramidal copper crystal grows in a lateral plane $\{1\ 1\ 1\}$ [8].

3.1.3. Influence of additives concentration

The influence of the additives concentration (thiourea, gelatin and chloride), on cathodic potential (cathodic peaks) and electrolytic deposit (nodulation phenomenon) was studied at $500\ A\ m^{-2}$ with four kind of solutions: industrial standard solution (4–11.5–40), solution A (4–2–40), solution B (4–6–40) and solution C (12–11.5–40). Immediate polarization lasting one hour without stirring and with a preheated electrode was conducted. The results are summarized in Table 3.

Decreasing the gelatin concentration, to 6 and $2\ mg\ l^{-1}$ (solutions B and A) compared with the reference solution resulted in a deposit free of nodules. The starting electrolysis potential became higher than $100\ mV$ (Figure 6). Depolarization occurred rapidly at the beginning of the electrolysis. After 750 s solution B (4–6–40) exhibited an abrupt potential increase in cathodic polarization while solution A (4–2–40) exhibited almost no change.

The crystalline structure of solution B is a pyramidal structure with pyramids which are approximately five times greater than those of the reference solution while the crystalline structure of solution A is a columnar structure. The increase in thiourea concentration to $12\ mg\ l^{-1}$ (solution C), compared with the reference solution, increases the cathodic polarization during the first 30 min of the electrolysis and shifts the formation of the cathodic peaks to shorter times. There are more nodules on the cathode and the pyramids are sharper than those of the reference solution.

Although the ratio of electrolyte volume on the cathodic surface is 100 times higher in our electrochemical cell than in industrial practice ($5511\ l\ m^{-2}$ compared to 63.59 and $53.62\ l\ m^{-2}$ for Kidd Creek and CCR, respectively) and we used a synthetic electrolyte with immediate polarization and without stirring, the results agree with those obtained in the pilot plant set-up [11]. With the industrial standard solution, cathodes were free of nodules at $300\ A\ m^{-2}$ but contained some at

Table 3. Influence of additives concentration, thiourea [TU], gelatin [G] and chloride ions [Cl⁻], on cathodic potential and the electrolytic deposit

Experimental conditions			Results			
Additives mg l ⁻¹			Cathodic potential peak/s	Electrolytic deposit		
[TU]	[G]	[Cl ⁻]		Crystalline structure		Morphology nodules
				Columnar	Pyramidal	
4	2	40	–	+	–	–
4	6	40	–	–	+	–
4	11.5	40	+	–	+	+
12	11.5	40	+	–	+	+

+ observed.

– not observed.

Bold type: reference.

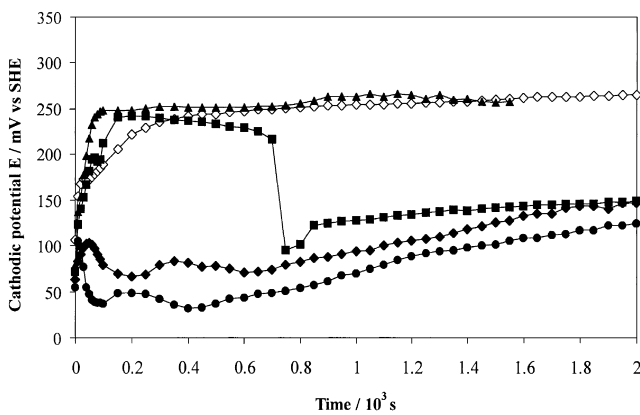


Fig. 6. Influence of additives concentration (thiourea–gelatin–chloride) (mg l⁻¹) at 500 A m⁻² with immediate polarization, without stirring and with a preheated electrode for 1 h of deposition: additive-free solution, (0–0–0), (◇); solution A, 4–2–40 (▲); solution B, 4–6–40, (■); industrial standard solution, 4–11.5–40, (◆); and solution C, 12–11.5–40, (●).

340 A m⁻². Cathodic potential values for the laboratory cell are similar to those obtained by the pilot plant set-up, only 20 mV higher or more positive. Therefore, it can be postulated that the ratio of electrolyte volume on

the cathodic surface does not seem to have a major influence on nodulation.

3.2. First stage of copper electrodeposition

A deposition period of 600 s was chosen to study the first stage of copper electrodeposition at 500 A m⁻² with additive-free A and industrial standard solutions. Experiments with immediate polarization without stirring and with a preheated electrode were conducted. Experiments with the industrial standard solution were the only ones that gave nodules after one hour of deposition (reference solution). A deposition period of 600 s corresponds to the appearance of the second cathodic peak. Three deposition times around T1 = 80 s, T2 = 180 s and T3 = 230 s were chosen to examine copper electrodeposition around the first cathodic peak (230 s) for the industrial standard solution at 500 A m⁻² (Figure 7). The results are summarized in Table 4.

3.2.1. Deposition period of 600 s and various additives concentration

With an additive-free solution, the structure appears crystalline with a columnar growth (Figure 8(a)). Columnar blocks seem to juxtapose themselves along

Table 4. Types of copper deposit at various concentration of additives, thiourea [TU], gelatin [G] and chloride ions [Cl⁻] or at various deposition times

Experimental conditions Time/s	Additives/mg l ⁻¹			Results		
	[TU]	[G]	[Cl ⁻]	Crystalline structure		
				Pyramidal	Columnar	Nodule
600	0	0	0	–	+	–
600	4	2	40	+	+	–
600	4	11.5	40	–	–	+
80	4	11.5	40	*	*	–
180	4	11.5	40	*	*	–
230	4	11.5	40	*	*	+
400	4	11.5	40	*	*	+

* crystalline structure is too small to be identified.

+ observed.

– not observed.

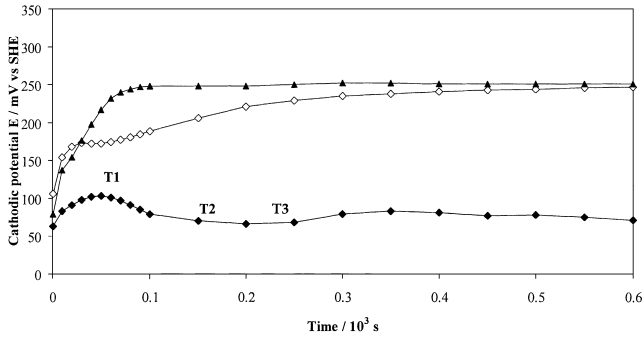


Fig. 7. First stage of copper electrodeposition at $Q = 300\,000\text{ C m}^{-2}$ ($j = 500\text{ A m}^{-2}$) for additive-free solution, 0–0–0, (◇); industrial standard solution, 4–11.5–40, (◆); and solution A, 4–2–40 (▲) with immediate polarization, without stirring and with a preheated electrode.

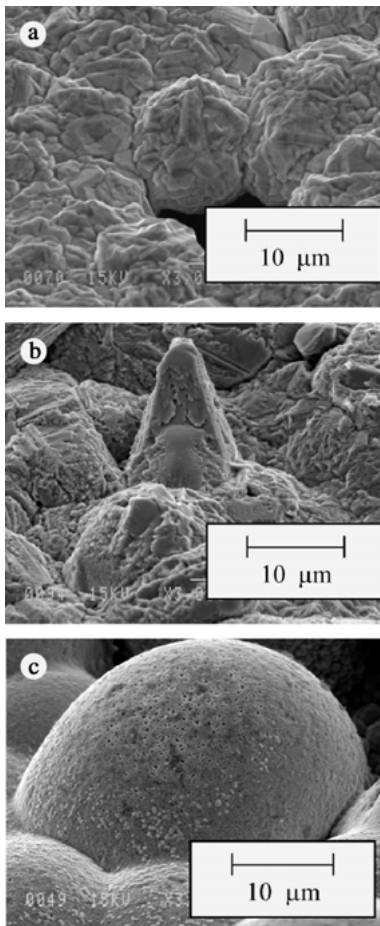


Fig. 8. SEM micrographs of cathodes produced at $Q = 300\,000\text{ C m}^{-2}$ ($j = 500\text{ A m}^{-2}$) with immediate polarization, without stirring and with a preheated electrode. (a) Additive free solution; (b) solution A, 4–2–40; (c) industrial standard solution, 4–11.5–40.

parallel lines on the cathodic surface and their juxtaposition shows many holes with a diameter of $10\ \mu\text{m}$ which gives the surface an irregular aspect. The size of the columnar blocks is equivalent to the one observed at the end of one hour of deposition (Figure 3(a)). A deposit

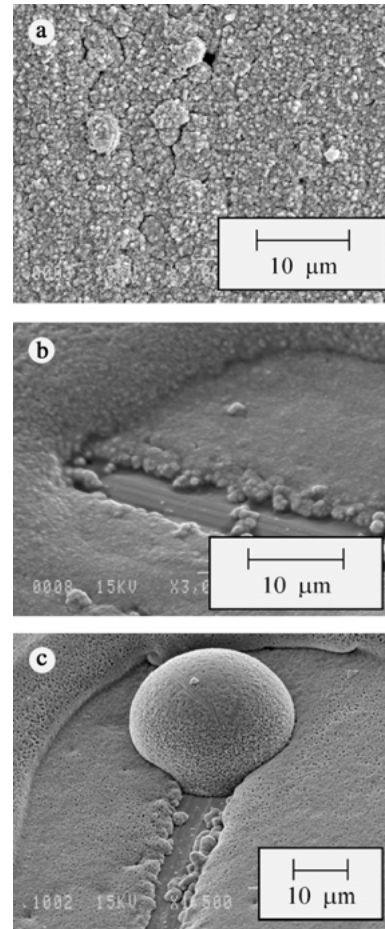


Fig. 9. SEM micrographs of cathodes produced at various times of copper deposition at 500 A m^{-2} with industrial standard solution with immediate polarization, without stirring and with a preheated electrode. (a) T1 = 80 s; (b) T2 = 180 s; (c) T3 = 230 s.

with columnar structure was assigned a BR structure according to Fisher [2].

With solution A (4–2–40), the structure appears crystalline with the coexistence of columnar and pyramidal structures (Figure 8(b)). At the end of an hour of deposition, it is only the columnar structure that remains. It seems that the gelatin concentration is not sufficient to promote the pyramidal structure.

With the industrial standard solution, nodules were formed about $10\ \mu\text{m}$ from the centre of the cathode and reach nearly $50\ \mu\text{m}$ on the edge (Figure 8(c)). After an hour of electrolysis, nodules in the centre will be blurred. The growth of nodules also decreases with time. At 500 A m^{-2} , 10 min of deposition gave deposits with nodules of $50\ \mu\text{m}$ in diameter compared to $150\ \mu\text{m}$ at the end of 60 min.

3.2.2. Various deposition times with the industrial standard solution at constant current density (500 A m^{-2})

At T1 = 80 s, the copper structure is crystalline and some microcracks appeared on the cathode (Figures 7 and 9(a)).

At T2 = 180 s, the copper structure becomes finer. There were a number of holes, about $5\ \mu\text{m}$ in diameter

at the centre of the cathode; and a number of hollows, about $100 \mu\text{m}^2$ at the edge of the cathode. On the bottom, copper crystallization had not occurred and the steel was still uncovered (Figures 7 and 9(b)).

At $T_3 = 230$ s, the bottom of the first cathodic peak corresponding to the maximum polarization, very few nodules had appeared. They seemed to initiate in the depressions on the surface, growing from the stainless steel cathode in the hollows and then overflowing the matrix extensively (Figures 7 and 9(c)).

4. Interpretation

4.1. Type of deposit

Fisher proposed characterizing stability domains of the electrolytic polycrystal deposit by taking four types of metallographic structures cut according to the current density and the intensity of inhibition [10]: (i) BR structure, basis reproduction, obtained at weak inhibition; (ii) at higher current density, the FI structure appears (field-oriented isolated crystals oriented in the field). Indeed, density of current promotes crystalline growth perpendicular to the electrode; (iii) FT structure, field-oriented texture type, obtained with stronger inhibition; and (iv) UD structure, nonoriented dispersion type, obtained at even stronger inhibition. Inhibitors promote lateral growth and lead to dense deposits. The best deposit has been obtained at the border of the FT–UD structures. This metallographic structure presents a preferential orientation $\langle 100 \rangle$ on the X-ray diagram [12].

Although we could not do a parallel observation of the electrode (metallographic cut of our deposits) but only a perpendicular observation, it is possible to confirm the previous results with the two types of structures obtained. Columnar structures can correspond to the BR structure. The pyramidal structures can correspond to the FT–UD structure.

4.2. Suggested mechanism for generating nodulation

Inhibitors or additives form ion complexes with copper that block the surface of the cathode and mediators that are adsorbed onto the surface of the electrode.

Inhibitors increase polarization resistance, their action is controlled by diffusion. Progressive desorption tends to occur as the average current density is increased. This shifts the deposition potentials to more cathodic values. Thus areas of low current density were relatively depolarized with respect to the areas of high current density. This gives a more uneven deposition and nodules can appear [13]. Nodules seem to start growing when the desorption of ion complexes start and leave behind hollows of about $100 \mu\text{m}^2$ where it is possible to see the steel of the cathode, giving rise to a new nucleation site (Figure 9(b)). Once the nucleus is

formed, the growth is systematically perpendicular to the cathode to offer the shortest path for current waves field, and nodular growth is greatly increased.

5. Conclusion

- (a) Electrochemical galvanostatic polarization appears to be a useful method of signalling the possibility of nodule formation. Galvanostatic studies of nodulation during copper electrolysis show that the nodule formation depends on: (i) the potential level of the starting potential (<100 mV vs SHE) (polarization value), and (ii) the shape of the polarization curve (a cathodic peak around 200 s).
- (b) Microscopic studies by a scanning electron microscope of nodulation during copper electrolysis (galvanostatic technique) show that nodules appear: (i) in solutions containing certain percentages of additives, (ii) at the beginning of the electrodeposition, around 200 s (very possibly after the desorption of the additive), and (iii) on a matrix made of pyramidal structure. However, the pyramidal structure does not always lead to nodule formation.
- (c) The pyramidal structure is only observed when the bath contains additives. The reverse is not true. Pyramidal structure can be identified as the result of a structural deposition of FT–UD type in the metallographic cut (border between the texture oriented in the field (FT) and nonoriented structure (UD)). To have a smooth and dense deposit, copper should grow showing a pyramidal shape.
- (d) An additive-free solution only gives the columnar structure. Columnar structure can be identified as structural deposition of BR type in the metallographic cut (basis reproduction). The FI structure is a particular shape of the columnar structure at high current densities. It can be found when the immediate cathodic potential is higher than 100 mV.
- (e) It is possible to decrease or even eliminate nodulation with depolarization (reducing cathodic potential value). The depolarization is due to the heating of the cathode to 65°C , stirring of the electrolytic bath, the delayed polarization (3 min after immersion) and a low gelatin concentration. There is a reduction of the diffusion overpotential (disappearance of concentration gradients and new nucleus appearance).

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