

Dendritic electrocrystallization and the mechanism of powder formation in the potentiostatic electrodeposition of metals

K. I. POPOV, M. D. MAKSIMOVIĆ, J. D. TRNJANČEV

Faculty of Technology and Metallurgy, University of Beograd, Beograd, Yugoslavia

M. G. PAVLOVIĆ

Institute for Electrochemistry ICTM, University of Beograd, Beograd, Yugoslavia

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A mechanism for metal powder formation, based on the theories of dendritic growth and nondendritic surface roughness amplification in potentiostatic deposition, is proposed. The mechanism takes into account all those variables recognized in practical systems.

Nomenclature

C_0	bulk concentration
C_{tip}	concentration around the tip of dendrite
D	diffusion coefficient
F	Faraday's constant
h	height of protrusion
h_i	initial height for dendritic growth
h_0	initial height for nondendritic amplification
I	limiting diffusion current
i	limiting current density
i_d	current density on the tip of dendrite of height h
i_0	exchange current density
N	number of elevated points
n	number of electrons
R	gas constant
r	dendrite tip radius
S	electrode surface area
T	temperature
t	time
t_i	induction time
V	molar volume
γ	surface tension
δ	thickness of diffusion layer
η	overpotential
η_c	critical overpotential for powder formation
η_i	critical overpotential for dendrite growth initiation
$2.3\eta_0$	slope of Tafel line
θ	fraction on flat surface

1. Introduction

It is well known [1] that the deposition of metals at current densities larger than a certain critical value leads to formation of powdered deposits. At current densities equal to the critical value i_c and larger, an induction period is observed. During this period a compact deposit is formed. The time when powder formation begins can be observed visually as the electrode is seen to turn suddenly from a lustrous to a black appearance.

It was shown [2, 3] that, keeping other conditions constant, the product of the current density used and the square root of the powder formation time is a constant quantity. The time before powder formation coincides with the transition time. This indicates that powder formation is caused by the slow transport of depositing ions. This is proved by analysis of powder deposition at vertical electrodes in the presence of natural convection [4, 5]. Despić [6] showed that copper deposits obtained at a cathodic overpotential of 300 mV are compact; at 600 mV they are irregular, dendritic, tree-like and formed mainly at the peaks of the original substrate irregularities. This means that powders are formed at overpotentials larger than a certain critical value η_c , because both overpotentials (300 and 600 mV) correspond to the limiting diffusion current plateau [6].

It is known that metal powder formation is enhanced by decreasing the concentration of

depositing ions, increasing the concentration of the electrolyte, increasing the viscosity of the solution, decreasing the temperature and decreasing the velocity of motion of the solution [1]. Regardless of this, a comprehensive theoretical explanation of these facts, i.e. a mechanism for powder formation, is apparently not yet available. The growth of the powder particles should probably be governed by the same laws as the amplification of surface roughness and the growth of dendrites [1]. In recent years a quantitative mechanism for dendritic growth [1, 7–9], as well as for nondendritic surface roughness amplification [1, 6, 9–11], has been proposed. Hence, it is to be expected that the mechanism of powder formation can be deduced on the basis of the above theories.

The yield of dendritic deposit varies with the overpotential of deposition [12–14]. Dendrites are not formed at overpotentials smaller than a certain value η_i . Increasing overpotential leads to an increase in the yield of dendritic deposit up to the overpotential at which all metal is deposited in the dendritic form. The overpotential η_c , at which compact metal is not formed and dendritic growth starts without an induction time, was earlier defined as the critical overpotential of powder formation [14].

Considering the dendritic electrocrystallization of zinc, Despić and Purenović [12] obtained η_i and η_c from a plot of $1/t_i$ against η . The induction time of dendritic growth was obtained by extrapolation of the linear phase of growth to zero height. Popov *et al.* [14, 15] assumed that the induction time of dendritic growth can be determined as the time in which the current density on the tip of the dendrite becomes equal to the limiting current density on the tip of a nondendritic protrusion of the same height inside the diffusion layer.

In our first paper [15] we pointed out that η_i can be determined from I - t dependences on the basis of the transformation of the growth mechanism inside the diffusion layer. In our second paper [14], we proposed the method of determination of the time, in which the approximation $\delta \gg h$ is valid was proposed, as well as a method of determination of the induction time of dendritic growth. Also an attempt has been made to determine η_c . In both cases [14, 15] the Barton–Bockris [7] approximation has been used to relate

overpotential and current density on the tip of the dendrite with optimal tip radius.

The purpose of the present paper is to give a more rigorous treatment of the problem, based on the Barton–Bockris model [7] extended to the Tafel region of overpotential by Diggle *et al.* [8].

2. Experimental

Copper and cadmium were deposited on a vertical, stationary, platinum-wire electrode (diameter 0.7 mm; length 24 mm) from 0.2 M CuSO_4 and 0.1 M CdSO_4 respectively in 0.5 M H_2SO_4 . The platinum electrode was previously electroplated with copper or cadmium, in a quantity which corresponds to 3.0 mA h cm^{-2} at overpotentials of 200 and 20 mV, respectively, in order to avoid hydrogen co-deposition during the covering of the platinum substrate at higher overpotentials.

The potentiostatic technique was used. The counter and reference electrodes were made of electrolytic copper and cadmium. All experiments were carried out at $22 \pm 1^\circ \text{C}$. Copper and cadmium were also deposited on a steel wire plated with copper from a copper pyrophosphate bath and on copper wire in some experiments. These electrodes were put in wax and metallographic samples were made by cutting and polishing in the usual manner. Photomicrographs were made using a magnification of $150\times$.

3. Results and discussion

Typical log (current)–time relationships obtained in this work are presented in Figs. 1 and 2. It is seen that each graph consists of two linear parts. The slope of the first part does not depend to any extent on overpotential and the slope of the second depends on overpotential. The limiting diffusion current I during the nondendritic surface roughness amplification is given by [14]

$$I = S\theta \frac{nFDC_0}{\delta} + \frac{S(1-\theta)}{N} \sum_{j=1}^{j=N} \frac{nFDC_0}{\delta - h_j}. \quad (1)$$

The height of each protrusion h_j inside the diffusion layer grows according to [1, 11] as

$$h_j = h_{0j} \exp(VDC_0 t / \delta^2) \quad (2)$$

if $\delta \gg h$. Equation 1 can be rewritten in the form

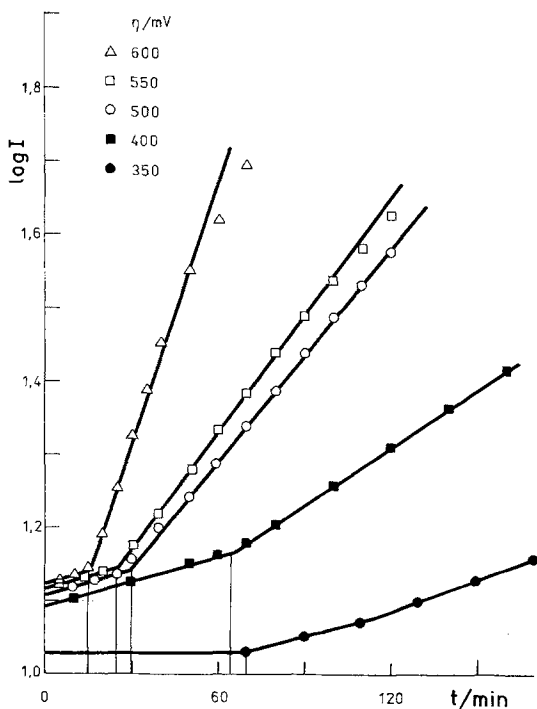


Fig. 1. Log I as a function of time for copper deposition.

$$\ln I = \ln \left(S\theta \frac{nFDC_0}{\delta} + \frac{S(1-\theta)}{N} \times \sum_{j=1}^{j=N} \frac{nFDC_0}{\delta - h_{0j} \exp(VDC_0 t/\delta^2)} \right) \quad (3)$$

It is easy to show that

$$\frac{d \log I}{dt} = \frac{VDC_0 (1-\theta)}{2.3 \delta^3 N} \sum_{j=1}^{j=N} h_{0j} \quad (4)$$

for $t \rightarrow 0$ if $\delta \gg h_{0j}$. Hence, the initial slope of the $\log I-t$ plot does not depend on overpotential as confirmed in Figs. 1 and 2.

The overpotential and the current density i_a on the tip of the dendrite [8] are related by

$$i_a = i_0 \frac{C_{tip}}{C_0} \exp \left(\frac{\eta - \Delta\eta}{\eta_0} \right) \quad (5)$$

where

$$\Delta\eta = \frac{2\gamma V}{nFr} \quad (6)$$

It is known that at sufficiently low values of i_0 there is a high possibility of the appearance of a protrusion with a radius in the required range for dendritic growth [1]. Hence it can be taken that the current density at the dendrite tip will be given by Equation 5 for all surface irregularities with $h \geq h_i$.

The concentration around the tip of the dendrite which grows inside the diffusion layer [8] is given by

$$C_{tip} = C_0 h/\delta \quad (7)$$

and Equation 5 can be rewritten in the form

$$i_a = i_0 (h/\delta) \exp [(\eta - \Delta\eta)/\eta_0]. \quad (8)$$

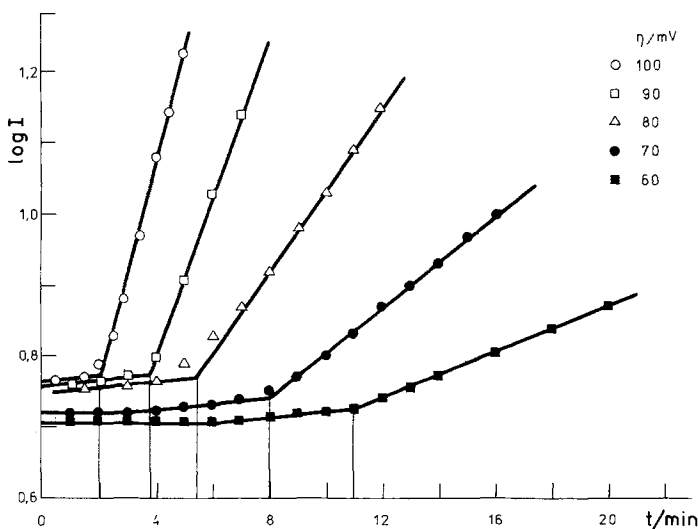


Fig. 2. Log I as a function of time for cadmium deposition.

The rate of propagation of the tip of the dendrite is given by

$$\frac{dh}{dt} = \frac{V}{nF} i_d = \frac{V h i_0}{nF \delta} \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right) \quad (9)$$

or

$$h = h_i \exp\left[\frac{V i_0 t}{nF \delta} \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right)\right] \quad (10)$$

Substitution of h from Equation 10 in Equation 8 gives

$$i_d = i_0 \frac{h_i}{\delta} \left\{ \exp\left[\frac{V i_0 t}{nF \delta} \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right)\right] \right\} \times \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right) \quad (11)$$

Assuming that the current on each dendrite is proportional to the tip current density, the total current is given by

$$I = K \frac{i_0}{\delta} \left\{ \exp\left[\frac{V i_0 t}{nF \delta} \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right)\right] \sum_{j=1}^{j=N} h_{i,j} \right\} \times \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right) \quad (12)$$

and

$$\ln I = \ln A + \frac{V i_0 t}{nF \delta} \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right) + \frac{\eta - \Delta\eta}{\eta_0} \quad (13)$$

where

$$A = K \frac{i_0}{\delta} \sum_{j=1}^{j=N} h_{i,j} \quad (14)$$

Hence

$$\frac{d \log I}{dt} = \frac{V i_0}{2.3 nF \delta} \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right) \quad (15)$$

and

$$\log \frac{d \log I}{dt} = \log \frac{V i_0}{2.3 nF \delta} - \frac{\Delta\eta}{2.3 \eta_0} + \frac{\eta}{2.3 \eta_0} \quad (16)$$

It is obvious that Equations 8–10 are valid if the rate of propagation of the dendrite tip is much larger than the rate of propagation of the flat sur-

face. It is seen that, if the rate of propagation of the flat surface can be neglected, the slope of $\log I$ versus t will be a function of overpotential. It is obvious that the intersection point of the two linear dependences determines the induction time of dendritic growth as shown in Figs. 1 and 2.

It was pointed out earlier [1] that the current density i on the tip of a nondendritic surface irregularity is given by

$$i = \frac{nFDC_0}{\delta - h} \quad (17)$$

if the spherical flux around the tip can be neglected or

$$i = \frac{nFDC_0}{\delta} \quad (18)$$

for $\delta \gg h$.

The height of a nondendritic protrusion varies with time according to Equation 2. It is seen from Equations 17, 18 and 8 that $i > i_d$ for $h \rightarrow 0$ and so the growth of surface irregularity will obey the mechanism of nondendritic surface roughness amplification. At a certain time the current density on the dendrite tip (given by Equation 8) will be equal to the current density on the tip of the nondendritic surface irregularity of the same height, given by Equation 17 or by Equation 18 for $\delta \gg h$. This happens when a protrusion growing according to Equation 2 reaches a height h_i given by

$$h_i = h_0 \exp\left(\frac{VDC_0}{\delta^2} t_i\right) \quad (19)$$

where t_i is the induction time of dendritic growth. Hence one can write, on the basis of Equations 8, 17, 18 and 19,

$$\frac{nFDC_0}{\delta} = \frac{i_0 h_0}{\delta} \exp\left(\frac{VDC_0}{\delta^2} t_i\right) \exp\left(\frac{\eta - \Delta\eta}{\eta_0}\right) \quad (20)$$

and

$$t_i = \frac{2.3 \delta^2}{VDC_0} \log \frac{nFDC_0}{i_0 h_0} - \frac{\delta^2}{VDC_0} \frac{\eta - \Delta\eta}{\eta_0} \quad (21)$$

It is obvious that $t_i = 0$ for

$$\eta_c = 2.3 \eta_0 \log \frac{nFDC_0}{i_0 h_0} + \Delta\eta \quad (22)$$

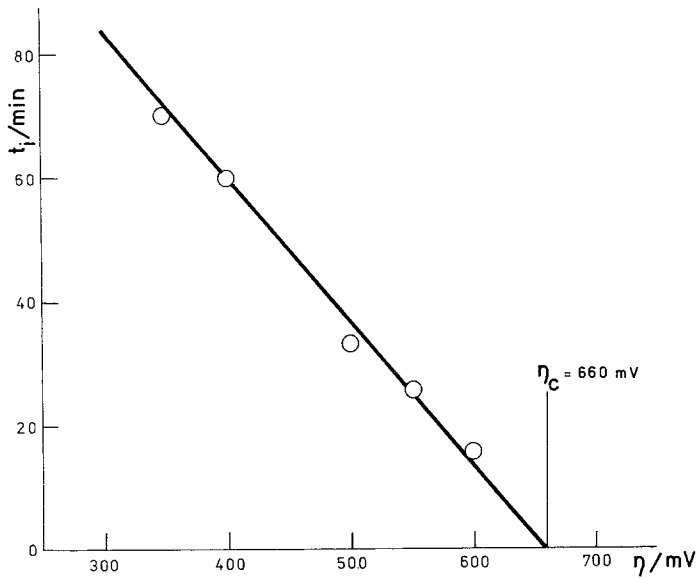


Fig. 3. Induction time as a function of overpotential for copper deposition.

This means that protrusions with initial height h_0 for $\eta \geq \eta_c$ will grow as dendrites immediately.

Induction times for dendritic growth extracted from the graphs in Figs. 1 and 2 are presented as a function of overpotential in Figs. 3 and 4. Straight lines on these figures confirm Equation 21 and the critical overpotentials of powder formation are obtained by extrapolation to zero value of the induction time.

The critical overpotential for powder formation in the systems where the current to the macro-

electrode is diffusion controlled in the steady state at all overpotentials [7] can be obtained in the same way. For sufficiently high i_0 , the current density to the macroelectrode is given by

$$i = \frac{(nF)^2 DC_0}{RT\delta} \eta \quad (23)$$

and the current density on the tip of the dendrite by

$$i_d = \frac{(nF)^3 DC_0 h_0}{8\gamma RT\delta} \eta^2 \quad (24)$$

taking into account Equation 7. It is seen that $i = i_d$ for

$$\eta_c = \frac{8\gamma V}{nFh_0} \quad (25)$$

The value of the lowest overpotential at which dendritic growth is possible can be evaluated in the following way. For $\delta > h$, but $\delta \not\gg h$, the transformation of growth mechanism will happen if

$$\frac{nFDC_0}{\delta - h} = i_0 \frac{h}{\delta} \exp \frac{\eta - \Delta\eta}{\eta_0} \quad (26)$$

for the mixed control and

$$\frac{(nF)^2 DC_0}{RT(\delta - h)} \eta = \frac{(nF)^3 DC_0 h}{8\gamma RT\delta V} \eta^2 \quad (27)$$

for pure surface energy and diffusion control. The solutions of Equations 26 and 27 are given by

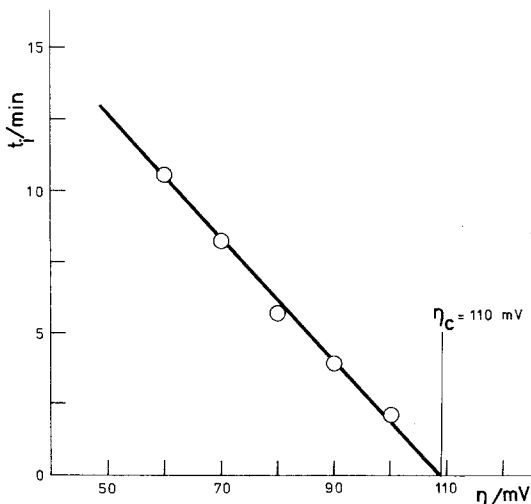


Fig. 4. Induction time as a function of overpotential for cadmium deposition.

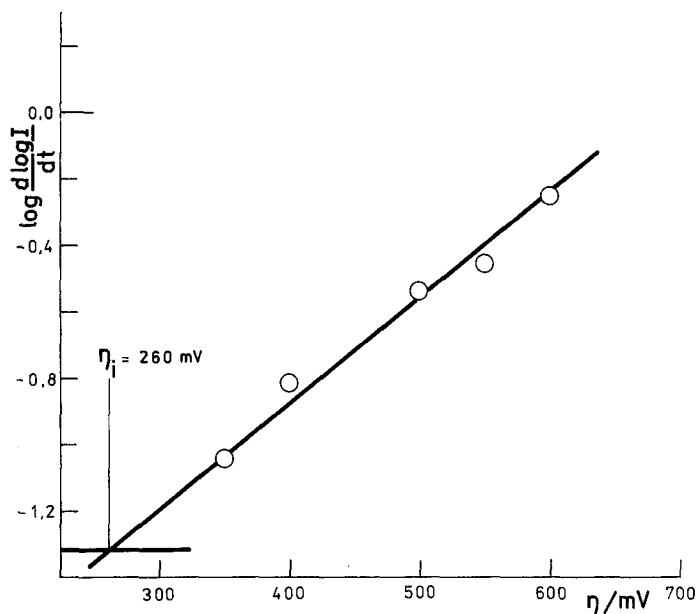


Fig. 5. $\log(d \log I / dt)$ as a function of overpotential for copper dendrite deposition.

$$2h_{1/2} = \delta \pm \left(\delta^2 - \frac{4nFDC_0\delta}{i_0 \exp[(\eta - \Delta\eta)/\eta_0]} \right)^{1/2} \quad (28)$$

at overpotentials

$$\eta_i = 2.3 \eta_0 \log(4nFDC_0/i_0\delta) + \Delta\eta \quad (31)$$

and

$$\eta_i = \frac{32\gamma V}{nF\delta} \quad (32)$$

$$h_{1/2} = \frac{1}{2} \delta \pm \frac{1}{2} \left(\delta^2 - \frac{32\gamma\delta V}{nF\eta} \right)^{1/2} \quad (29)$$

Equation 30 gives the maximum height of protrusion at which the mechanism of growth can be transformed, while Equations 31 and 32 give the corresponding values of overpotential.

It is seen that

$$h_1 = h_2 = \delta/2 \quad (30)$$

The critical overpotential of dendritic growth

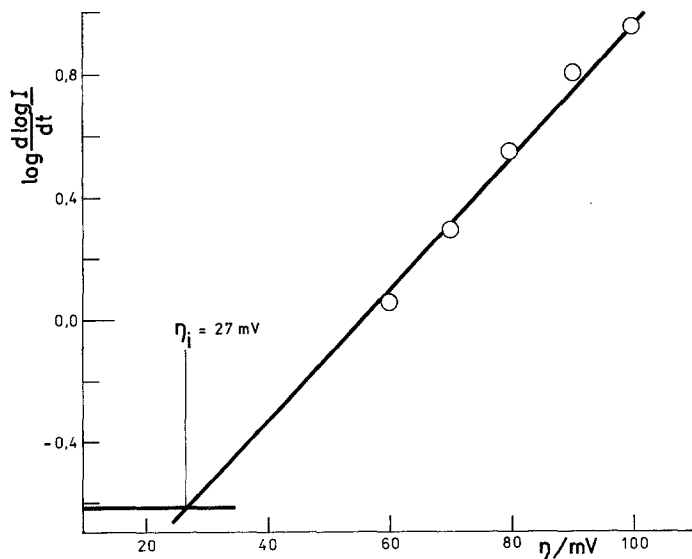


Fig. 6. $\log(d \log I / dt)$ as a function of overpotential for cadmium dendrite deposition.

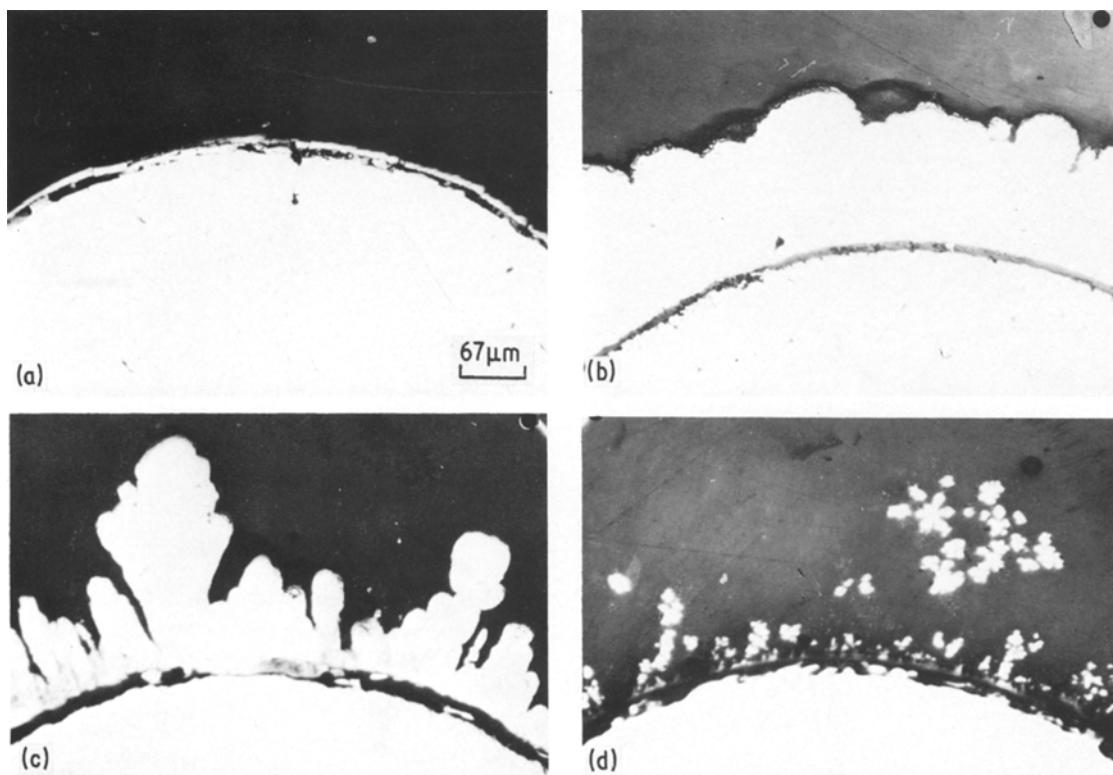


Fig. 7. Photomicrographs of copper deposited on to steel wire placed with copper from copper pyrophosphate bath. (a) Initial electrode, (b) overpotential 200 mV, deposition time 6 hours, (c) overpotential 300 mV, deposition time 5 hours, (d) overpotential 700 mV, deposition time 20 min.

initiation can be determined by plotting the logarithm of the slopes from Figs. 1 and 2, corresponding to dendritic growth, as a function of overpotential (see Equation 16) and by extrapolation of the logarithm of the slope corresponding to nondendritic growth from Figs. 1 and 2, as shown in Figs. 5 and 6. Straight lines with slopes of $1/160$ and $1/40 \text{ mV}^{-1}$ are obtained for copper and cadmium deposition, respectively, which are close to the expected slopes of $1/120 \text{ mV}^{-1}$ for copper [16] and $1/60 \text{ mV}^{-1}$ [17] for cadmium deposition.

The cross-section of the copper and cadmium deposits obtained at $\eta < \eta_i$; $\eta_i < \eta < \eta_e$ and $\eta > \eta_e$ are shown in Figs. 7 and 8, respectively. It is seen that at $\eta < \eta_i$ there is no dendrite formation, at $\eta_i < \eta < \eta_e$ both compact and dendritic deposits are formed, and at $\eta > \eta_e$ only powdered metal is deposited. In both cases η_i is close to the beginning of the limiting diffusion current plateau and η_e to the end of it.

This is a good proof of the proposed mechanism.

A quantitative analysis of the mechanism can be performed for copper deposition because surface energy effects can be neglected at sufficiently high overpotentials. Hence Equations 22 and 31 can be rewritten in the form

$$\eta_e \cong 2.3 \eta_0 \log \frac{nFDC_0}{i_0 h_0} = 2.3 \eta_0 \log \frac{i_L \delta}{i_0 h_0} \quad (33)$$

and

$$\eta_i \cong 2.3 \eta_0 \log \frac{4nFDC_0}{i_0 \delta} = 2.3 \eta_0 \log \frac{4i_L}{i_0} \quad (34)$$

From polarization curves and the Tafel line, the limiting diffusion current density, the exchange current density and the cathodic slope were determined as $i_L = 18 \text{ mA cm}^{-2}$, $i_0 = 1 \text{ mA cm}^{-2}$ and $2.3\eta_0 = 130 \text{ mV}$, respectively. Using these values and $\delta/h_0 = 10^3$ one obtains $\eta_i = 242 \text{ mV}$ and $\eta_e = 550 \text{ mV}$ from Equations 33 and 34, which are in good agreement with the experimentally

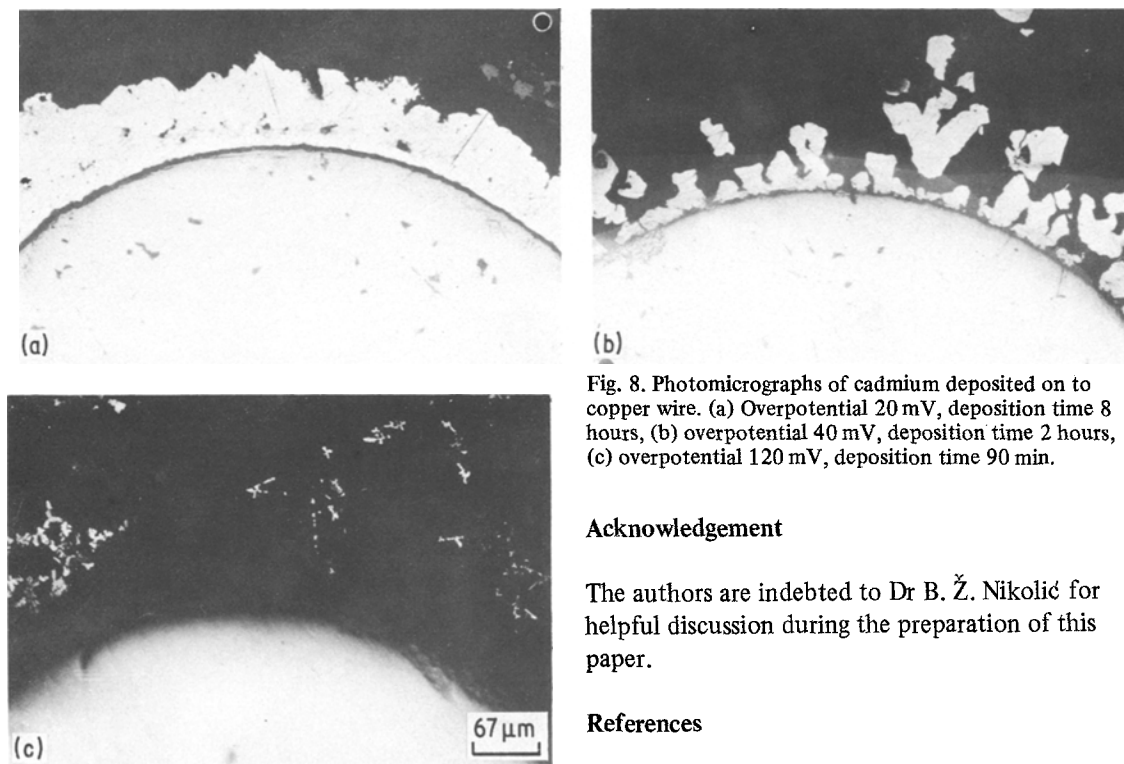


Fig. 8. Photomicrographs of cadmium deposited on to copper wire. (a) Overpotential 20 mV, deposition time 8 hours, (b) overpotential 40 mV, deposition time 2 hours, (c) overpotential 120 mV, deposition time 90 min.

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obtained values $\eta_i = 260$ mV and $\eta_e = 660$ mV.

An interesting test of Equations 25 and 32 can be performed by using the data of Barton and Bockris for deposition of silver dendrites [7]. Using $V = 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, $\delta = 10^{-4} \text{ m}$ and $\gamma = 10 \text{ J m}^{-2}$ (this value is calculated by Frenkel [18] for pure metals) one obtains $\eta_i = 0.5$ mV and $\eta_e = 8$ mV. This is in a good agreement with experimental results presented in Figs. 4 and 6 of [7].

It seems that the proposed mechanism explains all the effects of the electrolysis conditions discussed in the introduction, except for the effect of the motion of the electrolyte. This effect can be explained on the basis of Equation 30. The maximum height of a protrusion which can grow as a dendrite has a linear relationship with the diffusion layer thickness. It is reasonable to assume that h_0 , the minimum height of protrusion which can grow instantaneously as a dendrite, varies in a similar way. Hence stirring of the electrolyte leads to an increase in limiting diffusion current density, but the ratio h_0/δ remains approximately constant while the critical overpotential of powder formation increases with increasing motion of electrolyte.

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