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Spongy electrodeposit formation

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Nomenclature

f_1	$\exp(\eta/\eta_{0,c})$
f_2	$\exp(-\eta/\eta_{0,a})$
j_0	exchange current density
j_L	limiting current density
r	radius of growing nucleus
r_c	radius of growing nucleus at which deposition becomes mixed controlled
δ	thickness of diffusion layer
η	overpotential
$2{,}3\eta_{0,c}$	slope of cathodic Tafel line
$2{,}3\eta_{0,a}$	slope of anodic Tafel line

1. Introduction

According to recent theory [1, 2], spongy deposit formation on an inert substrate is caused by mass transfer limitations in conditions of diffusion control and low nucleation rate. A spherical diffusion layer is formed around the independently growing grains and amplification of surface protrusions in all direction is possible resulting in spongy deposit formation. This is possible, at a fixed value of overpotential, if

$$r > r_c = \left(\frac{j_L}{j_0}\right)\left(\frac{\delta}{4f_1 - 5f_2}\right) \qquad (1)$$

Obviously, r_c decreases with increasing overpotential as does the induction time of spongy growth initiation [1]. At $r < r_c$ the conditions of spherical diffusion control can be established only around the tip of growing grains leading to the growth of protrusions toward the bulk of the solution; this results in needle-like deposits [2]. A similar situation arises if grains with $r > r_c$ are so close to each other that the formation of a spherical diffusion layer is prevented.

The situation in which spongy deposit growth can start can easily be demonstrated in the following way. Grains of desired size and distribution can be grown at low overpotentials with activation-controlled deposition. This corresponds to growth of grains at $r < r_c$. The situation where $r > r_c$ can be simulated by increasing the overpotential to sufficiently high values to cause diffusion control around the growing grains. This is followed by nucleation over all the electrode surface and then formation of the diffusion layer at the macroelectrode. Establishment of a spherical diffusion layer around grains is very fast, as well as the amplification of protrusions [2]. This permits simulation of the initial stage of spongy growth initiation.

2. Experimental details

The electrolytes used throughout this work were $0.1\,\mathrm{mol\,dm^{-3}}$ zincate solution in $1.0\,\mathrm{mol\,dm^{-3}}$ KOH for the electrodeposition of zinc, and $0.1\,\mathrm{mol\,dm^{-3}}$ and $1.0\,\mathrm{mol\,dm^{-3}}$ $CdSO_4$ in $0.5\,\mathrm{mol\,dm^{-3}}$ H_2SO_4 for cadmium deposition. Zinc and cadmium were deposited onto planar copper electrodes. The experimental conditions were the same as described earlier [1]. Zinc was deposited at 40 mV and 60 mV; the nucleation of cadmium was initiated and grains were grown to the desired size in $1.0\,\mathrm{mol\,dm^{-3}}$ $CdSO_4$ at 12 mV and 20 mV. Diffusion control was simulated by exposing electrodes formed in $1.0\,\mathrm{mol\,dm^{-3}}$

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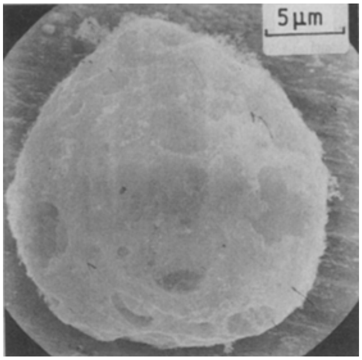

Fig. 1. Zinc deposit at 40 mV from 0.1 mol dm^{-3} zincate and 1.0 mol dm^{-3} KOH solution. Deposition time, 2 min; SEM, 60°.

$CdSO_4$ solution to overpotentials of 120 and 170 mV in 0.1 mol dm^{-3} $CdSO_4$ solution.

3. Results and discussion

The initial stage of spongy zinc formation from alkaline zincate solution is illustrated by Fig. 1. The development of a spongy deposit is illustrated by Fig. 2. Fig. 2a shows an initial cadmium grain obtained at 12 mV during a 15-min deposition from 1.0 mol dm^{-3} $CdSO_4$ on a planar copper electrode. A spherical diffusion layer can be formed around this grain. Similar grains, but after progressively longer deposition periods from 0.1 mol dm^{-3} $CdSO_4$ at 120 mV for 15, 30 and 60 s, are shown in Fig. 2b–d. The growth of protrusions in all directions is good proof that the initial stage of deposition on the grain is under spherical diffusion control. At higher deposition times the protrusions branch and interweave as shown by Fig. 3, causing the spongy appearance of the electrode. Needle-like deposit growth is illustrated by Fig. 4a. Deposition of cadmium from 0.1 mol dm^{-3} $CdSO_4$ at 120 mV for 70 s was performed on an electrode prepared by deposition of cadmium onto copper from 1.0 mol dm^{-3} $CdSO_4$ at 12 mV for 6 min. The

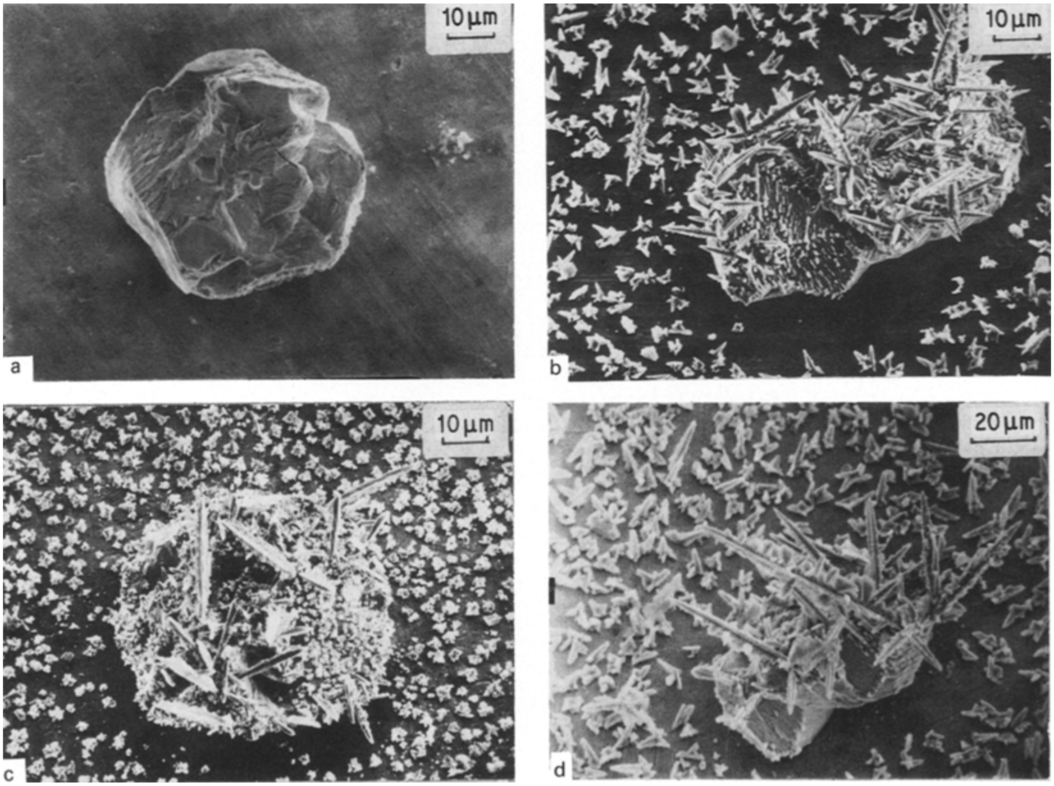

Fig. 2. Cadmium deposits. (a) From 1.0 mol dm^{-3} $CdSO_4$ and 0.5 mol dm^{-3} H_2SO_4 solution at 12 mV; deposition time 15 min; SEM, 30°. (b) The same as in Fig. 2a but after deposition from 0.1 mol dm^{-3} $CdSO_4$ and 0.5 mol dm^{-3} H_2SO_4 solution at 120 mV; deposition time, 30 s; SEM, 30°. (c) The same conditions as Fig. 2b but with a deposition time of 45 s. (d) The same conditions as Fig. 2b but with a deposition time of 60 s.

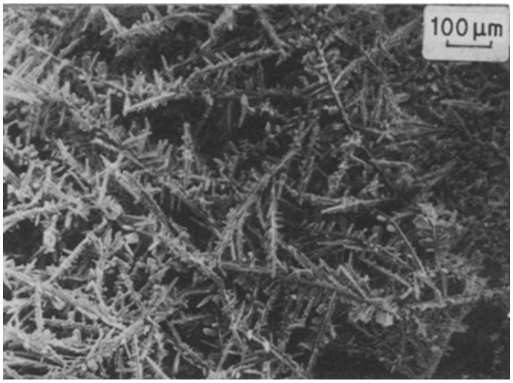

Fig. 3. The same as in Fig. 2b–d but after a deposition time of 120 s.

grain obtained in this way is considerably smaller than the grains in Fig. 2. It is obvious at 120 mV, with $r < r_c$, that a needle growing toward the bulk solution is formed instead of a spongy deposit. Deposition under the same conditions but at 170 mV for 30 s results in a spongy deposit that can be seen from Fig. 4b. It is also seen from Figs 2c and 4b that, at the same deposition time, protrusions are more developed at higher overpotentials. This means that the induction time is really lower at higher overpotentials as shown earlier [2]. Grains of similar size, but closer packed, are obtained by deposition from 1.0 mol dm^{-3} $CdSO_4$ at 20 mV for 15 min, and further deposition from 0.1 mol dm^{-3} $CdSO_4$, at 170 mV for 30 s produces a deposit similar to those of Fig. 4a with the protrusions growing toward the bulk of the solution and governed by the diffusional flux to the macroelectrode, as illustrated by Fig. 4c. It is obvious that because of interweaving and branching of protrusions that a spongy deposit will be obtained in prolonged deposition.

In zinc electrodeposition [1] in the overpotential range $40 < \eta < 80$ mV a compact deposit is formed over a relatively long induction time after which a spongy deposit can be formed. The deposit obtained during the induction time is shown in Fig. 5a and the initiation of spongy growth by Fig. 5b. Obviously, the situation is similar to that shown in Fig. 4c.

Hence, it can be concluded that at low over-potentials spongy growth is due to the

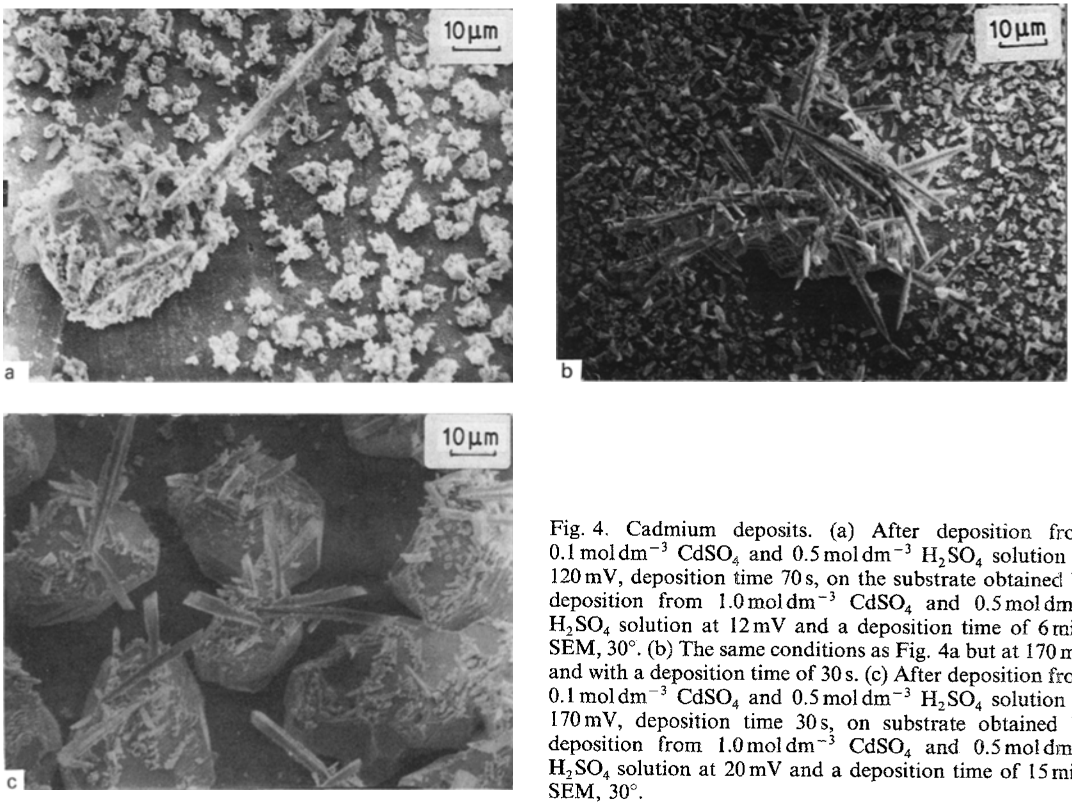

Fig. 4. Cadmium deposits. (a) After deposition from 0.1 mol dm^{-3} $CdSO_4$ and 0.5 mol dm^{-3} H_2SO_4 solution at 120 mV, deposition time 70 s, on the substrate obtained by deposition from 1.0 mol dm^{-3} $CdSO_4$ and 0.5 mol dm^{-3} H_2SO_4 solution at 12 mV and a deposition time of 6 min; SEM, 30°. (b) The same conditions as Fig. 4a but at 170 mV and with a deposition time of 30 s. (c) After deposition from 0.1 mol dm^{-3} $CdSO_4$ and 0.5 mol dm^{-3} H_2SO_4 solution at 170 mV, deposition time 30 s, on substrate obtained by deposition from 1.0 mol dm^{-3} $CdSO_4$ and 0.5 mol dm^{-3} H_2SO_4 solution at 20 mV and a deposition time of 15 min; SEM, 30°.

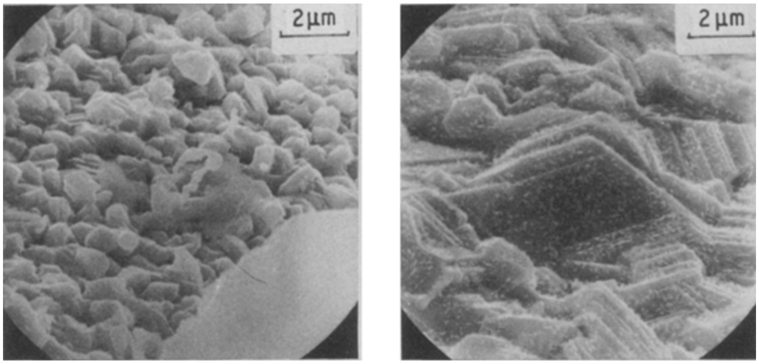

Fig. 5. Zinc deposits at 60 mV from 0.1 mol dm^{-3} zincate and 1.0 mol dm^{-3} KOH solution. (a) Deposition time, 150 min; SEM, 60°. (b) Deposition time, 260 min; SEM, 60°.

amplification of surface protrusions directly inside the spherical diffusion layer formed around each independently growing grain. Spongy deposit formation over an initial coating is due to the amplification of surface protrusions inside the diffusion layer of the macroelectrode.

There are at least two open questions related to spongy deposit formation.

1. Why is a spongy deposit not formed on foreign substrates at low overpotentials in all systems with high exchange current densities, as in the case of silver deposition for example [3]?

2. Why does spongy growth start over an initial coating after grains reach some critical value, as in the case of zinc deposition from zincate solution [1]?

It seems likely that those problems can be interpreted in terms of surface energy effects which will be the purpose of further investigations.

References

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