

The mechanism of copper powder formation in potentiostatic deposition

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A mechanism for copper powder formation in potentiostatic deposition is proposed, and the critical overpotential of copper powder formation is determined. A good agreement between theoretical and experimental results has been obtained.

List of symbols

C_0 bulk concentration (mol cm^{-3})	t_i induction time (s)
D diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	V molar volume ($\text{cm}^3 \text{mol}^{-1}$)
F Faraday's constant (C mol^{-1})	γ surface tension (J cm^{-2})
h height of protrusion (cm)	δ thickness of diffusion layer (cm)
h_c height at which dendrites crack (cm)	η overpotential (V)
h_i height (cm)	$\eta_{c,p}$ critical overpotential of powder formation (V)
h_0 initial height of protrusion (cm)	θ fraction of flat surface
$h_{j,t}$ elevation at point j and time t (cm)	τ apparent induction time (s)
$h_{j,0}$ initial elevation at point j (cm)	
I limiting diffusion current (A)	
I_0 initial limiting diffusion current (A)	
i limiting current density (A cm^{-2})	
i_d current density on the tip of dendrite of height h (A cm^{-2})	
i_t total current (A cm^{-2})	
j number	
k proportionality factor [$\text{cm} (\text{mol cm}^{-3})^m$]	
k' constant	
M number of dendrites	
m number	
N number of elevated points	
n number of electrons	
p concentration exponent	
Q_c quantity of electricity (C)	
R gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)	
S electrode surface area (cm^2)	
T temperature (K)	
t time (s)	
t_a longest time in which approximation $\delta \gg h$ is valid (s)	

1. Introduction

It is known that a copper powder deposit consists of dendritic copper particles [1–4]. In recent years a mechanism for dendritic growth, as well as for non-dendritic surface roughness amplification in potentiostatic deposition has been proposed [5–11]. The purpose of this paper is to discuss the mechanism of copper powder formation on the basis of above theories.

2. Theoretical considerations

Dendritic growth should be initiated under the same conditions and for the same reasons that lead to the non-dendritic amplification of any surface irregularity. It should therefore be governed by the same laws as non-dendritic surface irregularity amplification [9–11]. The current density, i , on the tip of a non-dendritic surface irregularity of height h , is given by

$$i = \frac{nFDC_0}{\delta - h} \quad (1)$$

and the height of the protrusion will vary with time according to

$$h = h_0 \exp\left(\frac{VDC_0}{\delta^2} t\right) \quad (2)$$

for $\delta \gg h$.

It was recently shown [12] on the basis of earlier papers [5–7] that the current density, i_d , on the tip of the dendrite (with optimal tip radius) of height h in the diffusion layer will be given by

$$i_d = \frac{n^3 F^3 DC_0}{8\gamma RTV} \frac{h}{\delta} \eta^2. \quad (3)$$

It is seen from Equations 1 and 3 that $i > i_d$ for $h \rightarrow 0$, and the growth of a surface irregularity will obey the mechanism of non-dendritic surface roughness amplification. At a certain time the current density on the dendrite tip given by Equation 3 will be equal to the current density on the tip of a non-dendritic surface irregularity of the same height given by Equation 1. This happens when the protrusion, growing according to Equation 2 reaches a certain height h_i given by

$$h_i = h_0 \exp\left(\frac{VDC_0}{\delta^2} t_i\right) \quad (4)$$

where t_i is the induction time for dendritic growth. Hence, from Equations 1, 3 and 4 it follows

$$t_i = \frac{C_0^{-1} \delta^2}{2.3VD} \log\left(\frac{8\gamma RTV}{n^2 F^2 h_0 \eta^2}\right). \quad (5)$$

It is known that the total current for metal deposition on to a vertical surface in solution under natural convection [13] can be presented as

$$i \sim C_0^{1.25} \quad (6)$$

Several authors [14] have reported a value of the concentration exponent in Equation 6 of less than 1.25. Ibl [15] showed that for very thin wire electrodes the concentration exponent has the value of 1.17. Systematic investigations of metal deposition on to vertical plates and vertical wires [16–19] have shown that the deposition process can be described by Equation 1 only under completely isothermal conditions. For even a small temperature difference the value of the exponent in Equation 6 decreases considerably and at

sufficiently large temperature differences tends to unity. Hence, depending on temperature difference, the concentration exponent varies in the limits

$$1 < p \leq 1.25.$$

This reasoning is also valid for deposition of rough and powdered deposits [20, 21]. In this way, Equation 6 can be rewritten in the form

$$i \sim C_0^p \quad (6a)$$

and consequently

$$\delta = kC_0^{-m} \quad (6b)$$

where $m = 1 - p$. Substitution for δ from Equation 6b in Equation 5 gives

$$t_i = \frac{k^2 C_0^{-(1+2m)}}{2.3VD} \log\left(\frac{8\gamma RTV}{n^2 F^2 h_0 \eta^2}\right). \quad (7)$$

The induction time of dendritic growth was earlier determined by extrapolation of the linear phase of growth to zero height [8, 10]. It is seen from Equation 7 that $t_i = 0$ for

$$\eta_{C, h_0} = \left(\frac{8\gamma RTV}{n^2 F^2 h_0}\right)^{1/2} \quad (8)$$

where η_{C, h_0} is the value of the overpotential corresponding to the instantaneous dendritic growth of protrusion with initial height h_0 .

3. Experimental

Copper was deposited onto a vertical stationary platinum wire electrode (diameter 0.7 mm, length 23 mm) from 0.05, 0.1 and 0.2 M solutions of CuSO_4 in 0.5 M H_2SO_4 . 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 the coverage of the platinum substrate with copper at higher overpotentials.

Copper was also deposited on copper wire electrodes in some experiments. These electrodes were put in wax and metallographic samples were made by cutting and polishing in the usual manner.

The potentiostatic technique was used through this work. The counter and reference electrodes were made of electrolytic copper. All experiments were carried out at $25.0 \pm 0.1^\circ \text{C}$. Room tempera-

ture was $22 \pm 1^\circ\text{C}$. Deposition was performed at constant overpotentials of 450, 500, 525, 550, 600, 650 and 700 mV. Quantities of deposited copper corresponded to quantities of electricity of 10, 20 and 30 mA h cm⁻². Copper powder was removed by tapping the electrode. Compact copper remaining on the electrode was dissolved in HNO₃ and determined analytically by titration with EDTA [22].

4. Results and discussion

The charge corresponding to compact copper, Q_c , as a function of deposition time at different overpotentials is given in Figs. 1-3. The limiting diffusion current, I , during the non-dendritic surface roughness amplification at time t of deposition is given by [12]

$$I = S\theta \frac{nFDC_0}{\delta} + \frac{S(1-\theta)}{N} \sum_{j=1}^{j=N} \frac{nFDC_0}{\delta - h_{j,t}} \quad (9)$$

and hence the charge for deposition of compact copper by

$$Q_c = S\theta \frac{nFDC_0}{\delta} t + \frac{S(1-\theta)}{N} \sum_{j=1}^{j=N} \int_0^{t_i} \frac{nFDC_0}{\delta - h_{j,t}} dt. \quad (10)$$

The largest irregularities on the electrode are caused by the mechanical pre-treatment of the surface. In the first approximation they are the same height. This is illustrated by the micro-photograph in Fig. 4. Dendritic growth will be initiated on the tips of all these protrusions at deposition times larger than the induction time. Hence, assuming that the irregularities are of the same height and for $\delta \gg h$, Equation 10 can be rewritten in the form

$$Q_c = S\theta \frac{nFDC_0}{\delta} t + S(1-\theta) \frac{nFDC_0}{\delta} t_i \quad (11)$$

or

$$Q_c = S \frac{nFDC_0}{\delta} t_i + S\theta \frac{nFDC_0}{\delta} (t - t_i) \quad (12)$$

and

$$Q_c = I_0 t_i + \theta I_0 (t - t_i) \quad (13)$$

because

$$I_0 = S \frac{nFDC_0}{\delta} \quad (14)$$

where I_0 is the initial limiting current for $\delta \gg h$. It is seen that

$$Q_c = 0 \quad (15)$$

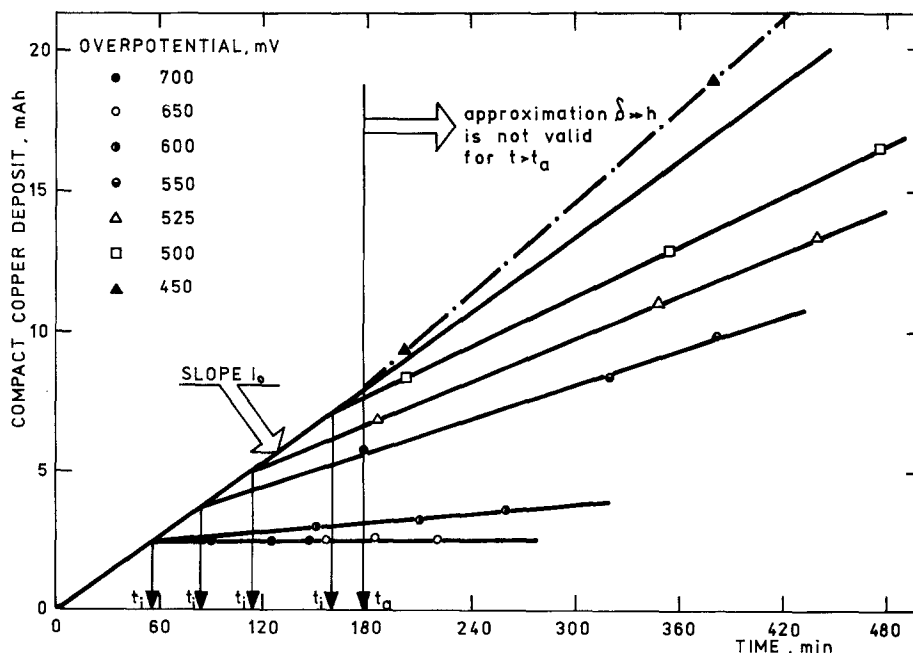


Fig. 1. The quantity of compact copper as a function of deposition time at different overpotentials. Concentration: 0.05M CuSO₄ in 0.5M H₂SO₄.

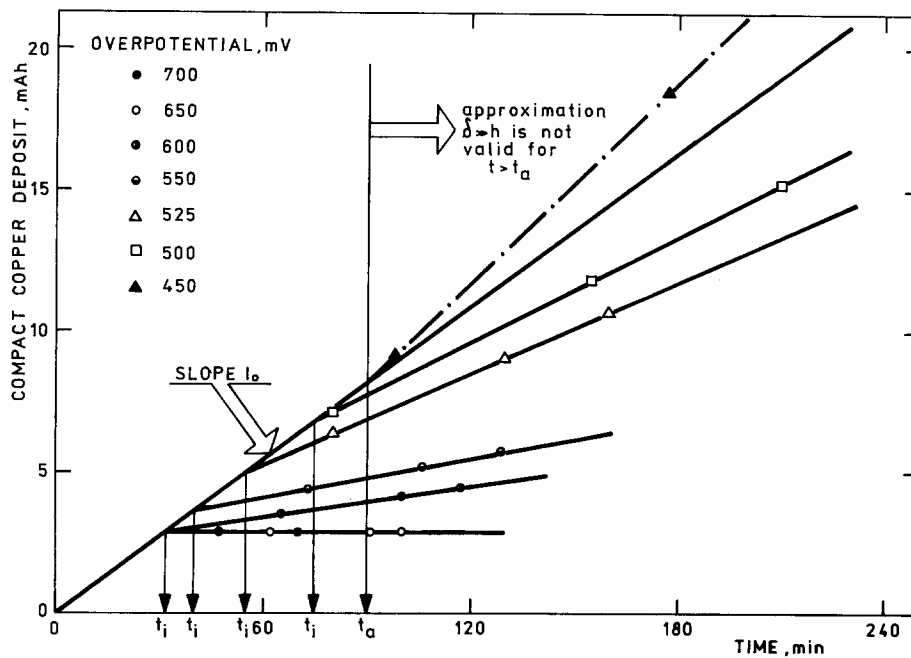


Fig. 2. The same as in Fig. 1 but for 0.1M CuSO_4 in 0.5M H_2SO_4 .

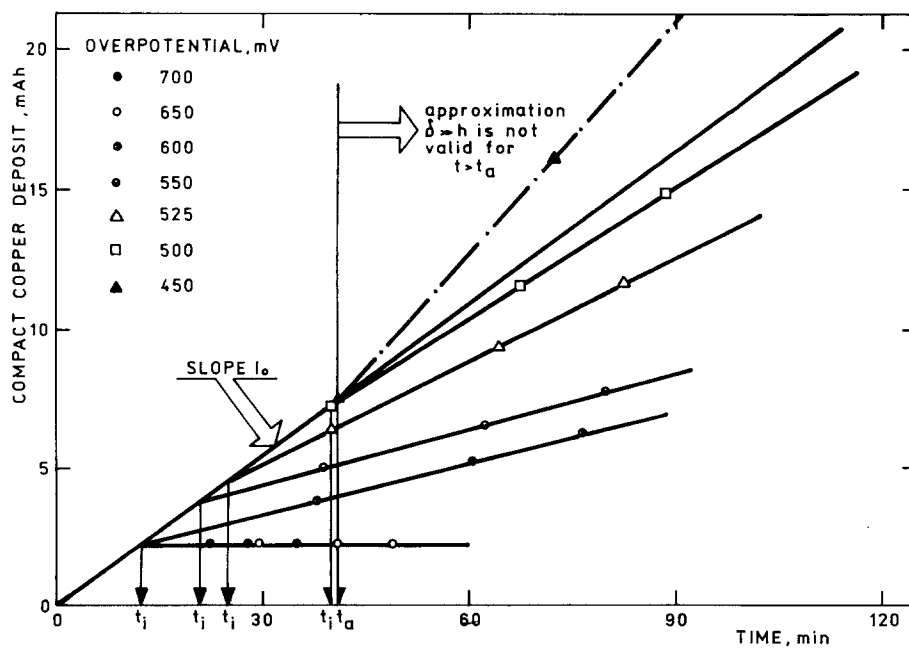


Fig. 3. The same as in Fig. 1 but for 0.2M CuSO_4 in 0.5M H_2SO_4 .

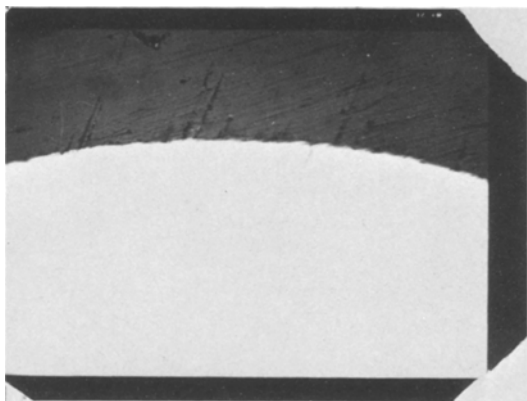


Fig. 4. Cross-section of copper wire electrode before copper deposition (× 240).

if

$$\theta = 0 \quad \text{and} \quad t_i = 0. \quad (16)$$

Hence, the critical overpotential for powder formation is a minimal overpotential at which Equations 15 and 16 are satisfied. The fraction of surface where compact copper is deposited, θ , can be determined by differentiation of Equation 13

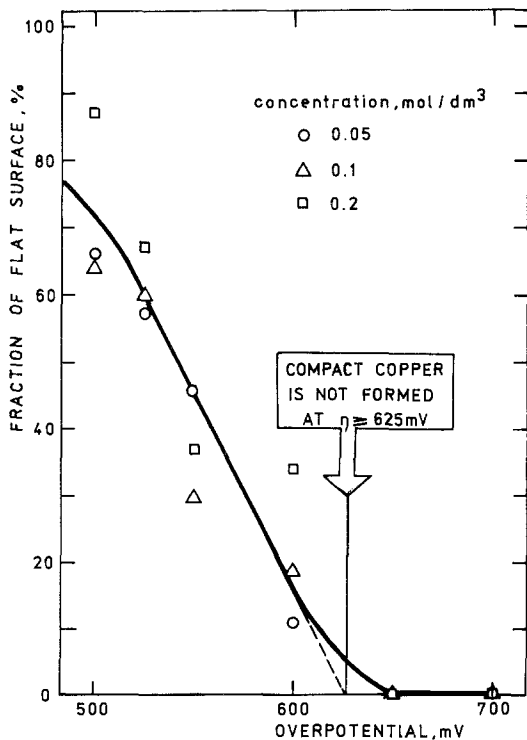


Fig. 5. Surface fraction θ , which remains flat and open to the diffusion of copper ion during deposition, as a function of overpotential.

$$\theta = \frac{1}{I_0} \frac{dQ_c}{dt} \quad (17)$$

and extracted from the slopes of the straight lines presented in Figs. 1-3. θ as a function of overpotential is shown in Fig. 5. Compact copper is not formed at $\eta \geq 625$ mV, at times larger than t_i . This is illustrated by the microphotographs in Fig. 6a and b. It is seen that for charges which correspond to an induction time of dendritic growth at 700 mV, and to 20 mA h cm^{-2} , a kind of Faradaic cage is formed by branching dendrites which prevent deposition on the original surface. At the same time and 525 mV the branching of dendrites is less pronounced and deposition on the initial electrode surface is not prevented. The value of $\theta \approx 0.65$ obtained from the slope of the Q_c-t dependence in Fig. 2 for 525 mV is close to $\theta \approx 0.5$ which can be roughly determined from Fig. 6c and d. Induction times for dendritic growth can be extracted by extrapolation of the Q_c-t dependences presented in Figs. 1-3 to the intersection point with the straight line with slope I_0 . If

$$t = t_i \quad (18)$$

Equation 13 becomes

$$Q_c = I_0 t_i. \quad (19)$$

Also from the Q_c-t dependences for deposition at an overpotential of 450 mV, the time interval in which the approximation $\delta \gg h_{j,t}$ is valid can be determined. In this case the quantity of compact copper deposit is larger than that which could be obtained with only the initial current during the same time of electrolysis. Now Equations 11-13 are not valid and the charge corresponding to compact copper should be calculated using Equation 10. The largest time, t_a , in which Equations 11-13 are valid can be obtained by extrapolation of the Q_c-t dependences to the intersection point with the straight line of slope I_0 . The mechanism of non-dendritic surface roughness amplification does not depend on overpotential. It is seen from Figs. 1-3 that for $\eta > 450$ mV, $t_i < t_a$ in all cases, and equations derived under the assumption $\delta \gg h_{j,t}$ are applicable.

Induction times extracted from Figs. 1-3 are plotted versus $\log \eta$ in Fig. 7. t_i is linear with $\log \eta$ up to some value of overpotential. At higher overpotentials t_i does not depend on $\log \eta$. In

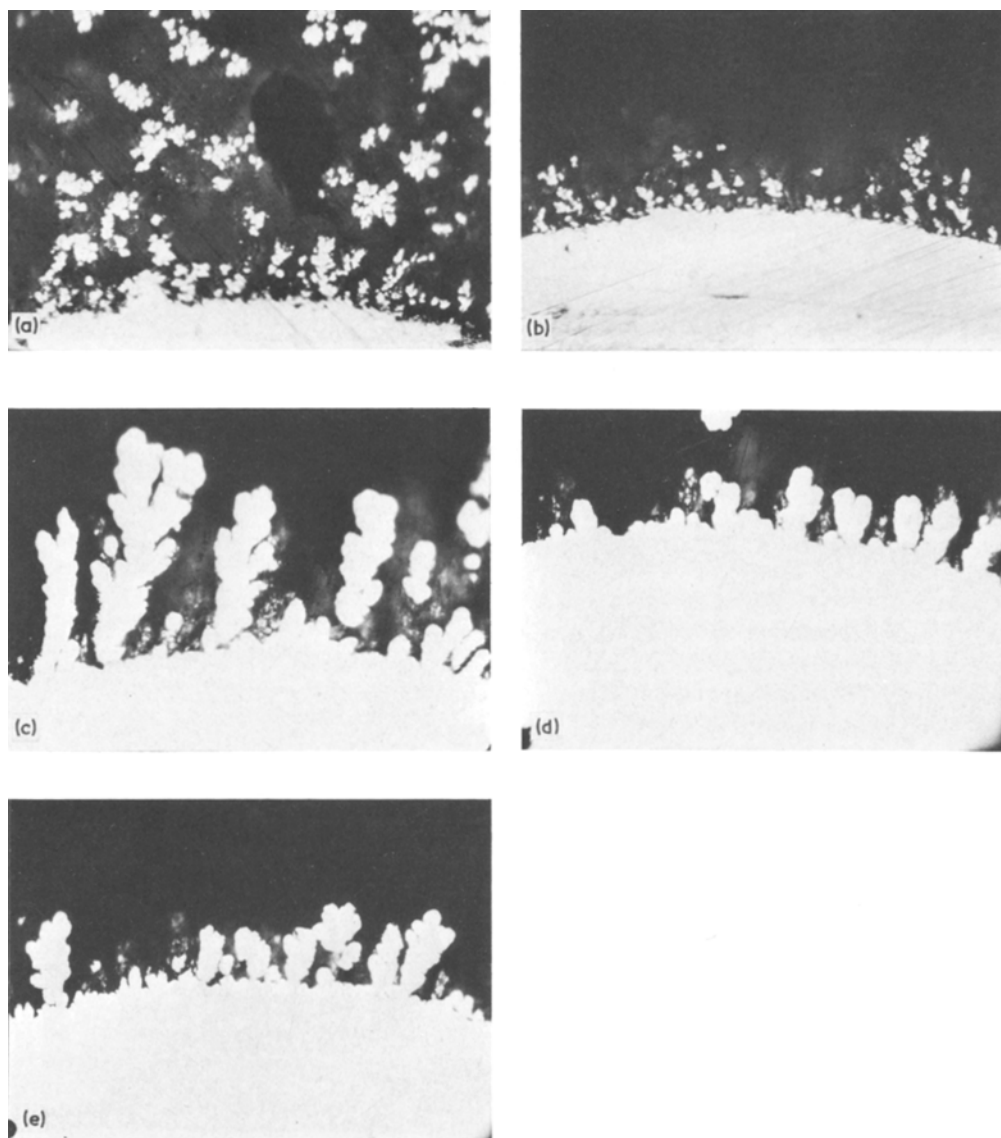


Fig. 6. Cross-sections of copper wire electrodes after deposition (a, c) and after removing of powdered deposits (b, d). Quantity of electricity 20 mA h cm^{-2} . (a, c) Overpotential 700 mV ; (b, d) overpotential 525 mV . Microphotograph (e) corresponds to deposition at 525 mV . Electrodeposition time was equal to induction time for dendritic growth ($\times 240$).

Fig. 8 the slopes of these lines are plotted versus concentration. A straight line with slope -1.10 is obtained. This slope, according to Equation 7, corresponds to $m = 0.05$. This value is expected for natural convection with a temperature difference between the surroundings and the electrolyte of $\sim 3^\circ \text{C}$ [18, 19]. The critical overpotential for instantaneous dendritic growth, i.e. powder formation, can be obtained by extrapolation of the straight lines in Fig. 7 to $t_1 = 0$, i.e. 625 mV .

$\eta_{c,p}$ does not depend on the concentration of copper ion, as predicted by Equation 8. It is seen from Fig. 7 that for 650 and 700 mV the induction times determined by the extrapolations shown in Figs. 1–3, have real values which do not depend on the overpotential. Extrapolation of the linear parts of Fig. 7 would suggest that the induction times would have zero values. It is seen from Fig. 6a and b that the copper dendrites deposited at 700 mV are not completely removed

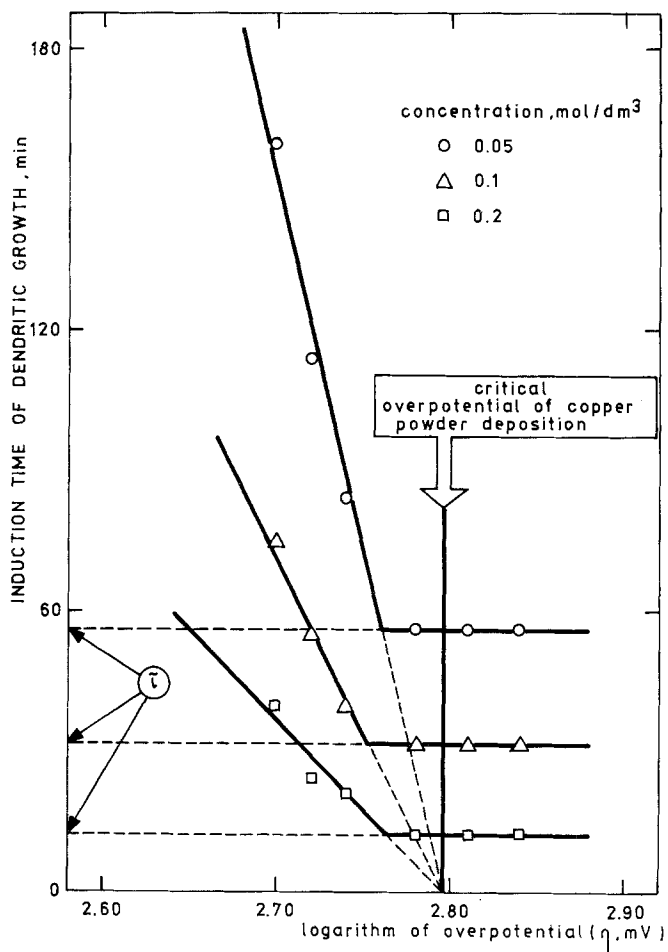


Fig. 7. Induction time for dendritic growth as a function of $\log \eta$.

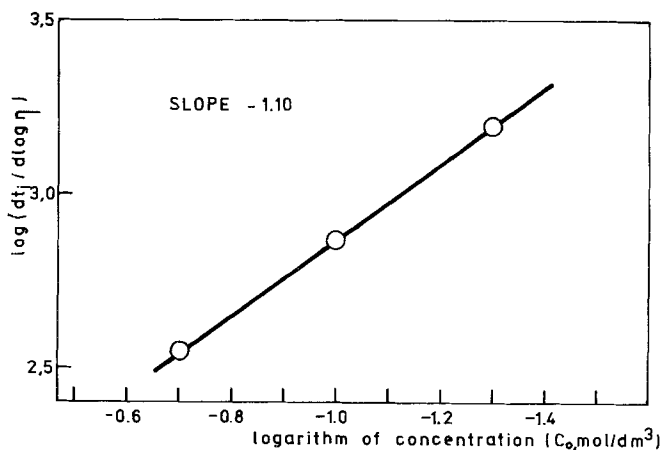


Fig. 8. The logarithm of the slopes of the lines from Fig. 6 as a function of $\log C_0$.

by tapping the electrode. If dendrites crack at approximately the same distance, h_c , from the initial electrode surface, apparent induction times of dendritic growth at 600, 650 and 700 mV can be discussed in the following way. The rate of dendrite propagation into the diffusion layer is given by

$$\frac{dh}{dt} = \frac{V}{nF} i_d \quad (20)$$

or, taking into account Equation 3

$$\frac{dh}{dt} = \frac{n^2 F^2 DC_0 \eta^2}{8\gamma RT \delta} h. \quad (21)$$

The integral form of Equation 21 is given by

$$h = h_0 \exp\left(\frac{n^2 F^2 DC_0 \eta^2}{8\gamma RT \delta} t\right) \quad (22)$$

or in the case of natural convection

$$h = h_0 \exp\left(\frac{n^2 F^2 DC_0^{1+m} \eta^2}{8\gamma RT k} t\right) \quad (23)$$

Hence, apparent induction time, τ , can be determined from Equation 23 for $h = h_c$ as follows

$$\tau = \frac{8\gamma k RT}{n^2 F^2 D \eta^2 C_0^{1+m}} \ln \frac{h_c}{h_0}. \quad (24)$$

In Fig. 9 apparent induction times of dendritic growth, extracted from the plots in Fig. 7 are presented as a function of concentration in a log-log graph. The straight line with a slope -1.06 ($m = 0.06$) confirms well Equation 24. The value of $m = 0.06$ obtained in this way is close to $m = 0.07$ determined from the slope of

the line in Fig. 8. At overpotentials at which non-dendritic amplification is followed by dendritic growth, dendrites are completely removed by tapping the electrode, as illustrated in Fig. 6c, d and e for deposition at 525 mV. Hence, in these cases the induction times extracted from the plots in Figs. 1-3 are real values and Equation 7 is directly applicable. Another proof that dendrites grow instantaneously after switching on at an overpotential of 650 or 700 mV can be given in the following way. It was shown earlier [12] that the total current i_t , on all dendrite surfaces is proportional to the current on the tip of the dendrite. Hence

$$i_t = k' \frac{n^3 F^3 DC_0 \eta^2 h_0}{8\gamma RT V \delta} \exp\left(\frac{n^2 F^2 DC_0 \eta^2}{8\gamma RT \delta} t\right) \quad (25)$$

and the total current, I , on the electrode if only dendrites are growing ($\theta = 0$) is given by

$$I = k' \frac{n^3 F^3 DC_0 \eta^2}{8\gamma RT V} \exp\left(\frac{n^2 F^2 DC_0 \eta^2}{8\gamma RT \delta} t\right) \sum_{j=1}^{j=M} h_{j,0} \quad (26)$$

where M is the number of dendrites, and $\log I$ will be linear with t . If dendritic and compact copper deposits are growing simultaneously ($\theta \neq 0$), $\log(I - I_0)$ is linear with t ; I_0 is the total initial current, as shown in a previous paper [12]. It may be noted that $\log(I - I_0)$ will also be linear with time in the case of powder formation at sufficiently large times of deposition, because of $I \gg I_0$. In the same time interval, before deposition on the flat surface is prevented

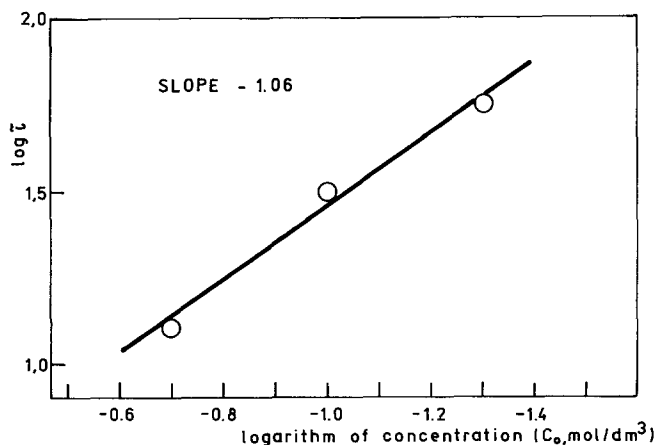


Fig. 9. The logarithm of the apparent induction times extracted from plots in Fig. 7 as a function of $\log C_0$.

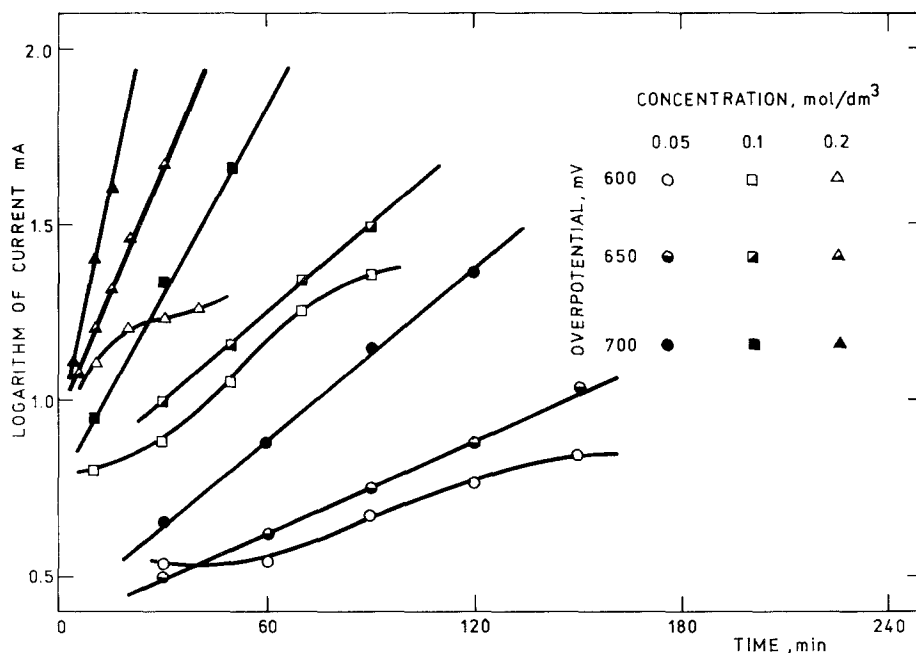


Fig. 10. The $\log I-t$ dependences for deposition from different electrolytes at different overpotentials.

by branching of the dendrites, $\log(I - I_0)$ will be linear even for powder deposition. Current-time relationships for deposition at 600, 650 and 700 mV are presented in Fig. 10 as $\log I-t$ plots. The straight lines obtained for the data at 650 and 700 mV confirm that dendrites grow from $t_i = 0$, as shown in Fig. 7. At 600 mV, $\theta > 0$ and $t_i > 0$, as can be seen from Figs. 5 and 7 respectively, and consequently $\log I$ is not linear with t . Hence a linear $\log I-t$ plot indicates that dendrites grow on the electrode instantaneously, and powder is formed (according to the definition of copper powder formation, given by Equations 15 and 16) at $\eta \geq 625$ mV. It may be noted that this value of the critical overpotential differs from the value obtained earlier by Popov *et al.* [12]. The earlier value resulted from the extrapolation of linear dependences of the dendritic growth time constant on the square of the overpotential to the value of the time constant for non-dendritic roughening. This critical overpotential (550 mV) corresponds to the inflection point on the $\theta-\eta$ dependence presented in Fig. 5 and it is to be concluded that it corresponds to the situation when dendritic growth becomes the dominant form of deposition, i.e., when all surface irregularities, after a relatively large induction time grow as dendrites.

The above discussion and derivation is valid for the formation of all metal powders.

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