

## ***The morphology of cadmium deposits obtained on foreign substrates at high overpotentials***

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Nomenclature			
		$k_1$	constant
		$k_2$	constant
$C_0$	bulk concentration	$n$	number of electrons
$C_s$	surface concentration	$N$	number of nuclei
$C_{\text{tip}}$	concentration at the top of growing protrusion	$N_0$	maximum number of nuclei
$D$	diffusion coefficient	$r$	radius of growing nucleus
$F$	Faraday constant	$r_c$	radius of growing nucleus at which deposition becomes mixed controlled
$f$	$\exp(\eta/\eta_{0,c}) - \exp(-\eta/\eta_{0,a})$	$t$	time
$f_1$	$\exp(\eta/\eta_{0,c})$	$t_i$	induction time for spongy growth initiation
$f_2$	$\exp(-\eta/\eta_{0,a})$	$t_{i,h}$	induction time for the formation of diffusion layer
$h$	the height of growing protrusion	$V$	molar volume
$h_0$	initial height of protrusion	$\delta$	thickness of diffusion layer
$i$	current density	$\eta$	overpotential
$i_0$	exchange current density	$2.3\eta_{0,c}$	slope of cathodic Tafel line
$i_L$	limiting current density		
$i_{\text{tip}}$	current density at the tip of growing protrusion		

### 1. Introduction

It is known that dendrites, spongy and needle electrodeposits are formed at high overpotentials [1–3]. The purpose of this work is to discuss these phenomena in the electrodeposition of metals on foreign substrates with special reference to cadmium.

### 2. Experimental details

The electrolyte used throughout this work was 0.1M CdSO<sub>4</sub> in 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The solution was prepared from AR-grade reagents and triple-distilled water. All experiments were carried out in an open glass cell at 20° C. Cadmium was deposited onto stationary vertical copper wires. Prior to each experiment the working surface of the electrode was mechanically polished with alumina powder (0.3 μm) and etched in 1:4 aq.

H<sub>2</sub>SO<sub>4</sub> solution. The counter electrode was a high purity (99.99%) cadmium plate; the reference electrode was a saturated sulphate electrode.

The experiments consisted of setting the electrode at a constant potential negative to the reversible potential of cadmium by means of a Wenking potentiostat, for a chosen period of time. A PAR-175-programmer and Tektronix (Type 564B) oscilloscope were employed to determine the ohmic drop correction. After a fixed time of deposition the electrode was taken out of the cell, washed and dried. The morphology of the deposits was investigated by scanning electron microscopy.

### 3. Results and discussion

The deposits of cadmium obtained at overpotentials of 300, 200 and 100 mV are presented

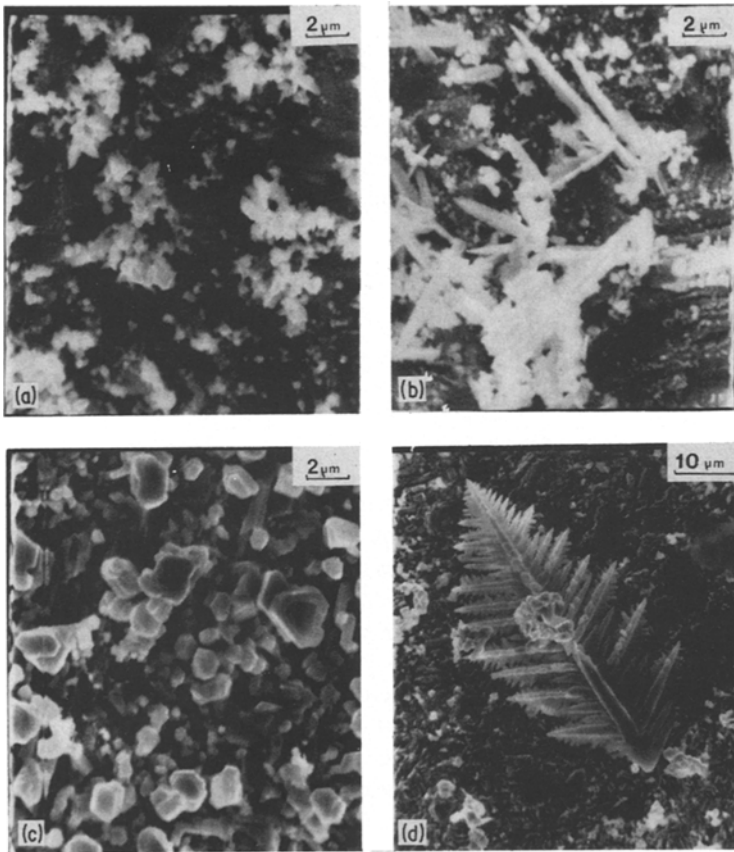


Fig. 1. Cadmium deposits obtained from 0.1M CdSO<sub>4</sub> and 0.5M H<sub>2</sub>SO<sub>4</sub> solution on copper substrate. (a) at 300 mV, 10 s; (b) at 200 mV, 20 s; (c) at 100 mV, 60 s; (d) at 100 mV, 120 s.

in Fig. 1. It is seen that spongy, needle and dendritic deposits are obtained. The appearance of such different forms of deposits can be explained in the following way. It was shown in a previous paper [4] that spongy deposits can be formed if the radius of the growing grain,  $r$ , is larger than some critical value  $r_c$  given by

$$r_c = \frac{i_L}{i_0} \frac{\delta}{4f_1 - 5f_2} \quad (1)$$

growing during an induction time,  $t_i$ , given by

$$t_i = \frac{i_L}{i_0^2} \frac{nF\delta}{Vf(4f_1 - 5f_2)} \quad (2)$$

if the condition

$$N < \frac{1}{(4r_c)^2} \quad (3)$$

permitting the independent growth of grains under spherical diffusion control is satisfied.

For a high overpotential where

$$f_1 \gg f_2 \quad (4)$$

Equations 1 and 2 can be rewritten as

$$r_c = \frac{i_L}{i_0} \frac{\delta}{4f_1} \quad (5)$$

and

$$t_i = \frac{i_L}{i_0^2} \frac{nF\delta}{4Vf_1^2} \quad (6)$$

The nucleation law can be written in the form [5]

$$N = N_0 [1 - \exp(-At)] \quad (7)$$

where

$$A = k_1 i_0 \exp(-k_2/\eta^2) \quad (8)$$

and spongy deposit formation is possible if

$$N_0 [1 - \exp(-At_i)] < \frac{1}{(4r_c)^2} \quad (9)$$

The condition of Equation 9 can be satisfied if

$$At_i \approx 0 \quad (10)$$

which happens at low overpotentials where  $k_2/\eta^2 \gg 1$ ,  $A \rightarrow 0$  and  $t_i > 0$ , and at high overpotentials where  $k_2/\eta^2 \ll 1$ ,  $A \rightarrow k_1 i_0$  and  $t_i \rightarrow 0$ .

Hence, the spongy deposit formation at high overpotentials starts at very low deposition times when the electrode surface is not completely covered with deposited metal. According to Equation 2 this happens at overpotentials larger than the critical one, which can be determined by substitution of  $r_c$  from Equation 1 and  $t_i$  from Equation 2 into Equation 9.

Steady-state spherical diffusion control around the grain with radius  $r$  is established at

$$t_{i,h} = \frac{10^2 r^2}{\pi D} \quad (11)$$

Substitution of  $r_c$  from Equation 5 into Equation 11 gives

$$t_{i,h} = \frac{100}{\pi D} \frac{i_L^2 \delta^2}{16 i_0^2 f_1^2} \quad (12)$$

and the combination of Equations 6 and 12 gives

$$t_{i,h} = \frac{1000 V C_0}{4\pi} t_i \approx 10^{-2} t_i \quad (13)$$

for  $V = 10 \text{ cm}^3 \text{ mol}^{-1}$  and  $C_0 = 0.1 \text{ mol dm}^{-3}$ .

Hence, it can be concluded that steady-state spherical diffusion is established instantaneously at  $r = r_c$ .

It is known that nondendritic surface coarseness amplification [6] in mixed activation-linear diffusion control follows the relationship

$$h = h_0 \exp \left[ \frac{VD(C_0 - C_s)}{\delta^2} t \right] \quad (14)$$

or

$$h = h_0 \exp \left[ \frac{VD(C_0 - C_s)}{r^2} t \right] \quad (15)$$

for spherical control of deposition on a microelectrode. It is obvious from Equation 15 that  $h = eh_0$  for

$$\tau = \frac{r^2}{VD(C_0 - C_s)} \quad (16)$$

Substitution of  $r_c$  from Equation 5 into Equation 16 gives

$$\tau = \frac{i_L^2}{i_0^2} \frac{\delta^2}{16VD(C_0 - C_s)f_1^2} \quad (17)$$

and further combination with Equation 6 gives

$$\tau = \frac{i_L}{4i} t_i \quad (18)$$

taking into account that

$$i = \frac{nFD(C_0 - C_s)}{\delta} \quad (19)$$

Equations 1 and 2 were derived under the assumption that the system enters mixed control at  $i \geq 0.2i_L$  and Equation 18 becomes

$$\tau \leq 1.25 t_i \quad (20)$$

This means that nondendritic surface roughness amplification is very fast in these conditions. The formation of spongy deposits confirms the assumption that deposition on independently growing grains is under spherical diffusion control because of the growth of protrusions in all directions. The formation of needles at 200 mV as presented in Fig. 1b, is possible to explain in a similar way. At overpotentials lower than the critical one for spongy formation the condition of Equation 9 is not satisfied because of the increase of  $t_i$  and  $r_c$  with decreasing overpotential. The conditions of spherical diffusion control can then be established only around the tips of growing grains, and the current density on the tip of the grain is given by

$$i_{\text{tip}} = \frac{nFDC_{\text{tip}}}{r} \quad (21)$$

which is minimum if the concentration around the tip is given by [2]

$$C_{\text{tip}} = C_0 \frac{h}{\delta} \quad (22)$$

which corresponds to steady-state conditions.

At the same time, according to Popov *et al.* [7] it is easy to show that this kind of growth can be changed to a dendritic one if

$$\frac{nFDC_0 h}{\delta} \frac{h}{r} < i_0 \frac{h}{\delta} \exp(\eta/\eta_{0,c}) \quad (23)$$

or at

$$\eta > \eta_{0,c} \ln \frac{i_L \delta}{i_0 r} \quad (24)$$

Hence, at sufficiently small  $r$  the tip of the pro-

trusion will grow under spherical diffusion control resulting in a needle deposit. The growth of needles is possible only if  $r_c$  is reached before the overlap of growing grains begins. After the beginning of the overlap of growing grains diffusion to the macroelectrode becomes the rate determining step, and considerable changes in morphology are not expected during the establishment of steady-state conditions [6]. At the same time the maximum difference in the height of points on the electrode surface will be lower than the grain tip radius and deposition to the grain will be controlled by linear diffusion because

$$\frac{nFDC_0}{\delta} > \frac{nFDC_0}{r} \frac{h}{\delta} \quad (25)$$

In this way the conditions suitable for dendritic growth initiation are established [7] which results in dendrite formation as illustrated by Figs. 1c, d.

Hence, the minimum overpotential at which needles can still be formed is determined from the relationship

$$N_0 [1 - \exp(-At_i)] \leq \frac{1}{(2r_c)^2} \quad (26)$$

At lower overpotentials (not lower than  $\eta_1$ ) dendrites will be formed. It is to be noted that the same situation appears in deposition on a cadmium substrate [2, 3]. This is probably due to the same reasons as in the deposition on foreign substrates, because the deposit does not replicate the original substrate as can be seen from Figs. 4, 11 and 13 in Reference 3.

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## SHORT COMMUNICATION

### *Scanning electron microscopic study of some nickel electroplates*

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#### 1. Introduction

Electrodeposition of bright nickel using organic brighteners has been the subject of much research [1–4]. Some of the recent publications correlate the surface irregularities and surface roughness to brightness of electroplate. For example Weil and Paquin [1] and Weil [4] have reported that the bright electroplates do not have extensive irregularities or well-developed facets on their surface. The investigations carried out in our laboratory also show that the bright electroplates are smooth [5]. The present investigation was undertaken to study the surface topography of

nickel electroplates obtained in the presence and absence of combination of brighteners using both standard SEM and a Y-modulation technique [6] to show the difference in the information provided by the two types of display.

#### 2. Experimental details

The composition and pH of the Watts bath used and the other experimental conditions were the same as reported earlier [5]. Sodium benzene sulphonate was prepared and purified by the method of Vogel [7]. Acrylamide (SD, LR) was purified by recrystallization from chloro-