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Comparison of the critical conditions for initiation of dendritic growth and powder formation in potentiostatic and galvanostatic copper electrodeposition

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Critical current densities for the initiation of dendrite growth and powder formation in potentiostatic and galvanostatic deposition are determined. Induction times for dendritic growth formation in potentiostatic and galvanostatic deposition are discussed.

Nomenclature

C_0	bulk concentration
D	diffusion coefficient
F	Faraday constant
h	height of a protrusion
h_i	height of ith protrusion
h_0	initial height of a protrusion
i	current density
i_c	current density at which dendrites appear instantaneously
i_i	minimal current density at which dendritic growth becomes possible
i_L	limiting current density
i^0	initial current density
i_0	exchange current density
k	proportionality factor
n	number of electrons
N	number of protrusions
R_t	tip radius
S	electrode surface area
S_0	initial electrode surface area
t	time
t_i	induction time
V	molar volume
δ	thickness of the diffusion layer
η	overpotential
η_c	critical overpotential of instantaneous dendritic growth
$\eta_{c,t}$	critical overpotential of dendritic growth following non-dendritic roughness amplification
η_i	critical overpotential for the initiation of dendritic growth
η_0	initial overpotential
$2.3\,\eta_0$	slope of the Tafel line
$\Delta\eta$	quantity defined by Equation 3
γ	surface tension
τ	time constant

1. Introduction

All metals which can be electrodeposited exhibit a tendency to appear in the form of powders at current densities larger than a certain critical value, i_c. This value is equal to the limiting diffusion current density in galvanostatic deposition, as shown by Hirakoso [1, 2] and Ibl [3, 4]. At the same time Kudra *et al.* [5, 6] observed that the product of the current density used and the square root of the time of powder formation t_i is a constant quantity. The time for powder formation at current densities equal to i_c and larger can be observed visually as the electrode is seen to turn suddenly from a lustrous to a black appearance. During this induction period a compact deposit is formed. Ibl and Schadegg [7] showed that at sufficiently high deposition times, powdered deposits can be obtained at all overpotentials which correspond to the limiting diffusion current plateau. It is known that the limiting diffusion current plateau covers a wide range of overpotentials, because of a large change of overpotential for extremely small changes of current density. Therefore, as pointed

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out by Calusaru [8], the formation of electrolytic powder cannot be localized at a certain point on the current density versus polarization curve by using only current density measurements. Calusaru *et al.* [8–10] showed, that there are three ranges of overpotential which can be determined from studies of deposit structure. Similar facts were reported by Russev [11] and Theis *et al.* [12]. According to Calusaru [8], there are regions of overpotential in which compact, rough and really powdered deposits are obtained. Popov *et al.* [13] showed recently that in potentiostatic deposition two critical values of overpotential can be determined: the critical overpotential for dendrite growth initiation, η_i, and the critical overpotential for powder formation, η_c. It was shown at the same time, that dendritic deposits are obtained at all overpotentials between η_i and η_c after a sufficiently long induction period, which is in agreement with the findings of Ibl and Schadegg [7]. It was also shown [8] that in potentiostatic deposition, dendritic and powdered deposits can be obtained at current densities lower than the limiting diffusion value at sufficiently long deposition times. This is not possible in the case of galvanostatic deposition. The purpose of this work is to discuss this phenomenon.

2. The statement of the problem

At a macroelectrode the minimum overpotential η_i at which dendritic growth, is possible is given by

$$\eta_i = \eta_0 \ln \frac{4i_L}{i_0} + \Delta\eta \tag{1}$$

and the minimum overpotential at which instantaneous dendritic growth is possible is given by

$$\eta_c = \eta_0 \ln \frac{i_L \delta}{i_0 h_0} + \Delta\eta \tag{2}$$

according to Popov *et al.* [13]. $\Delta\eta$ in Equations 1 and 2 is given by

$$\Delta\eta = \frac{2\gamma V}{nFR_t} \tag{3}$$

and represents the difference in the reversibile potential of the tip of the dendrite and a planar surface [14].

The relationship between overpotential and current density in mixed controlled metal electrodeposition is given by

$$\eta = \eta_0 \ln \frac{i}{i_0} \frac{1}{(1 - i/i_L)}. \tag{4}$$

Current densities i_i and i_c which correspond to η_i and η_c can be obtained by elimination of η from Equations 1, 2 and 4 as

$$i_i = \frac{4i_L \exp(\Delta\eta/\eta_0)}{1 + 4\exp(\Delta\eta/\eta_0)} \tag{5}$$

and

$$i_c = \frac{i_L (\delta/h_0) \exp(\Delta\eta/\eta_0)}{1 + (\delta/h_0)\exp(\Delta\eta/\eta_0)} \tag{6}$$

or

$$i_c = i_L \tag{7}$$

for $\delta/h_0 \gg 1$. Hence, because $\exp(\Delta\eta/\eta_0)$ cannot be significantly larger than 1 [14] it can be concluded that dendritic growth is not possible at

$$i < i_i \tag{8}$$

but growth is possible after an induction time at

$$i_i \leqslant i < i_L \tag{9}$$

and instantaneous growth is possible at

$$i \geqslant i_L \tag{10}$$

in potentiostatic deposition. The fact that dendritic growth in potentiostatic depositon is possible at $\eta < \eta_c$, and hence $i < i_L$ (regardless $i \sim i_L$), was explained by the effect of non-dendritic surface roughness amplification during the induction time of dendritic growth [13].

This effect in galvanostatic deposition will be in the opposite direction. It was shown recently by Maksimović *et al.* [15, 16] that the surface roughness amplification of a protrusion with an initial height, h_0, in galvanostatic deposition (for $t \ll \tau$) obeys the same relation as that in the case of potentiostatic deposition [17–22], i.e.

$$h = h_0 \exp(t/\tau) \tag{11}$$

where $\tau = (\delta^2/VDC_0)$, if the condition $\delta \gg h$ is satisfied. It is easy to show that for the electrode surface presented in Fig. 1 the real electrode surface area will increase with time according to

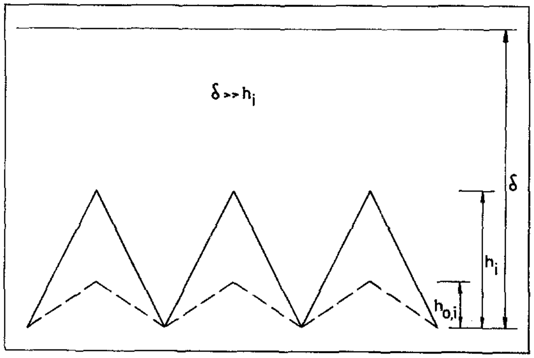

Fig. 1. Schematic representation of a rough electrode surface area.

$$S = S_0 \exp(t/\tau) \tag{12}$$

since

$$S = k \sum_{i=1}^{N} h_i \tag{12a}$$

and

$$S_0 = k \sum_{i=1}^{N} h_{0,i} \tag{12b}$$

and Equation 11. Obviously, the real current density will decrease according to

$$i = i^0 \exp(-t/\tau) \tag{13}$$

where i^0 is initial current density, and the overpotential will decrease according to

$$\eta = \eta_0 \ln \frac{i^0 \exp(-t/\tau) i_L}{i_0 \left[i_L - i^0 \exp(-t/\tau)\right]}. \tag{14}$$

Equation 14 is obtained by substitution of i from Equation 13 into Equation 4.

The critical overpotential for instantaneous dendritic growth is given by Equation 2 for protrusions with an initial height h_0. In potentiostatic deposition, an overpotential lower than η_c can belong to the limiting diffusion range. Non-dendritic surface roughness amplification in the limiting diffusion current density range does not depend on overpotential, leading to an increase of height of the protrusion. Substitution of h from Equation 11 in Equation 2 shows the change of critical overpotential of instantaneous dendritic growth with time, caused by non-dendritic surface roughness amplification as

$$\begin{aligned} \eta_{c,t} &= \eta_0 \ln \frac{i_L \delta}{i_0 h} \exp(\Delta\eta/\eta_0) \\ &= \eta_c + \eta_0 \ln \exp(-t/\tau). \end{aligned} \tag{15}$$

Hence, the overpotential of deposition remains constant and the critical overpotential of instantaneous dendritic growth decreases, and at $t = t_i$ these values become equal and dendritic growth starts. In galvanostatic conditions, non-dendritic amplification causes a decrease in the critical overpotential for dendritic growth according to Equation 15, but at the same time the overpotential of deposition decreases according to Equation 14. The time t_i in which these two overpotentials become equal can be obtained by elimination of η from Equations 14 and 15 as

$$t_i = -2.3\,\tau \log \frac{i_L}{i^0} \tag{16}$$

if $\delta \gg h_0$. Hence, $t_i = 0$ for $i^0 = i_L$ and instantaneous dendritic growth is possible at $i^0 < i_L$, for $t_i < 0$ dendritic growth is not possible. In this way the induction period for the dendritic growth becomes equal to the transition time.

3. Experimental procedure

Copper was deposited potentiostatically and galvanostatically on to a vertical stationary platinum wire electrode. The counter and reference electrodes were made of electrolytic copper. The platinum electrode was previously electroplated with copper in a quantity which corresponded to 3.0 mA h cm^{-2} at an overpotential of 200 mV in order to avoid hydrogen co-deposition during coverage of the platinum substrate with copper which occurs at higher overpotentials.

Deposition was carried out from 0.2 mol dm^{-3} $CuSO_4$ in 0.5 mol dm^{-3} H_2SO_4 at room temperature in an open cell. The solution was prepared from reagent grade chemicals and distilled water. The limiting diffusion current was determined in each experiment potentiostatically. Deposition was performed at current densities equal to 0.7 i_L, 0.95 i_L and 1.1 i_L in galvanostatic deposition. In the potentiostatic experiments the potentials were selected so that the initial current densities had these values. Microphotographs of the electrode were made at a magnification of x 20.

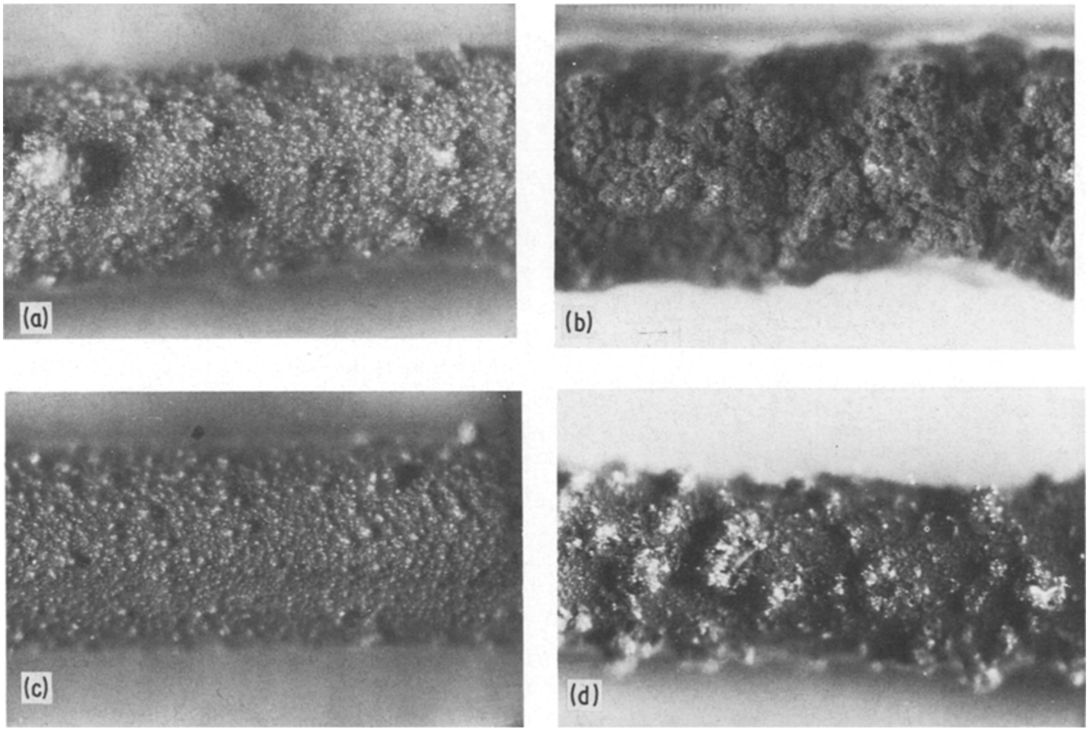

Fig. 2. Photomicrographs of copper deposits. (a) Potentiostatic deposition, initial current density 0.7 i_L, deposition time 210 min. (b) Potentiostatic deposition, initial current density 1.1 i_L, deposition time 15 min. (c) Galvanostatic deposition, current density 0.7 i_L, deposition time 210 min. (d) Galvanostatic deposition current density 1.1 i_L, deposition time 15 min.

4. Results and discussion

Copper deposits obtained potentiostatically and galvanostatically at initial current densities, 0.7 i_L and 1.1 i_L are presented in Fig. 2. In both cases a non-dendritic deposit is obtained at 0.7 i_L and a dendritic one at 1.1 i_L. In this way the validity of Equations 8, 10 and 16 is shown, because the overpotential corresponding to 0.7 i_L is 200 mV and the overpotential corresponding to 1.1 i_L is 750 mV ($\eta_i = 260$ mV and $\eta_c = 660$ mV in this system [13]).

Deposits obtained potentiostatically and galvanostatically at an initial current density of 0.95 i_L (corresponding overpotential = 500 mV) for different deposition times are shown in Fig. 3. Corresponding log (current)–time and overpotential–time relationships are presented in Figs 4 and 5, respectively. The induction time for dendritic growth in this system is about 28 min, as seen from Fig. 4 using the procedure described earlier [13]. In the galvanostatic case, the overpotential decreases with increasing deposition time as predicted by Equation 14. Deposits obtained in potentiostatic (Fig. 3a) and galvanostatic (Fig. 3b) cases are similar in morphology for a deposition time less than the induction time for dendritic growth. At deposition times greater than the induction time of dendritic growth during potentiostatic deposition, a change of deposit from non-dendritic to dendritic can be observed (Fig. 3c, e). In the galvanostatic case (Fig. 3d, f) the morphology of deposits remains constant in quality, i.e. surface roughness changes according to the mechanism of non-dendritic amplification. After 55 min of deposition, as from Fig. 5, the overpotential becomes less than the critical overpotential of dendritic growth initiation and further change in morphology is not possible. These facts are in a good agreement with Equations 9 and 16. In this way the necessity of a current density greater than the limiting diffusion current [23–

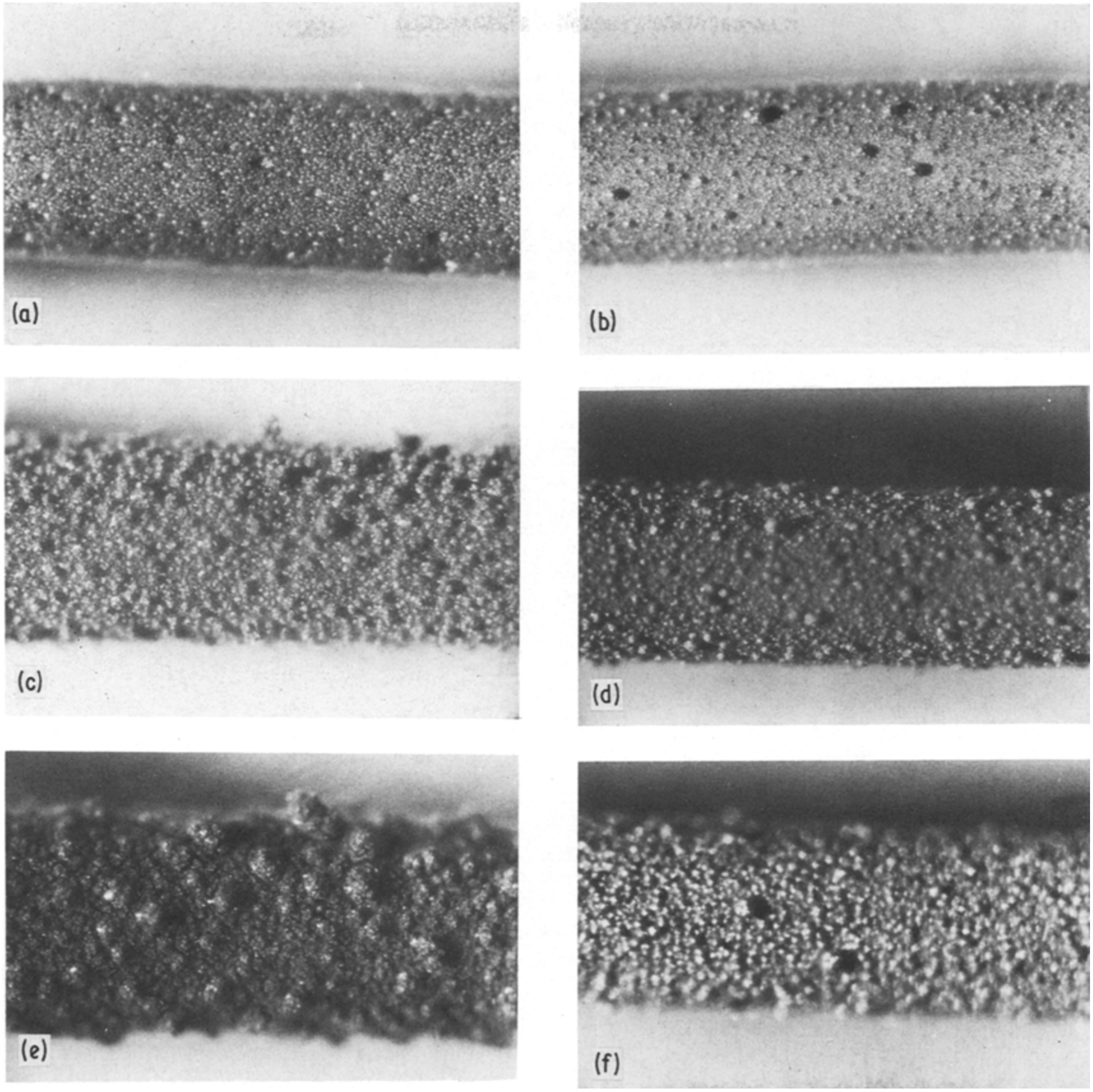

Fig. 3. The same as in Fig. 2, but for an initial current density 0.95 i_L. (a) Potentiostatic deposition, deposition time 20 min. (b) Galvanostatic deposition, deposition time 20 min. (c) Potentiostatic deposition, deposition time 40 min. (d) Galvanostatic deposition, deposition time 40 min. (e) Potentiostatic deposition, deposition time 60 min. (f) Galvanostatic deposition, deposition time 60 min.

26] in galvanostatic powder deposition is explained.

It was also pointed out by Calusaru [8] that the critical value of overpotential does not depend strongly on the concentration of the species in solution. This can be demonstrated in the following way. It is known that for copper 2.3 $\eta_0 =$ 120 mV dec^{-1} and $i_0 \sim C_0^{0.75}$ [27]. On the other hand, it is known that in metal electrodeposition under natural convection [28], i_L varies with concentration according to

$$i_L \sim C_0^{1.25}. \tag{17}$$

Substitution of these values into Equations 1 and 2 and further rearranging gives

$$\eta_i = \text{constant} + 60 \log C_0 + \Delta\eta \tag{18}$$

and

$$\eta_c = \text{constant}' + 30 \log C_0 + \Delta\eta. \tag{19}$$

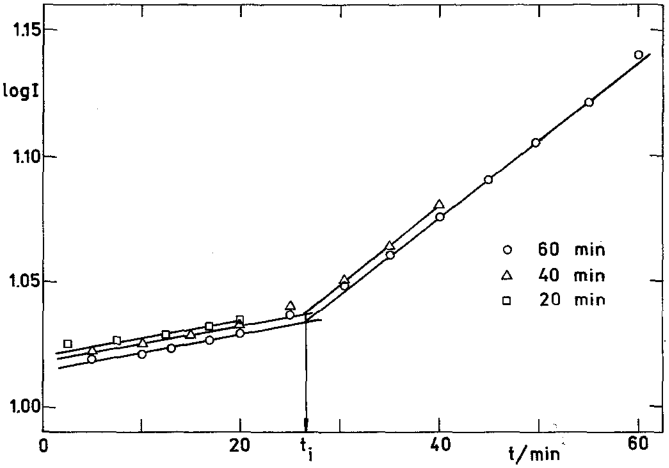

Fig. 4. Log *i* as a function of time in potentiostatic copper deposition.

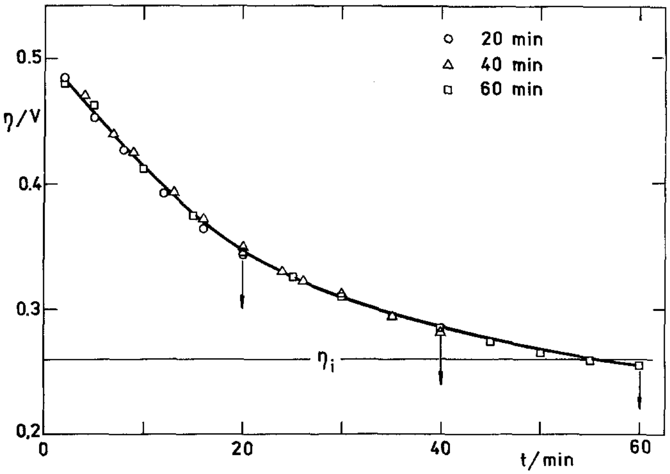

Fig. 5. η as a function of time in galvanostatic copper deposition.

It is obvious that Equations 18 and 19 explain the data of Calusaru [8] well.

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