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The critical overpotential for copper dendrite formation

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The difference between surface roughness amplification and dendritic growth in copper electrodeposition in the limiting current density range is shown. The critical overpotential of copper dendrite growth is determined as 550 mV.

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1. Introduction

It is well known that powdery metal deposits are very loosely connected with the substrate at which they are formed. Also, they have a very high degree of dispersion, i.e., consist of very small crystallites. It was shown by Ibl [1], that metal powders are formed if the deposition process is controlled by diffusion. Atanasiu and Calusaru [2, 3] showed that powders do not form at the initial part of the limiting current plateau, but only at higher overpotentials. Despić [4] showed that the copper deposit obtained at a cathodic overpotential of 300 mV is rough, but compact, and that obtained at 600 mV is irregular, dendritic, tree-like and formed only at peaks of the original substrate irregularities. Hence, some correlation between dendritic growth and copper powder formation can be expected. The critical overpotential of copper dendrite growth has not previously been determined, and the purpose of this work was to try to determine it.

2. Experimental

Copper was deposited on the vertical platinum wire electrode (diameter 0·7 mm, length 23 mm) from 0·1 M $CuSO_4$ in 0·5 M H_2SO_4, previously plated with copper from the same electrolyte at a cathodic overpotential of 200 mV for 15 minutes. Copper was deposited at 200 mV in order to avoid hydrogen co-deposition when the electrode is taken to high overpotentials.

The potentiostatic technique was used throughout the study. The counter and reference electrodes were made of electrolytic copper. All experiments were carried out at 25·0 ± 0·1° C.

Deposition was performed at overpotentials of 300, 350, 400, 450, 500, 550, 575, 600, 625 and 650 mV and current–time relationships were recorded. It should be noted that occasional oscillations of current were observed due to hydrogen bubbles.

3. Results and discussion

Current–time relationships for copper deposition are presented in Fig. 1. The log $(I_{L,t} - I_{L,0})$ values, extracted from the data presented in Fig. 1 are plotted versus time in Fig. 2, ($I_{L,0}$ is the initial limiting diffusion current and $I_{L,t}$ the limiting diffusion current at time t). It is seen that in some intervals the log $(I_{L,t} - I_{L,0})$ are linearly dependent on time.

According to Despić *et al.* [4, 5], the amplification of surface roughness follows an exponential time dependence. The time constant of this process was shown to be a very simple function of diffusion parameters and independent of the overpotential of deposition in the diffusion-limited current range. The time constant can be obtained from the slopes of the log $(I_{L,t} - I_{L,0})$ versus t relationships. Hence, the slopes of the lines presented in Fig. 2 give the time constants of the surface roughness amplification. It can be seen that up to some overpotential the time constant is independent of the overpotential for deposition. This can be explained using the theory of ampli-

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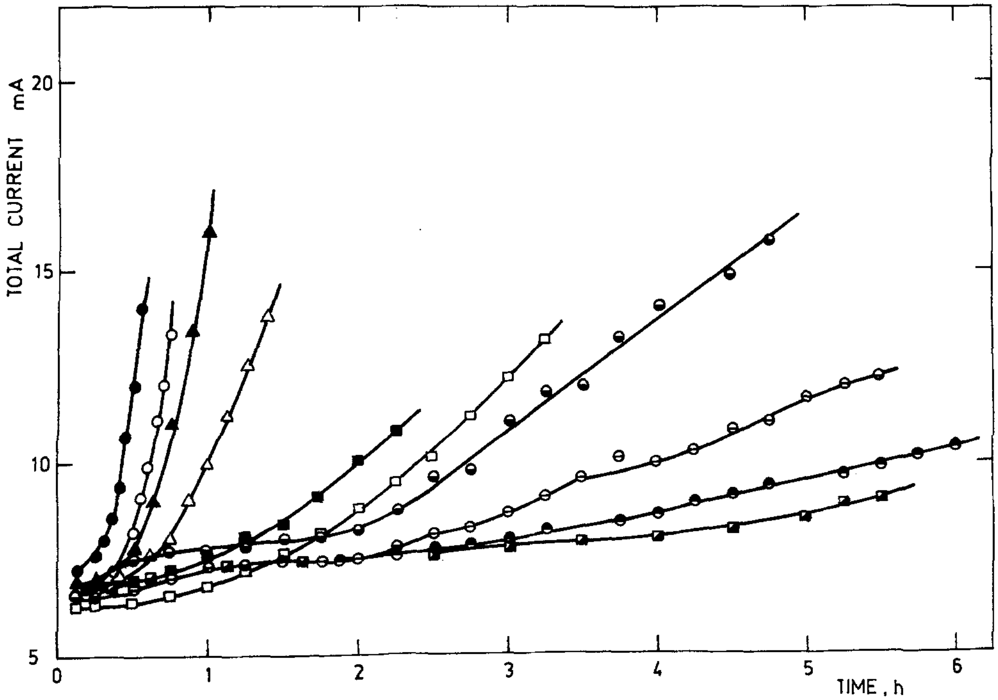

Fig. 1. Current–time relations for copper deposition at different overpotentials (mV): 650 (●), 625 (○), 600 (▲), 575 (△), 550 (■), 500 (□), 450 (◒), 400 (⊖), 350 (◓) and 300 (◩).

fication of surface irregularities [5]. If the spherical flux around the tips of protrusions can be neglected, initial current $I_{L,0}$ will be given by

$$I_{L,0} = S\theta \frac{nFDC_0}{\delta} + \frac{S(1-\theta)}{N} \sum_{i=1}^{N} \frac{nFDC_0}{\delta - h_{i,0}} \tag{1}$$

and current in time t of deposition, $I_{L,t}$, by

$$I_{L,t} = S\theta \frac{nFDC_0}{\delta} + \frac{S(1-\theta)}{N} \sum_{i=1}^{N} \frac{nFDC_0}{\delta - h_{i,t}} \tag{2}$$

where θ is the fraction of the flat surface, N the number of elevated points, $h_{i,0}$ the initial elevation at point i, $h_{i,t}$ the elevation at point i after time t of deposition, S the electrode surface area, and the other symbols have their usual meaning.

The first term in Equations 1 and 2 corresponds to the diffusion limited current on the flat part of the surface, and the second one to the average diffusion-limited current on the elevated points on the surface. The diffusion-limited current on the flat part of the surface does not vary with time, and the increase of current is due to the increase in current on the elevated points of the surface. Hence, the increase of current with time is given by

$$I_{L,t} - I_{L,0} = \frac{S(1-\theta)}{N} \sum_{i=1}^{N} \frac{nFDC_0}{\delta - h_{i,t}} - \frac{S(1-\theta)}{N} \sum_{i=1}^{N} \frac{nFDC_0}{\delta - h_{i,0}} \tag{3}$$

or

$$I_{L,t} - I_{L,0} = nFDC_0 \frac{S(1-\theta)}{N} \times \sum_{i=1}^{N} \left(\frac{1}{\delta - h_{i,t}} - \frac{1}{\delta - h_{i,0}} \right) \tag{4}$$

and

$$I_{L,t} - I_{L,0} = nFDC_0 \frac{S(1-\theta)}{N} \times \sum_{i=1}^{N} \frac{h_{i,t} - h_{i,0}}{(\delta - h_{i,0})(\delta - h_{i,t})}. \tag{5}$$

The elevation of point i varies with time according to [4, 5]

$$h_{i,t} = h_{i,0} \exp(t/\tau) \tag{6}$$

where

$$\tau = \frac{\delta^2}{(M/\rho)C_0 D}$$

with the assumption that $\delta \gg h_{i,0}$ and $\delta \gg h_{i,t}$. Hence, Equation 5 can be rewritten in the form

$$I_{L,t} - I_{L,0} = nFDC_0 \frac{S(1-\theta)}{N} \times \sum_{i=1}^{N} \frac{h_{i,0} \exp(t/\tau) - h_{i,0}}{\delta^2} \qquad (7)$$

or

$$I_{L,t} - I_{L,0} = A\,[\exp(t/\tau) - 1] \qquad (8)$$

where

$$A = nFDC_0 \frac{S(1-\theta)}{N\delta^2} \sum_{i=1}^{i=N} h_{i,0} \qquad (9)$$

For $\exp(t/\tau) \gg 1$ Equation 8 can be rewritten as

$$\log(I_{L,t} - I_{L,0}) = \log A + \frac{1}{2{\cdot}3}\frac{t}{\tau} \qquad (10)$$

and the same slope can be expected for the linear parts of the $\log(I_{L,t} - I_{L,0})$ versus t relationships, regardless of applied overpotential in the diffusion-limited current density range. This corresponds to the amplification of the initial surface roughness, as shown by Despić [4, Fig. 13a], in the overpotential range where dendrites do not grow. At higher overpotentials [4, Fig. 13b] deposition occurs only at the elevated peaks and exhibits clearly a dendritic character. It was shown by Barton and Bockris [6] that dendrites with optimal tip radius grow under pure diffusion and surface energy control according to

$$\frac{dh}{dt} = KC_{\text{tip}}\eta^2. \qquad (11)$$

Equation 11 gives the maximum rate of growth of a dendrite tip. C_{tip} is the ion concentration around the tip of the dendrite and the other symbols have their usual meaning. Because C_{tip} varies with the diffusion layer thickness [5, 7] according to

$$C_{\text{tip}} = C_0 \frac{h}{\delta} \qquad (12)$$

where C_0 is the bulk concentration of the copper ion and h the height of the dendrite, Equation 11 can be rewritten as

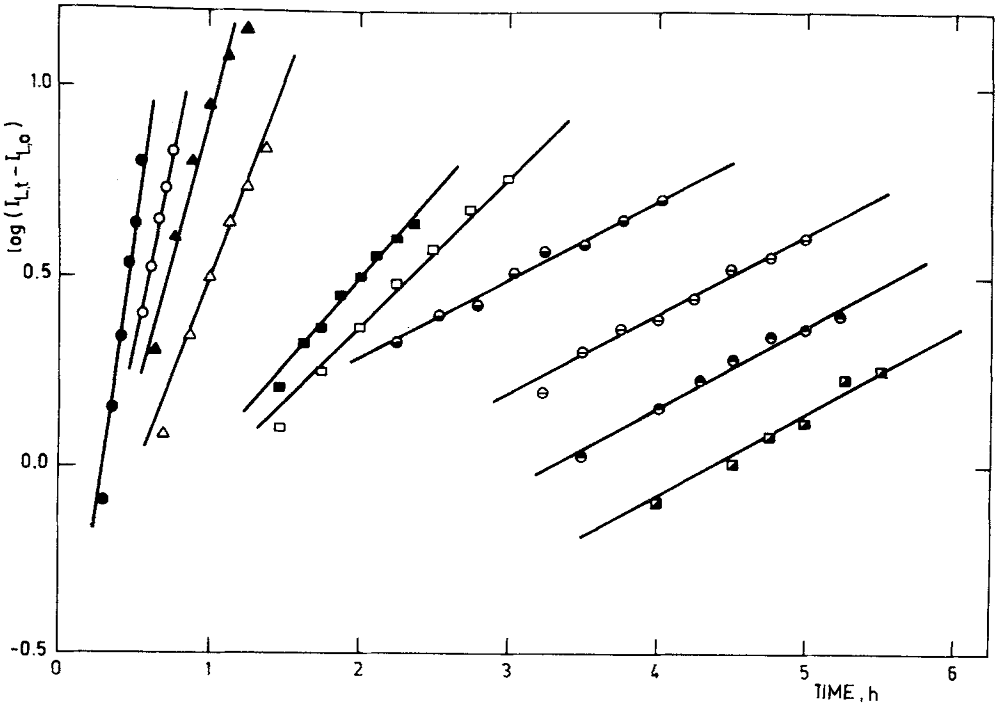

Fig. 2. Log $(I_{L,t} - I_{L,0})$ versus time relationships for copper deposition at different overpotentials (mV): 650 (●), 625 (○), 600 (▲), 575 (△), 550 (■), 500 (□), 450 (◒), 400 (⊖), 350 (◓) and 300 (◪).

$$\frac{\mathrm{d}h}{\mathrm{d}t} = K'\eta^2 h \tag{13}$$

or in the integral form

$$h = h_0 \exp(K'\eta^2 t) \tag{14}$$

where $K' = KC_0/\delta$ and h_0 is the initial height of the surface irregularity. Hence, because of dendrite propagation the current density of the tip, i_{tip}, as a function of time will be given by

$$i_{\mathrm{tip}} = k\eta^2 h_0 \exp(K'\eta^2 t) \tag{15}$$

where k is a constant,

The current densities at other points will be proportional to the tip current density for dendrite growth with a constant topography of the growing surface [6] and total current, i_{t}, on all the dendrite surface can be written as

$$i_{\mathrm{t}} = k' i_{\mathrm{tip}}. \tag{16}$$

This reasoning is valid if the optimal tip radius growth is faster than the change of ion concentration around the tip of the growing dendrite, because the optimal tip radius depends on the ion concentration for constant overpotential of deposition. Barton and Bockris [6] showed, that in this case the diffusion equations for a stationary sphere can be used. Hence, the above approximation is appropriate.

With the assumption that the number of dendrites with non-optimal tip radius can be neglected compared to the number of those with optimal tip radius it can be shown that

$$\log(I_{\mathrm{L},t} - I_{\mathrm{L},0}) = \log B + \log\left[\exp(K'\eta^2 t) - 1\right] \tag{17}$$

where $I_{\mathrm{L},0}$ is the total initial and $I_{\mathrm{L},t}$ the total current at time t and

$$B = \frac{1-\theta}{N} k\eta^2 \sum_{i=1}^{i=N} h_{i,0} \tag{18}$$

where N is the number of dendrites. For $\exp(K'\eta^2 t) \gg 1$ Equation 17 can be rewritten as

$$\log(I_{\mathrm{L},t} - I_{\mathrm{L},0}) = \log B + \frac{1}{2{\cdot}3} k\eta^2 t \tag{19}$$

and the slope of the linear part of the $\log(I_{\mathrm{L},t} - I_{\mathrm{L},0})$ versus t relationships will be dependent on the square of the deposition overpotential.

In order to check the validity of Equations 10

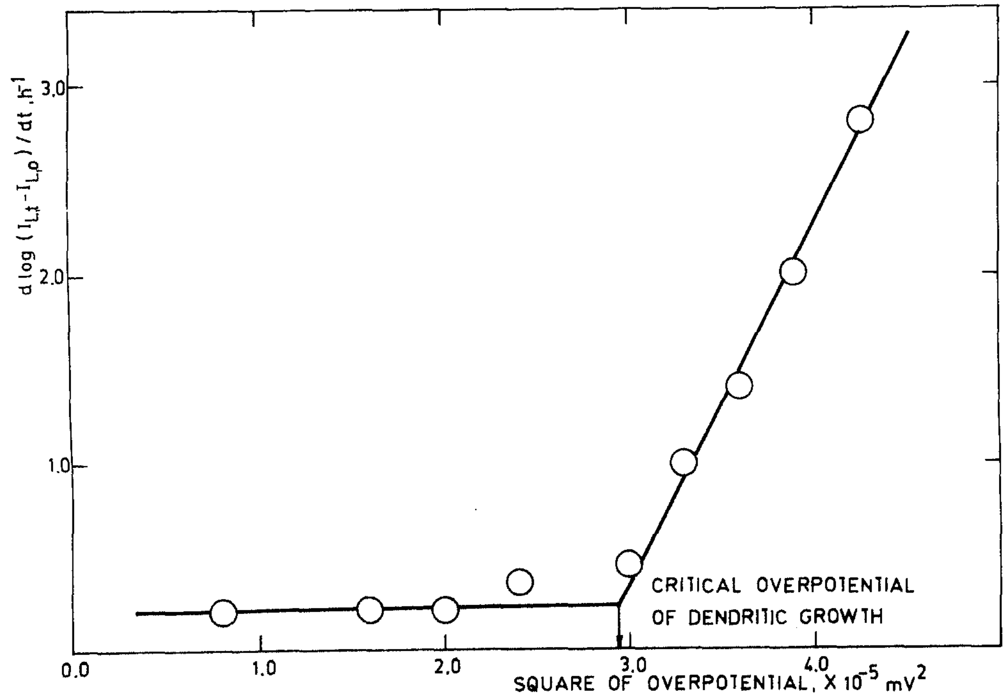

Fig. 3. The plot of slopes of lines presented in Fig. 2 as a function of square of overpotential.

and 19 d log $(I_{L,t} - I_{L,0})/dt$ extracted from the linear part of the graphs given in Fig. 2 are presented in Fig. 3 as a function of the square of the overpotential. It is seen, that ~ 550 mV can be taken as the critical overpotential for dendritic growth in this system.

The possible correlation between this overpotential and the critical overpotential of copper powder formation will be the object of further investigations.

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