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Effect of surface active agents on the initial formation of electrodeposited copper layers

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The kinetics of formation and the structure of copper layers are investigated in the presence of a complex additive for bright acid copper plating. It is shown that, in the presence of additive, two maxima are observed on the voltammetric curve. The first may be explained in terms of the formation of a complex between the components of the additive and the cuprous ion. The structure of the initial copper deposits is studied using the double pulse technique. It is shown that the size of separate crystallites strongly decreases in the presence of the additive which also blocks vertical growth and favours lateral growth.

1. Introduction

In recent decades, numerous detailed investigations on the effects exerted by additives with different composition upon sulfuric acid copper plating electrolytes have been carried out. Many papers dealing with the behaviour of surface active agents during the electrodeposition of copper coatings with good physical–mechanical properties have been published [1–11], but a complete picture of the mechanisms by which the respective additives influence the formation of the layers is still lacking.

Compact polycrystalline metallic layers are highly complex structures and, according to Baraboshkin [12], when deposited on substrates, three stages can generally be observed as a function of time. These are: (i) the nucleation of separate crystallites on the substrate, (ii) the growth of separate crystallites until they merge into a compact layer, and (iii) the collective growth of crystallites in the compact layer.

These stages depend on the conditions and regime of electrodeposition. For example, the second stage terminates with the merger of crystallites in a compact layer only in cases when their size, up to the moment they merge, has not reached dimensions at which the growth becomes unstable, that is, it is transformed into a dendrite.

After the merger into a compact layer, the crystallites continue their growth. At this stage the anisotropy of growth rate begins to exert a strong effect. The so-called geometrical selection becomes active: crystallites with favourable orientations with respect to the electrical field lines start growing faster and, as a result, a predominant orientation of crystalline grains appears. Thus, compact metallic layers with a columnar structure are formed.

When morphological stability is disturbed, that is, when the size of crystallites reaches a certain critical value [13] skeletal growth starts and the crystal layer is transformed into a dendritic polycrystalline structure. This suggests that single crystals, compact layers and dendritic layers are cognate structures, since they are developed from crystallites initially originating on the substrate.

The present paper is aimed at the *in situ* investigation of the effect of surface active agent upon the initial stages of copper layer formation. The complex additive (CA) for bright acid copper plating [14] was investigated.

2. Experimental details

The investigations were carried out by applying a method [15] which combines both microscopic-interferometry and electrochemical (potentiodynamic) techniques, shown in Fig. 1. It offers the possibility of studying both the initial stages of metal deposition *in situ* and to modelling the levelling processes caused by surface active agents, dendritic formation, etc. The basic element of the method is the 'two-dimensional' glass cell, provided with a Luggin capillary ($d = 100\,\mu m$) for fixing the SSE reference electrode (Hg-sulfate, potential $+678\,mV$). This approach offers the possibility of monitoring changes in the concentration during the process by interferometry. Due to the small distance between the plane-parallel glass plates (the gap is less than $600\,\mu m$) and the uniform temperature of 20° C, natural convective flows are thought to be negligible for the case of vertically placed electrodes [16, 17] while in other geometries [18] the convection may play a crucial role. The lack of convection permits us to use low scan rates ($1–2\,mV\,s^{-1}$). The cathodes were made of platinum or nickel $300\,\mu m$ thick foil fixed in the cell at a distance $30–50\,\mu m$ from the Luggin capillary. The anodes were copper plates. The nickel electrodes were coated in advance with an amorphous Ni–P layer to eliminate any epitaxial effect of the substrate (area about $10\,mm^2$). The effect of oxygen was eliminated by purging the electrolytes

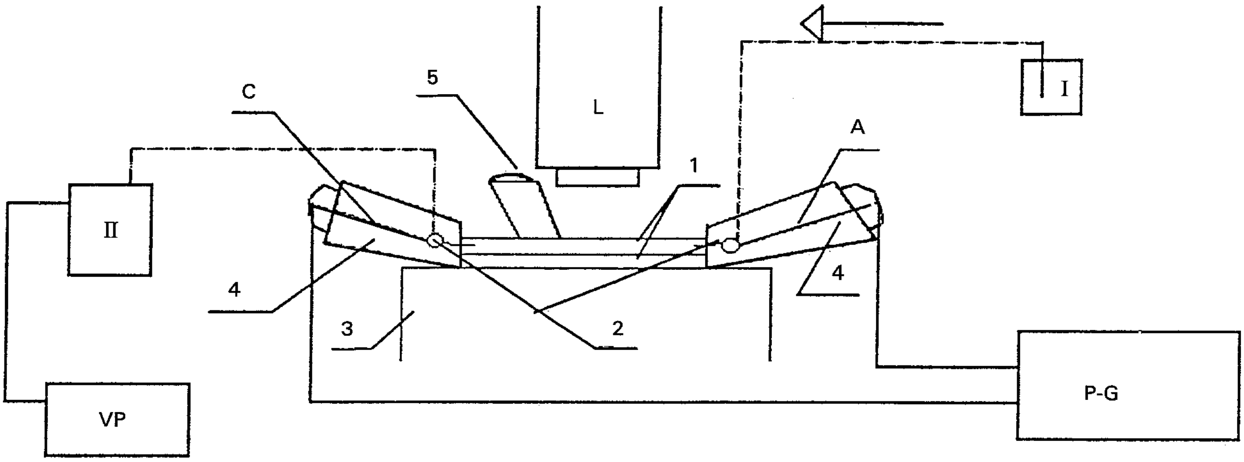

Fig. 1. Experimental setup: (L) lens, (P–G) potentiostat-galvanostat, (I, II) containers, (VP) vacuum pump, (C) cathode, (A) anode; (1) plan-parallel glasses, (2) tubes, (3) microscope stage, (4) ground glass joint, (5) counter electrode.

with argon. For the investigation of the initial stages of copper crystallite nucleation the double pulse method [19] was applied. Simultaneously, the crystallite growth was followed by SEM in the presence or absence of the additive. The electrolytes used contained 0.8 M $CuSO_4 \cdot 5H_2O$ and 0.5 M H_2SO_4, as the basic electrolyte ((1) BE) and the additive (CA) electrolyte ((2) BE + CA). The additive contained the following components: three-block type co-polymers of ethylene and propylene oxides with molecule mass about 10 000 (called 'polymer' with the concentration in the additive: $0.2\,g\,dm^{-3}$), disodic 3,3-dithiobispropanesulphonate ('disulphide': $0.022\,g\,dm^{-3}$) and poly N,N'-diethylsaphranin ('dye-stuff': $0.01\,g\,dm^{-3}$). It is known that these concentrations are optimal for obtaining bright copper coatings [16]. In the absence of additives (pure BE) the first pulse at overvoltage $\eta_1 = 40\,mV$ and duration 0.5 s was sufficient to create nuclei. According to the double pulse method, the following pulses with a smaller overvoltage, $\eta_2 = 20\,mV$, are insufficient to initiate new nucleation, but are necessary for the growth of already existing nuclei. The durations were 5, 10 and 20 s. It was experimentally established that, due to the increased polarization in the presence of the additive, higher η_1 and η_2 values are required for initiation of the growth of crystallites, namely 70 and 40 mV, respectively.

3. Results and discussion

3.1. *Voltammetric curves*

The effect of each separate component of the additive upon the I/E curves was investigated. As shown by the cyclic I/E curves in Fig. 2, the shapes in the presence of separate components of CA are similar to that of the basic electrolyte. The only exception is the curve of the 'polymer', which shows very high polarization within the entire deposition range. But when all three components participate simultaneously (CA), two maxima are observed (Fig. 3), probably corresponding to the following

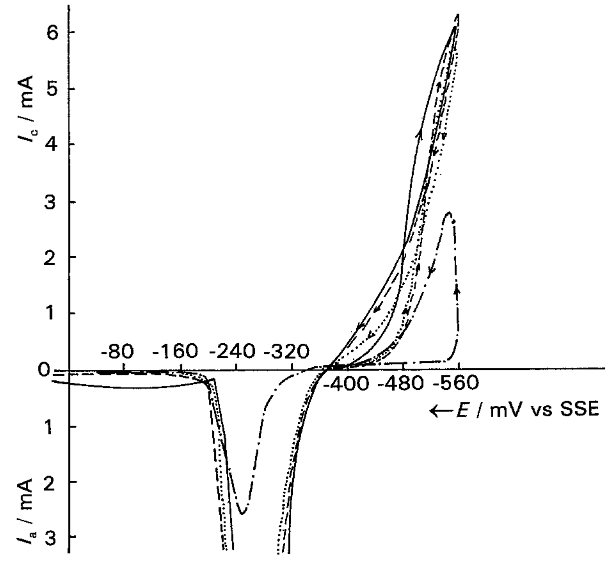

Fig. 2. Cyclic voltammetric curves: (· · ·) basic electrolyte, (— — —) dyestuff, (———) disulphide; (— · — · — ·) polymer.

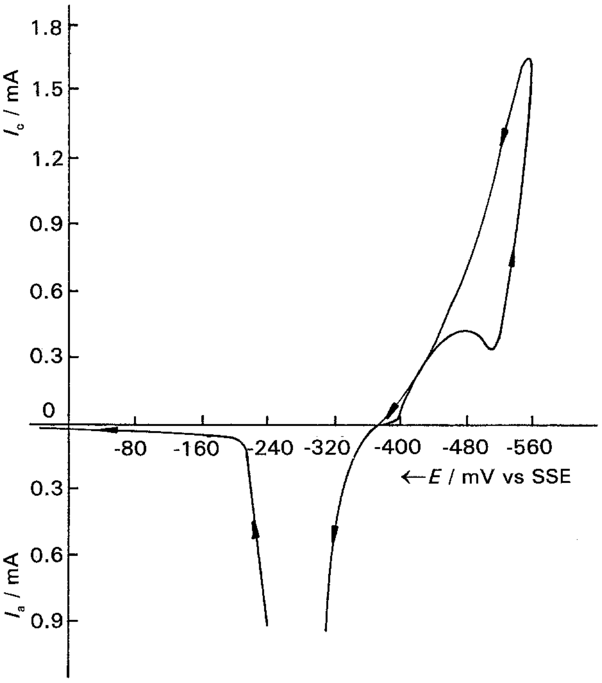

Fig. 3. Basic electrolyte and the additive CA.

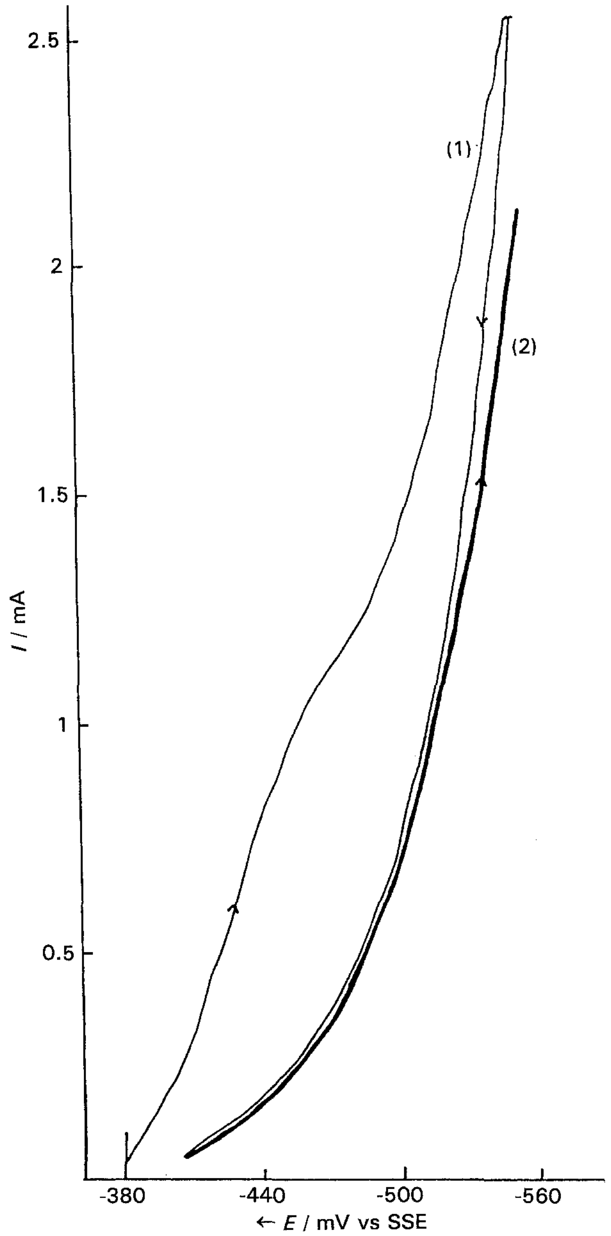

Fig. 4. Cyclic voltammetric curve of basic electrolyte + additive CA + KJ. Scan rate 2 mV s^{-1}; (1) first scan, (2) second scan.

reactions:

$$\mathrm{Cu^{+} + e^{-} \longrightarrow Cu^{0}(+0.520\,V)} \tag{1}$$

$$\mathrm{Cu^{2+} + e^{-} \longrightarrow Cu^{+}(+0.160\,V)} \tag{2}$$

In standard conditions the equilibrium potential of Equation 1 is 520 mV instead of the 200 mV in the present experiment. This difference is due to complexation between the CA and the cuprous-ion.

Milchev and Vasileva [20] have observed a decrease in Cu^{+} concentration in the presence of an additive, while other authors, for example, Paidovsky [21] and Pearson and Dennis [22], have proposed different schemes for the formation of complexes involving the cuprous ion. Stoychev and Tsvetanov [23] have proved the existence of complexes between copper ions (Cu^{2+} and mostly Cu^{+}) and the polymer of the additive [23]. To confirm this we added KJ (with concentration 0.03–0.04 g dm^{-3}) to electrolyte 2. Consequently the available cuprous ions precipitate as CuJ, for example, the cuprous-ion is eliminated from the solution. In this case the complexation between the cuprous ion and the CA is not possible. The shape of the curve in Fig. 3 is changed; the first maximum disappears, as shown in Fig. 4, which confirms the above assumption.

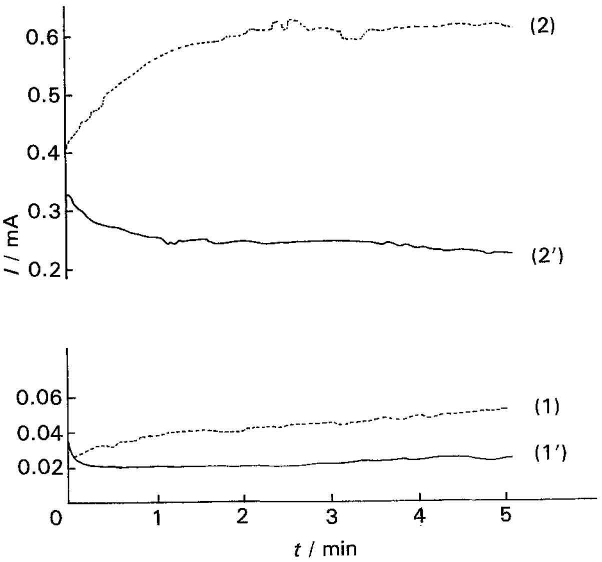

Fig. 5. Current transients at 380 mV: (1) BE and (1′) BE + CA; and at 420 mV: (2) BE and (2′) BE + CA.

3.2. *Current transients*

It was of interest to follow the influence of CA with time at different potentials. The current transients are shown in Figs 5–9. The form of the curves is as expected, since in the presence of additive the transients shift to lower current values due to the inhibitive effect [6, 7]. The curves within the potential range 480–500 mV are of particular interest. According to Stoychev [3], the most efficient adsorption of CA and its brightening action appears in this region. In the case of pure electrolyte (BE), the current increases (nucleation of separate crystallites) and then becomes constant, Fig. 6. In the presence of CA three regions occur, Fig. 7. This behaviour may be explained in

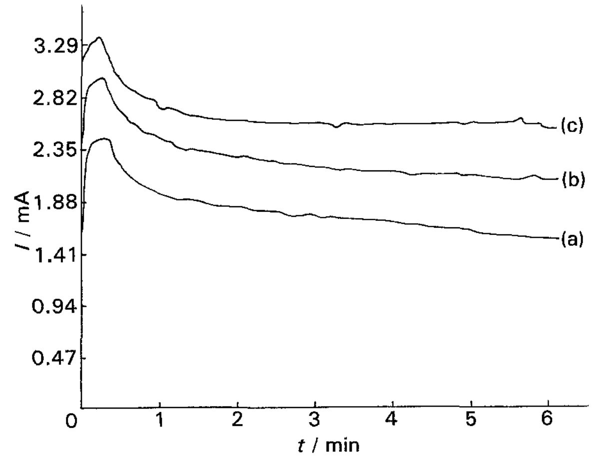

Fig. 6. Current transients of basic electrolyte: (a) 480, (b) 490 and (c) 500 mV.

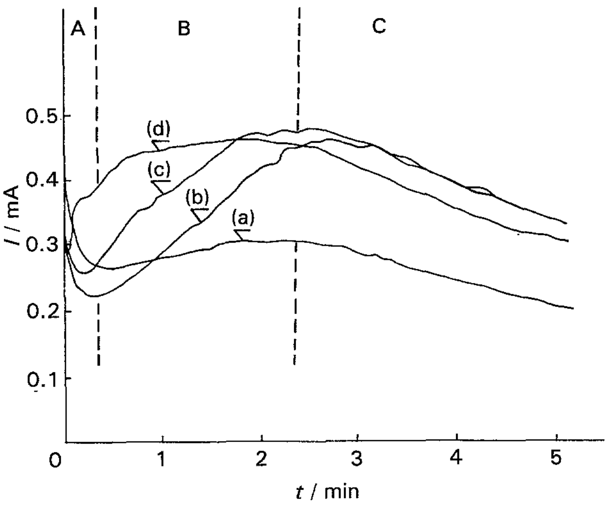

Fig. 7. Current transients of basic electrolyte and the additive CA: (a) 480, (b) 485, (c) 490 and (d) 500 mV.

the following way. Initially, when the potentiostatic pulse is switched on, the current increases abruptly up to 0.3–0.4 mA, which is considerably lower than the current obtained in the case of pure conditions 1.5–3.0 mA (Fig. 6). Then the current decreases (region A) due to strong adsorption of CA. The next increase may be attributed to the formation of new nuclei, growing to a certain size (region B), or, most likely, to lateral crystal growth as a result of the inhibition effect of CA (blocked tops and edge growth). This is followed by a slow decrease (region C) corresponding to a dense coating. At higher potentials (550–650 mV) processes proceed at such a high rate that the appearance of primary nuclei, their growth, blocking and secondary nucleation occurs within a very short period of time, followed by a steady current value, Fig. 8 and Fig. 9.

3.3. *Surface morphology*

The coating is characterized by its brightness at potentials above 480 mV in the presence of additive. An attempt was made to study the effect of the latter during the formation of the macro-grains, their

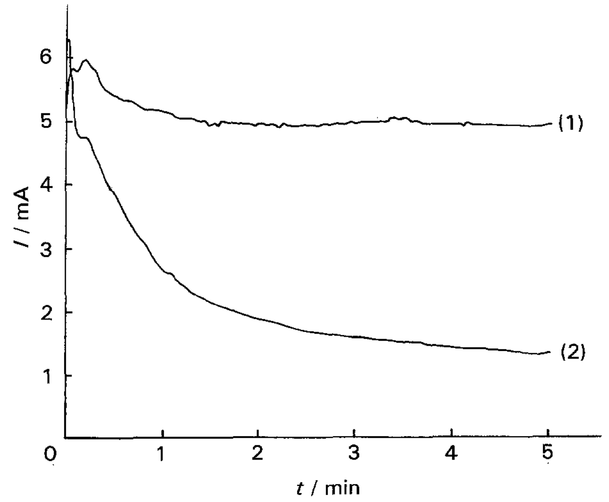

Fig. 8. Current transients at potential of 550 mV: (1) BE and (2) BE + CA.

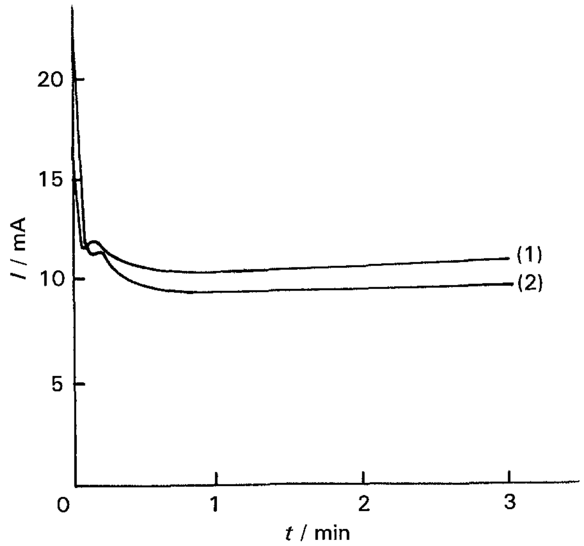

Fig. 9. Current transients at potential of 650 mV: (1) BE and (2) BE + CA.

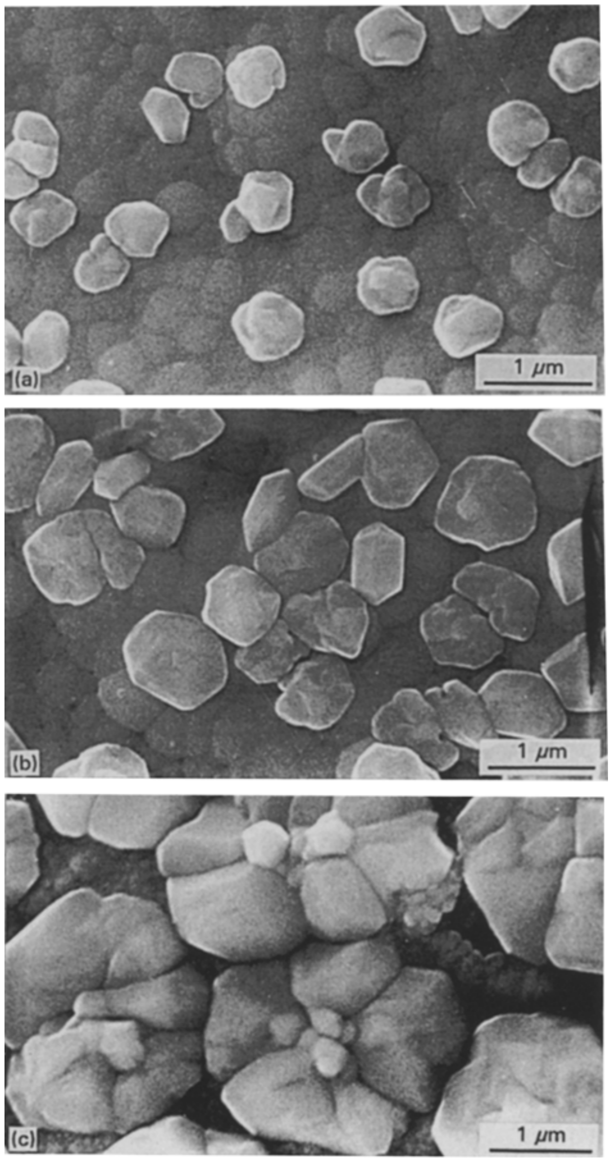

Fig. 10. SEM micrographs of the layer deposited from BE. Time of second pulse: (a) 5, (b) 10 and (c) 20 s.

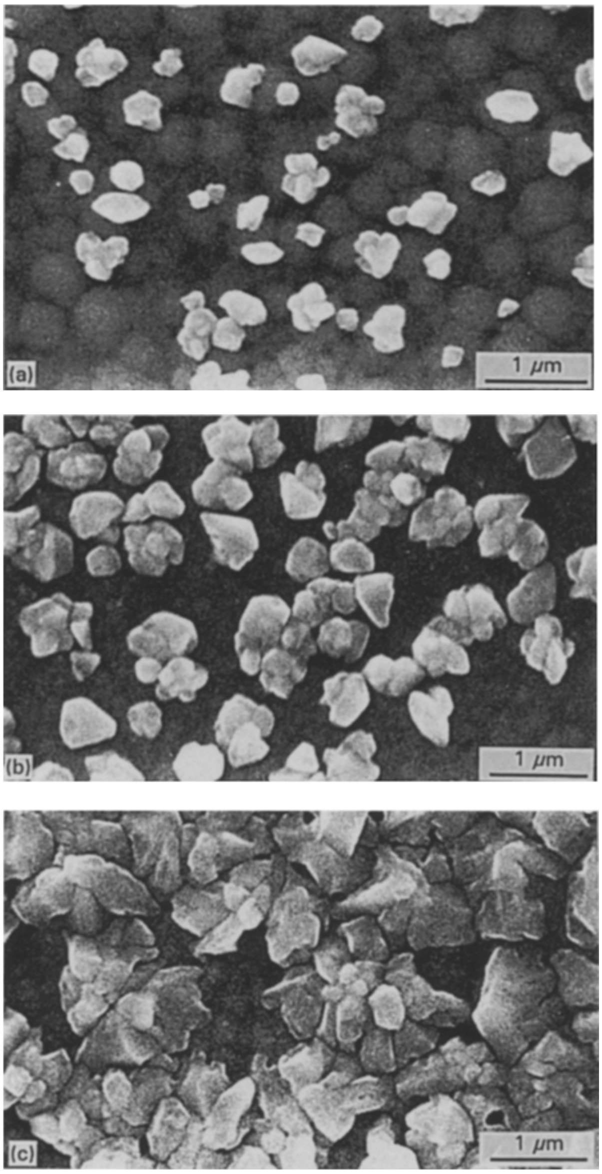

Fig. 11. SEM micrographs of the layer deposited from BE + CA. Time of second pulse: (a) 5, (b) 10 and (c) 20 s.

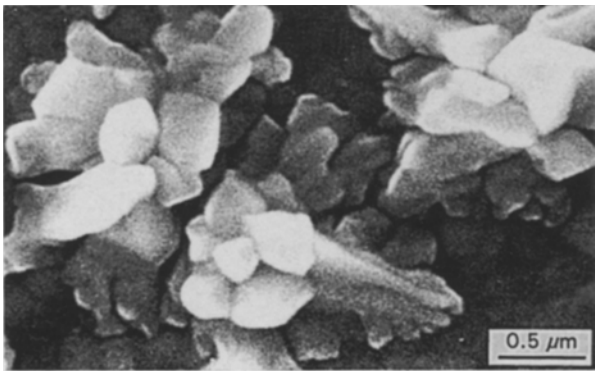

Fig. 12. Morphology of the grains from BE + CA at high magnification.

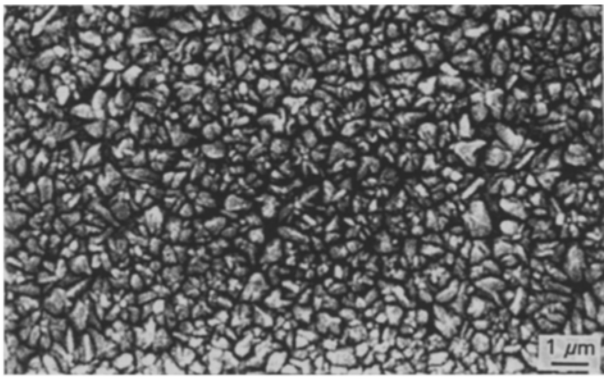

Fig. 13. Bright zone of the layer.

structure and growth by the double pulse technique [19]. The difference in the morphology is obvious, as shown by Figs 10 and 11. In the case of pure electrolyte (BE, Fig. 10) grain size is almost twice as big. Well formed grains have been observed, when the duration of η_2 is 10 s (Fig. 10(b)). After the next 10 s the intergrain boundaries are merged and the distinct geometry disappears, Fig. 10(c). The presence of additive increases polarization, enhancing fine-grained structure (Fig. 11(a)) and regular geometry is no longer observed (Fig. 11(b)). A characteristic feature, however, is the growth of smooth layers (parallel to the substrate) at the base of the grain, as shown at high magnification in Fig. 12. These crystallites overlap and form a dense film. Regardless of the appearance of secondary grown nuclei, a bright zone is observed visually (Fig. 13), confirming previous investigations [4] concerning the changes in the size of crystallites in the dense layers in the perpendicular direction, leading to the development of a lateral structure.

4. Conclusion

The separate components of the additive CA exert different effects on the I/E curves. The strongest effect is observed with the polymer component, confirming previous results by other authors. In the presence of additive two maxima are observed on the voltammetric curve. The first may be explained by the formation of a complex between the components of the additive and the cuprous ion.

The initial stages of copper layer deposition on applying the double pulse technique were investigated by SEM and it is shown that the size of separate crystallites decreases strongly in the presence of the additive, which also blocks vertical growth and favours lateral growth.

Acknowledgements

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