Electroplating of bright cadmium from an optimized acetate bath under the influence of superimposed alternating current

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A systematic study of the electroplating of bright cadmium from an acetate bath is described. The process was carried out in electrolytes containing cadmium acetate with inclusion of boric acid, acetic acid and sodium acetate, in addition to gelatin and toluene-4-sulphonic acid as organic additives. The effects of the bath constituents on the cathodic polarization and the current efficiency of cadmium deposition from each bath as well as on the surface morphology of the as-formed cadmium electroplates is discussed. The optimum acetate bath composition is suggested. The influence of a superimposed sinusoidal a.c. with the d.c. on the above-mentioned characteristics of cadmium electroplating from the optimum bath was also examined.

1. Introduction

The industrial electroplating of cadmium is practised in order to provide an attractive corrosion protective coating on various metals. The process is achieved successfully from cyanide baths which are easy to control and produce uniform, fine-grained and bright electroplates [1]. Nevertheless, the toxicity of cyanide has prompted a long search for alternative non-cyanide electrolytes. Accordingly, several attempts have been made to obtain satisfactory deposits from sulphate–fluoborate [2], sulphate [2–4], chloride [5] and bromide [6] acidic baths. In fact, cadmium electroplates from the latter baths are of lesser quality than those from cyanide baths. The electroplating of cadmium from aqueous acetate baths is rare and only one study describes the deposition from a solution of cadmium acetate in methanol [1].

Continuing our investigations on the electroplating of cadmium from sulphate [7], chloride [8–10] and bromide [11] acidic baths, we have investigated the electroplating of cadmium from aqueous acidic acetate baths.

2. Experimental details

All plating baths were freshly prepared from distilled water and AR grade chemicals (BDH). The composition of and symbols for these baths are given in Table 1. The experimental set-up for the electrodeposition consisted of a rectangular Perspex cell provided with a copper sheet cathode placed midway between two plane-parallel platinum sheet anodes; all electrodes were of the same geometrical area (2.3 × 2.0 cm each). In some experiments, a sinusoidal a.c. was superimposed on the d.c. This was supplied by a TRIO AG 203 CR oscillator and connected directly to the cathode and the anodes. To achieve separation of the external d.c. and a.c. circuits, an induction coil (2.5 H, 0.25 A) was introduced into the d.c. circuit and a condenser (100 μF, 12 V) to the a.c. circuit.

The cathodic potentials were measured relative to a saturated calomel electrode (SCE) through a bridge filled with solution under test to avoid contamination. The potential was recorded using a potentiometer (type EIL 23 AUK). The cathode current efficiency, f, was determined by

Table 1. Composition and pH of the cadmium electroplating solutions and the corresponding percentage current efficiency from each solution (j = 2 A dm⁻² and t = 10 min)

Solution	Concentration (mol l⁻¹)						pH	f (%)
	$Cd(CH_3COO)_2 2H_2O$	H_3BO_3	CH_3COOH	$CH_3COONa\ 3H_2O$	gelatin[a]	TSA[a]		
1a	0.10	–	–	–	–	–	7.00	102.0
1b	0.20	–	–	–	–	–	7.00	102.4
1c	0.30	–	–	–	–	–	7.00	103.8
1d	0.40	–	–	–	–	–	7.00	103.3
1e	0.50	–	–	–	–	–	7.00	103.6
2a	0.40	0.05	–	–	–	–	6.20	99.4
2b	0.40	0.10	–	–	–	–	6.25	98.1
2c	0.40	0.20	–	–	–	–	6.30	98.4
2d	0.40	0.30	–	–	–	–	6.30	97.5
3a	0.40	0.30	0.10	–	–	–	5.40	98.0
3b	0.40	0.30	0.20	–	–	–	5.10	98.5
3c	0.40	0.30	0.30	–	–	–	5.05	98.5
4a	0.40	0.30	0.20	0.10	–	–	5.00	96.1
4b	0.40	0.30	0.20	0.20	–	–	5.00	96.3
4c	0.40	0.30	0.20	0.30	–	–	5.00	96.0
5	0.40	0.30	0.20	0.10	1	–	5.00	98.9
6	0.40	0.30	0.20	0.10	–	1	5.00	98.0
7	0.40	0.30	0.20	0.10	1	1	5.00	98.4

[a] The concentrations of these compounds are expressed in g l⁻¹.

means of weight-gain of the cathode. The quantity of electricity passed during plating was checked by means of a copper coulometer which was connected in series with the cell. The surface morphology of the as-plated cadmium was examined using a scanning electron microscope (JEOL Model JSM-T 20). All experiments were performed at $25° \pm 1°$ C, with temperature maintained by an air thermostat.

3. Results and discussion

3.1. Polarization curves

The cathodic polarization curves for cadmium electrodeposition from 0.1–0.5 M cadmium acetate solutions (1a–e) were irregular and non-reproducible. This could be attributed to the formation of cadmium hydroxide and basic oxide films on the cathode surface in the absence of a buffering agent in the solutions. Nevertheless, solutions 1a–e showed a general trend of shifting of the cathodic polarization curves in the more noble direction with increasing concentration of Cd^{2+} ions in the solution. The
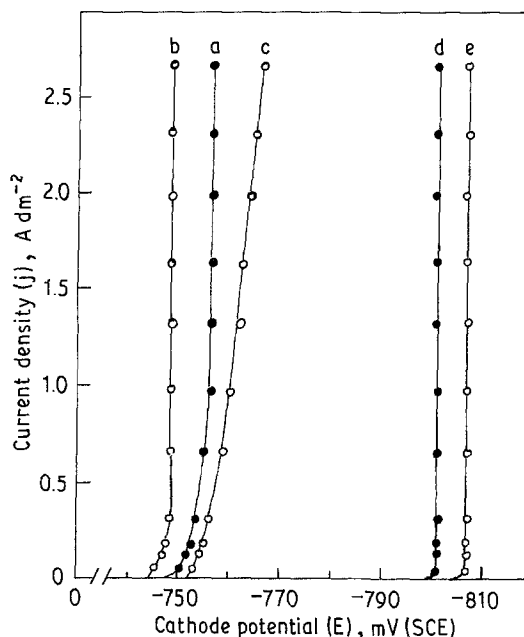

Fig. 1. Effect of the bath constituents on the polarization curves of cadmium electroplating from solutions. Curve a, 0.4 M cadmium acetate + 0.3 M H_3BO_3; curve b, 0.4 M cadmium acetate + 0.3 M H_3BO_3 + 0.2 M acetic acid; curve c, 0.4 M cadmium acetate + 0.3 M H_3BO_3 + 0.2 M acetic acid + 0.1 M sodium acetate; curve d, as c + gelatin; curve e, as d + TSA.

0.4 M solution (1d) produced a better coverage of the cathode with a reasonable metallic deposit when compared with the other solutions.

Progressive addition of boric acid, used as a buffer (solutions 2a–d), did not alter the position of the polarization curves. Consequently, the concentration of 0.3 M boric acid in solution 2d was chosen to ensure a satisfactory buffering action. Fig. 1 (curve a) shows that the electrodeposition of cadmium from solution 2d is attended by a relatively low polarization. Moreover, there is no change in the cathode potential with increasing current density, indicating the absence of activation polarization [12].

The addition of an increasing concentration of acetic acid to solution 2d shifted the cathodic polarization curves to less negative values and improved the quality of the deposit, up to an upper limit of 0.2 M found in solution 3b. This positive potential shift (Fig. 1, curve b), achieved

by lowering the pH of the solution, may be due to a decrease in the hydrogen overvoltage [13]. Consequently, the rate of hydrogen evolution becomes so high that most of the gas formed escapes as bubbles. However, at higher pH values bubble formation is not fast enough for the gas to escape and, accordingly, hydrogen adsorption occurs giving rise to an increase in the cathodic potential [14].

In contrast, the polarization curves shift to more negative potentials with increase in the concentration of sodium acetate added (solutions 4a–c). This may be due to the formation of soluble Cd^{2+} acetate complex ions with a stability constant of $\log K_1 = 1.34$ [15] and the consequent decrease in the concentration of the free Cd^{2+} ions in the solution. Actually, at concentrations of sodium acetate higher than 0.1 M (solution 4a) the deposit started to turn black. The polarization curve corresponding
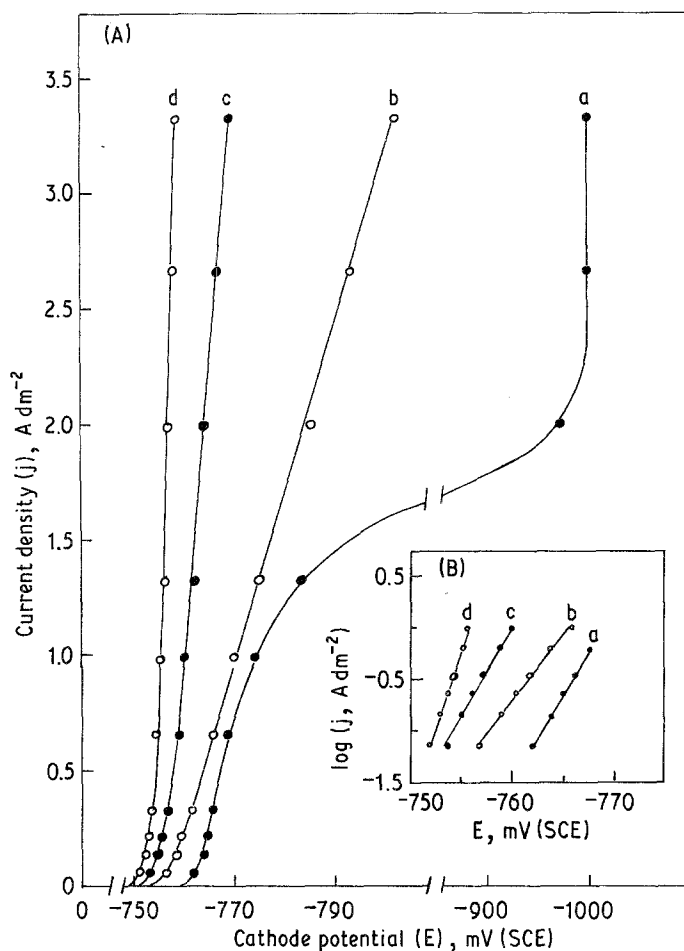
Fig. 2. Effect of cadmium acetate concentration in solution 4a on (A) the polarization curves and (B) Tafel lines of cadmium electroplating. Curve a, 0.1 M; curve b, 0.2 M; curve c, 0.4 M; curve d, 0.5 M.

to this solution is shown plotted in Fig. 1 (curve c).

A series of solutions of similar composition to solution 4a, except for the concentration of Cd^{2+} ions, was selected in order to examine the influence of cadmium acetate within the concentration range 0.1–0.5 M on the polarization curves. The results are illustrated in Fig. 2A which shows that as the concentration of Cd^{2+} ions increases the electrodeposition of cadmium is attended by a lower polarization. This could be partly due to the decrease of the concentration polarization. Furthermore, at the lowest concentration of cadmium acetate (curve a) an arrest corresponding to the limiting diffusion current of Cd^{2+} ion deposition is observed before the evolution of hydrogen. Inspection of Fig. 2B shows also that the activation polarization of cadmium deposition decreases with increase in the concentration of Cd^{2+} ions in the solutions used. Since there is no considerable ennobling of the polarization curves at concentrations higher than 0.4 M (curve c), solution 4a was considered the optimum for cadmium electroplating.

Some organic additives were introduced into solution 4a in order to improve the quality of the deposits. The most efficient of these additives were gelatin and toluene-4-sulphonic acid (TSA). Fig. 1 (curve d) shows that the addition of $1\,g\,l^{-1}$ gelatin into solution 5 caused a considerable shift (about 40 mV) in the cathodic polarization in the negative direction. This effect may be attributed to the formation of a very thin protein membrane in the cathode layer [16]. This membrane results in hinderance of the migration and discharge of the Cd^{2+} ions. A further polarization increase is observed (Fig. 1, curve e) as a result of the combined effect of both gelatin and TSA in solution 7.

The data of Fig. 3 show that a superimposed a.c. (at constant a.c. frequency of 50 Hz) shifts the cathodic polarization curve of cadmium deposition from solution 7 to less negative values and the depolarizing effect increases with increase of the a.c. density ($j_\sim$). Moreover, at the same a.c. density the depolarizing effect decreases with increasing d.c. density. Similar results have been reported for the electrodeposition of cobalt, nickel and cobalt–nickel alloys from Watts [17] and ammoniacal complex [18] baths. However,
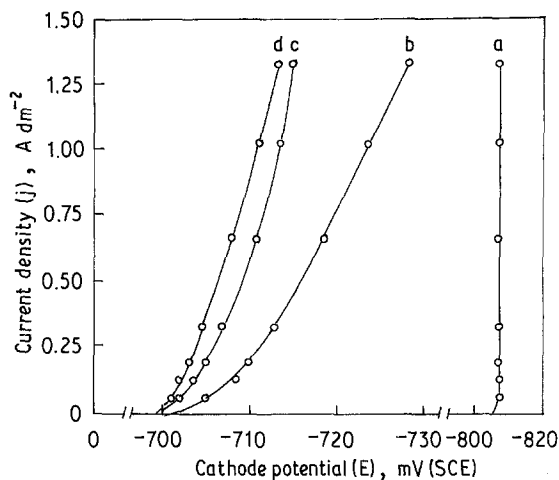

Fig. 3. Effect of superimposed a.c. density ($\omega = 50\,Hz$) on the polarization of cadmium electroplating from solution 7. Curve a, d.c. only; curve b, $j_\sim = 0.2$; curve c, $j_\sim = 0.5$; curve d, $j_\sim = 1.33\,A\,dm^{-2}$.

it was found experimentally during the electroplating of cadmium from solution 7 that the anodic polarization is markedly greater than the cathodic polarization. Therefore, the electrode can be considered as an electrically non-linear element [19–22]. Consequently, the sine wave of the a.c. suffers distortion at the electrode surface. In turn, the potential fluctuates periodically giving rise to an average potential value which is less negative than the potential corresponding to d.c. only. Moreover, the data of Fig. 4 show that
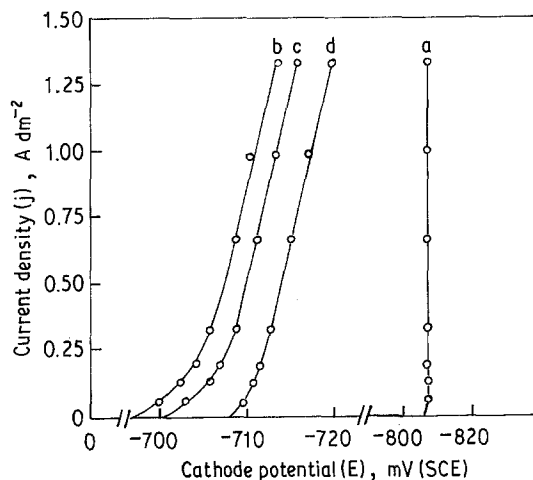

Fig. 4. Effect of superimposed a.c. frequency ($j_\sim = 0.66\,A\,dm^{-2}$) on the polarization curves of cadmium electroplating from solution 7. Curve a, d.c. only; curve b, $\omega = 50$; curve c, $\omega = 250$; curve d, $\omega = 1000\,Hz$.

the depolarizing effect of a.c. (at a constant a.c. density of $0.66\,A\,dm^{-2}$) decreases with increasing a.c. frequency (ω). It is probable that at a higher frequency the perodic fluctuation of the potential would not be able to follow the fast change in current and, accordingly, the effect of a.c. becomes gradually diminished.

3.2. Current efficiency

The cathodic current efficiency, f, of cadmium deposition from these solutions was determined at a constant current density of $2\,A\,dm^{-2}$ for 10 min, and the results are given in Table 1. Regardless of the concentration of Cd^{2+} ions in solutions 1a–e, f is apparently over 100%. This could be due to the incorporation of cadmium hydroxide and basic oxide into the cadmium deposit formed in these non-buffered cadmium acetate solutions.

On the contrary, f decreases gradually as a result of the increasing addition of boric acid in solutions 2a–d and reaches a minimum of 97.5% at 0.3 M. This decrease may be ascribed to prevention of the formation of the basic compounds in the presence of a buffer. A slight improvement in f with increase of the concentration of acetic acid in solutions 3a–c was observed. This effect is in good agreement with the shifting of the cathodic polarization curves to less negative potentials (Fig. 1) which is expected to facilitate the discharge of Cd^{2+} ions. The inclusion of sodium acetate in solutions 4a–c leads to a slight decrease in f. This feature can be ascribed to the formation of soluble Cd^{2+}– acetate complex ions [15] and the consequent

increase in the overvoltage of Cd^{2+} deposition (Fig. 1).

It is observed that f from either solution 5 or 6, containing gelatin or TSA respectively, is marginally higher than that from the corresponding additive-free solution 4a. A similar result is also observed for the combined effect of both additives in solution 7. This feature is at variance with the fact that the electrodeposition of cadmium from the additive-containing solutions is attended by a greater polarization than from the additive-free solution. This effect may be due to the incorporation of small amounts of these additives and/or their reduction products into the metallic deposit.

In general, Table 2 shows that a superimposed a.c. decreases f of cadmium electroplating from solution 7. Moreover, the higher the a.c. density and the lower its frequency the greater is the decrease in f. This decrease may be attributed to the possibility of dissolution of some of the cadmium deposit during the anodic half-cycle of the a.c.

3.3. Surface morphology

The surface morphology of the as-plated cadmium deposits from these solutions was examined and some of the electron micrographs taken are shown in Fig. 5. The deposits from solutions 1 to 3 consisted of irregularly shaped hexagonal crystals with large holes between them. These deposits were dull, coarse-grained and loosely adherent to the cathode.

Fig. 5a shows that the cadmium deposit from solution 4a is polycrystalline. Moreover, most of the crystals grow outward in a spiral hexagonal shape, some of which exhibit distortion and twinning. Such a hexagonal structure is typical for cadmium electrodeposits from acidic baths [7]. The electrodeposition of cadmium from acidic solutions takes place readily at potentials that favour adsorption of anionic species [23]. Therefore, the morphology data mentioned above could be correlated to the specific adsorption of the acetate anions at the cathode surface and thus the cathode is expected to be partially inhibited. Consequently, once a cadmium nucleus of sufficient size is formed its surface is relatively uninhibited compared with the surrounding

Table 2. Effect of superimposed a.c. on the percentage current efficiency of cadmium electroplating from cadmium solution 7 (j = 1.46 A dm^{-2} and t = 10 min)

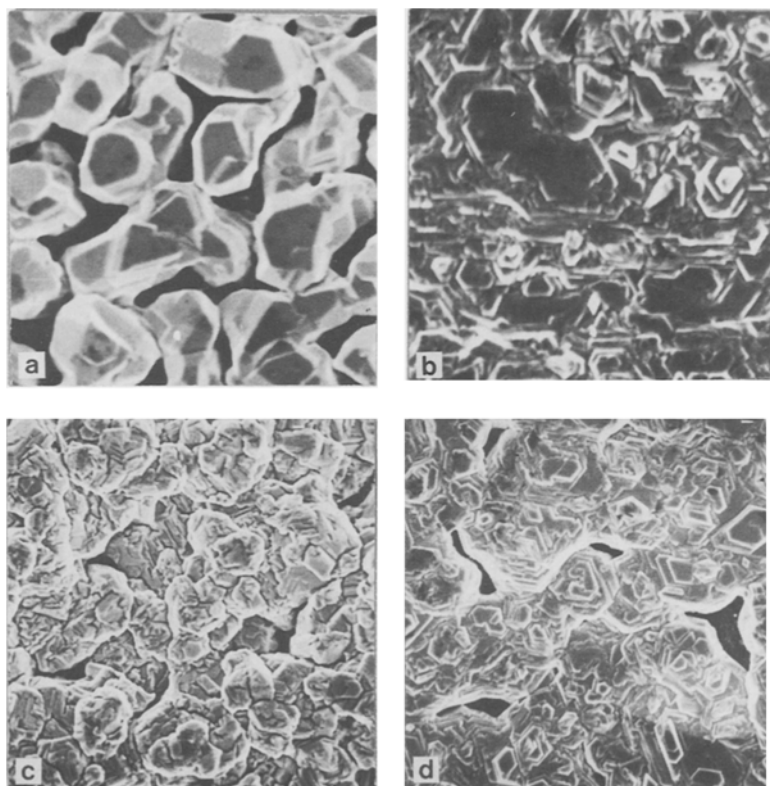| Superimposed a.c.		$f(\%)$
$j_\sim$ (A dm^{-2})	ω(Hz)	
0.00	0	98.4
0.20	50	99.6
0.46	50	95.3
1.33	50	94.7
0.66	1000	98.5
0.66	250	97.3
0.66	50	95.0

Fig. 5. Electron micrographs of cadmium deposited from: (a) solution 4a; (b) solution 5; (c) solution 6; (d) solution 7. Magnification, $\times 650$; j, $2\,A\,dm^{-2}$; t, 10 min.

copper cathode surface so that it grows more readily, giving rise to larger polycrystals leaving holes between them.

The inclusion of $1\,g\,l^{-1}$ gelatin in solution 5 leads to supression of the outgrowth of the isolated crystals and the production of a more coherent and levelled electroplate (Fig. 5b). Nevertheless, the characteristic hexagonal structure of cadmium is still obvious. It is well known that gelatin solutions coagulate in neutral media and dissolve in acids. Accordingly, the effect of gelatin could be due to the formation of membrane-like films in the cathode layer. These films are thicker in the higher current density areas, due to discharge of H^+ ions, than they are in the lower current density areas [16]. Consequently, they are responsible for hinderance of the migration and discharge of Cd^{2+} ions in the higher current density areas, giving rise to the levelling action.

As can be seen in Fig. 5c, the electroplate from solution 6 containing $1\,g\,l^{-1}$ TSA consists of a coherent accumulation of small crystallites without any preferred grain orientation. In addition,

the surface is characterized by irregularities and the occurrence of large holes is also observed. However, it would be expected that the existence of six lone pairs of electrons on the sulphonic group enhances the specific adsorption of TSA on metallic surfaces. The effects exerted by TSA may be explained by its adsorption both at the cathode surface (giving rise to holes) and at the cadmium deposit (resulting in irregularly shaped crystals).

$$H_3C \!-\!\!\!\bigcirc\!\!\!-\!\! \overset{\displaystyle :\ddot{O}:}{\underset{\displaystyle :\ddot{O}:}{\overset{\|}{\underset{\|}{S}}}}\!-\!\ddot{O}^- \qquad H^+$$
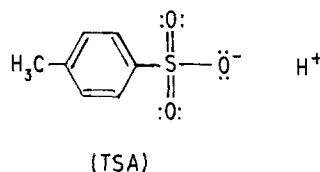
(TSA)

Fig. 5d reflects the combined effects of both gelatin and TSA on the deposit from solution 7. A correlation of Fig. 5b, c, and d with Fig. 5a shows an increase in the nucleation density and grain refinement of cadmium deposition as a result of the inclusion of these additives either individually or in combination. These results are in agreement with shifting of the polarization
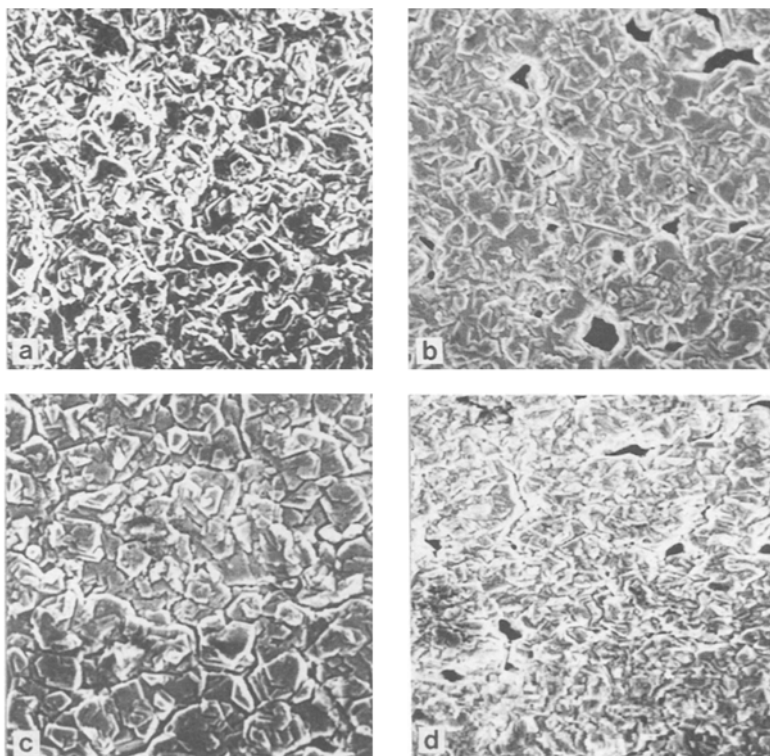
Fig. 6. Electron micrographs of cadmium deposited from solution 7 under the influence of superimposed a.c. (a) $j_\sim = 0.20$, $\omega = 50$; (b) $j_\sim = 0.66$, $\omega = 50$; (c) $j_\sim = 1.33$, $\omega = 50$; (d) $j_\sim = 0.66\,A\,dm^{-2}$, $\omega = 1000\,Hz$. Magnification, $\times 650$; $j_\sim$, $2\,A\,dm^{-2}$; t, 10 min.

curves of cadmium deposition to more negative direction in the presence of these additives.

Fig. 6a–d indicates, in general, that cadmium deposited under the influence of a superimposed a.c. is more level and characterized by a smoother texture. The figures reveal that the levelling action increases with increase of the a.c. density (at a constant a.c. frequency). This may be due to, firstly, the increase of the depolarizing effect of the a.c. which renders the cathode relatively uninhibited towards the discharge of Cd^{2+} ions. Another reason could be the expected redissolution of cadmium from the top of the outgrown spiral crystals during the anodic half-cycle of the a.c. and its consequent deposition at the less inhibited cathode areas during the cathodic half-cycle of the a.c. On the other hand, an increase of the a.c. frequency at a constant a.c. density leads to an increased nucleation density (Fig. 6b, d) which may be related to the decrease of the effect of a.c. Although the finest texture is obtained at the highest a.c. frequency used (Fig. 6d), some small holes can still be seen.

4. Conclusions

It has been possible to obtain pale grey, semi-bright cadmium electroplates from an optimum acetate bath containing $0.4\,M$ $Cd(CH_3COO)_2$, $0.3\,M$ H_3BO_3, $0.2\,M$ CH_3COOH and $0.1\,M$ CH_3COONa. The operating conditions at $25°\,C$ were: j, $2\,A\,dm^{-2}$; t, 10 min and pH 5.

The addition of $1\,g\,l^{-1}$ gelatin and $1\,g\,l^{-1}$ TSA to the optimum bath led to the formation of a bright silverish-white electroplate. A superimposed a.c. with the d.c. increased the brightness of the deposits from the additive-containing bath. The influence of the a.c. increased with increase of the a.c. density and lowering of its frequency.

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