

Electroplating of cadmium from acidic bromide baths

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Earlier work on the electroplating of cadmium from acidic bromide solution containing 0.3M $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, 0.1M HCl, 0.4M H_3BO_3 and 2.0M KBr (Bath I) has been reviewed and extended to an examination of the influence of the organic additives 5 g gelatin l^{-1} and 2.5 g melamine l^{-1} (Bath II). The effects of the plating current density, plating time and pH on the cathodic polarization and the current efficiency of cadmium electroplating from Bath II, as well as on the morphology and the micro-hardness of the as-plated cadmium electrodeposits are discussed. It was observed that the additive-containing Bath II yields more coherent, brighter and harder cadmium plates than the additive-free Bath I. The optimum operating conditions for obtaining satisfactory plates from Bath II at 25° C are: $i = 0.6\text{--}1.6 \text{ A dm}^{-2}$; $t = 10\text{--}15 \text{ min}$ and pH 3.6-1.9.

1. Introduction

Over the last fifty years, cadmium has been electroplated successfully with cyanide baths [1, 2]. In the course of the search for non-polluting electrolytes with good characteristics to replace the cyanide baths, successful deposition has been reported from many non-cyanide acidic electrolytes including sulphate solutions [3-5], chloride solutions [6] and iodides in non-aqueous media [7]. In a recent paper [8] we reported that cadmium electroplating from acidic solutions is influenced to some extent by the nature of the anion of the salt employed in the bath. Of the various systems investigated, the bromide and chloride baths are much more promising than the corresponding sulphate and iodide baths. They have good cathodic efficiencies and moderate throwing powers and they produce deposits of reasonable appearance and micro-hardness. Surprisingly, cadmium electroplating from bromide baths has not received adequate attention and only one patent has been published in this respect [9].

Taking into consideration the earlier advantages of the bromide bath and the rare literature available, the present study is devoted to finding the optimum bath composition and conditions for satisfactory cadmium electroplating.

2. Experimental details

The experimental details such as the plating cell, materials and treatments of the electrodes and the experimental set-up have been reported elsewhere [8, 10]. The electrolytes were prepared in doubly distilled water using highly pure chemicals (BDH); their compositions are given in Table 1. The pH of these electrolytes was measured when required with a Corning Research Model 12 pH meter which was also used for the measurements of the cathodic potentials.

The steady-state cathodic polarization curves were measured relative to the saturated calomel electrode (SCE) and the cathodic efficiencies ($f\%$) were determined coulometrically.

The morphology of the as-formed cadmium deposits was examined with a scanning electron microscope (JEOL Model JSM 35). The micro-hardness of the plated cathodes was measured by a Lietz-Wetzlar microhardness tester and was expressed as the Vickers hardness, H_v , in kilogrammes-force per square millimeter. The corresponding average thickness, d (in micrometers), of each plate was also calculated.

The electroplating experiments were carried out at various current densities, i (A dm^{-2}), durations, t (min), and pH values. One variable was changed while the other two were held

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Table 1. Composition of the bromide-based cadmium electroplating solutions

Constituent	Compositions of the following solution numbers										
	1	2	3	4	5	6 ^a	7	8	9	10	11 ^b
CdBr ₂ ·4H ₂ O (mol l ⁻¹)	0.30	0.30	0.30	0.30	0.30	0.30	0.10	0.05	0.30	0.30	0.30
HCl (mol l ⁻¹)	-	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
H ₃ BO ₃ (mol l ⁻¹)	-	-	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
KBr (mol l ⁻¹)	-	-	-	0.50	1.00	2.00	2.00	2.00	2.00	2.00	2.00
Gelatin (g l ⁻¹)	-	-	-	-	-	-	-	-	5.00	-	5.00
Melamine (g l ⁻¹)	-	-	-	-	-	-	-	-	-	2.50	2.50

^a This solution is denoted Bath I.

^b This solution is denoted Bath II.

constant. All measurements were made at 25°C using stationary electrodes.

3. Results and discussion

3.1. Polarization curves

The data of the steady-state cathodic polarization for cadmium electrodeposition from Solutions 1–8, of the compositions given in Table 1, are represented graphically in Fig. 1. Inspection of Curves 1 and 2 reveal that the electrodeposition

of cadmium from pure CdBr₂ (Solution 1) or from Solution 2 is accompanied by a slight overpotential and that the two curves coincide with each other. It must be noted that HCl is added (Solution 2) in order to prevent the formation of cadmium hydroxide and basic compounds at the cathode surface. On addition of boric acid (Solution 3) as a buffering agent [11], a further increase in the cathodic polarization is observed (Curve 3). The data of Curves 4–6, respectively, show that the additions of increasing amounts of KBr as an indifferent salt (Solutions 4–6)

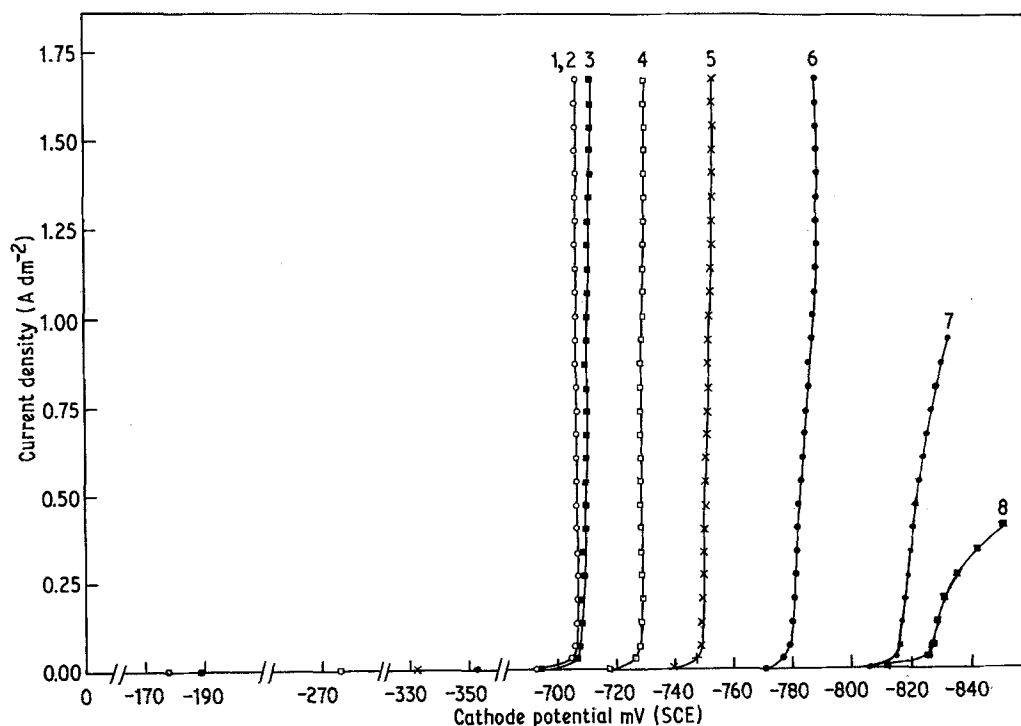


Fig. 1. Polarization curves for cadmium electrodeposition from Solutions 1–8, respectively.

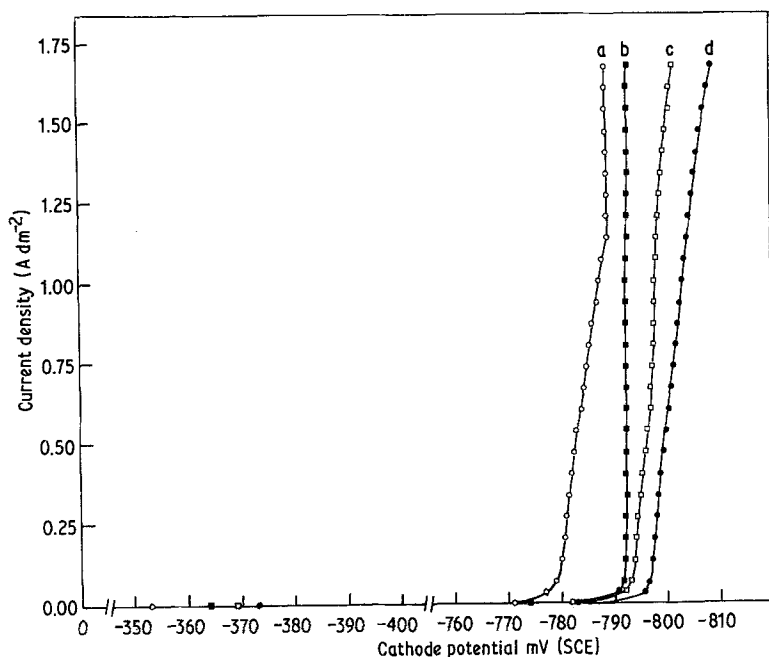


Fig. 2. Polarization curves for cadmium electrodeposition from Bath I (Curve a), Solution 9 (Curve b), Solution 10 (Curve c) and Bath II (Curve d).

produce correspondingly increasing polarization effects. This feature could be accounted for by the activation overpotential arising from complex formation between Cd^{2+} ions and the excessive Br^- anions [8]. This complex is characterized by a stability constant $\log K_1$ of 1.6 [12].

In order to determine the optimum CdBr_2 concentration producing the maximum polarization and at the same time the best electroplate, the polarization curves from Solutions 7 and 8 were also traced. However, as the concentration of CdBr_2 decreases (Solutions 6–8) an extra-overpotential is created and reaches about 50 mV (Curves 6–8) but the polarization curves extend over a shorter range of current density after which it was difficult to measure the cathode potential. This discontinuity of the cathodic polarization curves could be attributed to the depletion of Cd^{2+} ions in the cathode layer and the preferential evolution of hydrogen. These results show that 0.3M CdBr_2 can be regarded as the optimum concentration which allows a wide range of the plating current density. Therefore, the composition corresponding to that of Solution 6 was chosen to fulfil the requirements for the cadmium electrodeposition electrolyte and it is denoted the bromide Bath I.

Some additives (Solutions 9–11) were added to Bath I in an attempt to improve the quality of the former cadmium electroplates. Fig. 2 shows the effects of these additives on the cathodic polarization curves for cadmium electrodeposition from Bath I (Curve a). The addition of either gelatin (Solution 9) or melamine (Solution 10) to Bath I created a slight shift of the cathodic polarization to more negative values (Curves b and c, respectively). The shift in cathodic polarization for gelatin may be ascribed to the widespread occurrence of a very thin protein membrane in the cathode layer [13]. This membrane would result in hindrance, to some extent, of the migration and discharge of the cadmium ions. On the other hand, the shift in cathodic polarization for melamine may be referred to the adsorption of the melamine molecules at the active sites on the cathode surface and the consequent inhibition of cadmium electrodeposition [14]. The combined effects of both gelatin and melamine (Solution 11) seem to be simply additive (Curve d). The characteristics of the cadmium electroplates obtained from Solution 11 are superior to those obtained from any of Solutions 1–10. Therefore, Solution 11 was selected for further investigations and is denoted the bromide Bath II.

Table 2. Effect of the bath constituents on the efficiency, hardness and thickness of cadmium electroplates

Property	Solution number					
	6 (Bath I)	7	8	9	10	11 (Bath II)
f (%)	99.40	90.20	88.20	99.00	99.10	98.40
H_v (kgf mm ⁻²)	125.20	–	–	134.50	136.20	145.90
d (μ)	6.69	6.08	5.95	6.66	6.67	6.63

$i = 1.665 \text{ A dm}^{-2}$ and $t = 10 \text{ min}$.

3.2. Cathodic current efficiency

The effects of the bath constituents CdBr₂ (of varying concentration), gelatin and melamine on the percentage cathodic efficiency (f %) of cadmium electrodeposition were investigated and the results can be seen in Table 2.

On decreasing the concentration of cadmium bromide within the range 0.30–0.05 mol l⁻¹ (Solutions 6–8) the efficiency decreases about 11%. Also, the additions of either gelatin or melamine and a combination of both additives into Bath I (Solutions 9–11, respectively) lead to a very slight decrease in the efficiency. These features could be attributed to the corresponding polarization-increasing effects resulting from the shortage in Cd²⁺ ion concentration and the additions of gelatin and melamine (see Fig. 1). The observed high efficiency range (88–90%) is a common feature of cadmium electrodeposition from simple acidic electrolytes [8]. This is due to the relatively high hydrogen overvoltage on cadmium [11].

The effects of the plating variables i , t and pH on the cathodic efficiency of cadmium deposition from Bath II were also examined and the results are given in Tables 3–5, respectively.

Table 3. Effect of i on the efficiency, hardness and thickness of cadmium electroplates from Bath II

i (A dm ⁻²)	f (%)	H_v (kgf mm ⁻²)	d (μ)
0.165	91.1	–	0.61
0.660	97.7	–	2.61
1.665	98.4	145.9	6.63
1.995	97.3	147.3	7.85

$t = 10 \text{ min}$ and $\text{pH} = 3.58$.

The cathodic current efficiency increases with increasing current density until it reaches a maximum at 1.665 A dm⁻² and then starts to fall again (Table 3). Similar results are observed in several acidic plating electrolytes [11, 15]. The decrease of efficiency above a certain current density limit ($i = 1.665 \text{ A dm}^{-2}$) is due to increased evolution of hydrogen.

Table 4 shows that the cathodic efficiency increases slightly with increasing plating time. A similar trend of increasing efficiency with t was observed for the electrodeposition of cadmium from a corresponding chloride-based bath [10]. This feature would be attributed to accumulation of Cd²⁺ ions as the difference between the anodic efficiency which is close to 100% [1] and the measured cathodic efficiency which is less than 100%. Such an increase of Cd²⁺ ion concentration in the bath leads to a consequent decrease in the cathodic polarization and hence an increase in the efficiency. Therefore, it is recommended that this bath be operated at current densities in the range 0.6–1.6 A dm⁻² where the cathodic efficiency is maximum to avoid changes in the Cd²⁺ ion concentration in the bath.

On addition of HCl to Bath II, the decrease in pH of the bath is accompanied by a slight decrease

Table 4. Effect of t on the efficiency, hardness and thickness of cadmium electroplates from Bath II

t (min)	f (%)	H_v (kgf mm ⁻²)	d (μ)
3	97.5	–	1.97
10	98.4	145.9	6.63
25	99.2	152.3	16.70

$i = 1.665 \text{ A dm}^{-2}$ and $\text{pH} = 3.58$.

Table 5. Effect of pH on the efficiency, hardness and thickness of cadmium electroplates from Bath II

pH	HCl (mol l^{-1})	η (%)	H_v (kgf mm^{-2})	d (μ)
5.35	0.00	99.3	—	6.69
3.58	0.10	98.4	145.9	6.63
1.92	0.40	97.8	161.7	6.59

$i = 1.665 \text{ A dm}^{-2}$ and $t = 10 \text{ min}$.

in the cathodic efficiency (Table 5). Although simple metallic ions are only slightly sensitive to changes in the pH of the solution [16], the slight decrease of the efficiency with lowering of pH could be associated with the decrease of the hydrogen overvoltage and the preferential evolution of hydrogen gas [17]. On the other hand, the highest efficiency is obtained from the

non-acidified solution (see Table 5). This feature may be ascribed to the incorporation of hydroxide or basic oxides of cadmium, which are formed favourably at such a high pH value, into the electro-deposited metal. However, these results are in good agreement with those obtained for the electrodeposition of cadmium and cobalt from acidic chloride solutions [10, 18].

3.3. Surface morphology

The electronmicrographs in Fig. 3 show the influences of the bath constituents on the morphology of the as-formed cadmium electroplates at a current density of 1.665 A dm^{-2} and a plating time of 10 min. In the absence of the inert salt KBr (Solution 3) the cadmium electroplate consists of spiral hexagonal crystals sparsely

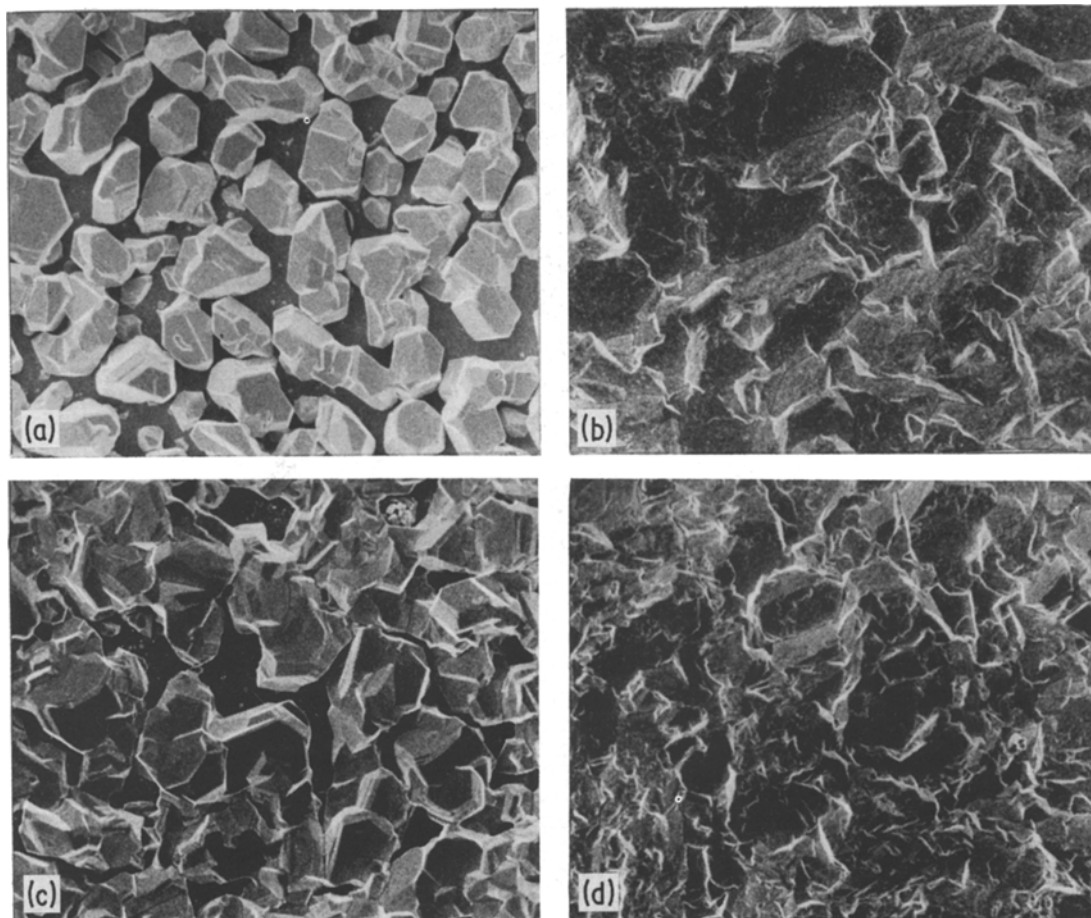


Fig. 3. Electronmicrographs of cadmium from Bath I (a), Solution 9 (b), Solution 10 (c) and Bath II (d); $i = 1.665 \text{ A dm}^{-2}$, $t = 10 \text{ min}$ and magnification $\times 1200$.

covering the cathode. On addition of 2.0 mol KBr l⁻¹ (Bath I) the nucleation density increased to a high extent and the cathode is nearly completely covered with spiral hexagonal crystals leaving holes between them (Fig. 3a). The increase of the nucleation density could be due to the polarization-increasing effect arising from complex formation between Cd²⁺ ions and the excess of Br⁻ anions as discussed above in Section 3.1. The inclusion of 5 g gelatin l⁻¹ in Bath I (Solution 9) leads to suppression of the crystal growth and production of a coherent deposit spreading over the substrate (Fig. 3b). The growth habit modification achieved by gelatin could be explained by the formation of membrane-like films in the cathode layer, these films are thicker in the higher current density areas due to the preferable discharge of H⁺ ions [10, 13]. The addition of 2.5 g melamine l⁻¹ to Bath I (Solution 10) gives rise to relatively larger polycrystals of cadmium (Fig. 3c) than those obtained from the additive-free Bath I. This feature may be associated with the preferential adsorption of melamine on the substrate surface so that the latter becomes relatively inhibited towards cadmium electro-deposition. For this reason, once a cadmium nucleus is formed its surface is relatively clean in comparison with the substrate surface and thus it grows more readily. The combined effect of both gelatin and melamine in Bath II results in the production of a finer texture of coherent crystallites without any preferred grain orientation (Fig. 3d).

The influences of the plating variables i , t and pH on the morphology of cadmium electroplates from Bath II were examined and the electromicrographs taken are shown in Figs. 4–6 respectively. However, only one variable was changed whereas the other two were held constant.

At low current density, the cathode is sparsely covered with a thin layer of irregularly shaped fine-grained deposit (Fig. 4a). This is thought to be due to inhibition of the cathode surface to some extent resulting from the adsorption of Br⁻ anions and melamine molecules as well as the formation of a membrane-like gelatin film in the cathode layer. Under such conditions, the electroplating takes place only by some random deposition [19]. Therefore, the deposit grows on some isolated centres where the local current density is strong enough to overcome the inhibition [20]. However, as the current density increases there is a regular trend of increasing the coverage of the substrate surface with coherent cadmium deposit such as that shown in Fig. 4b. This change may be correlated to the increase of the nucleation density in correspondence to the increase of the overpotential with the current density [21].

On increasing the plating time within the range 3–25 min, there is a corresponding increase in the grain size of the cadmium deposit and improvement of the coverage of the substrate (Figs. 5a, b). However, similar results were obtained for electro-deposition of cadmium from acidic chloride baths [10]. These results could be due to the fact that

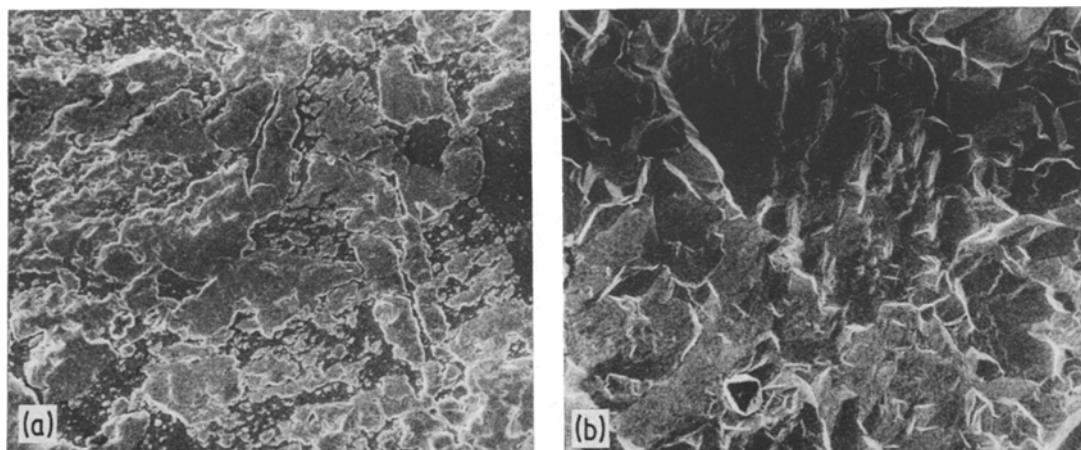


Fig. 4. Electronmicrographs of cadmium from Bath II at $i = 0.165$ (a) and $i = 1.995 \text{ A dm}^{-2}$ (b); $t = 10 \text{ min}$, $\text{pH} = 3.58$ and magnification $\times 1200$.

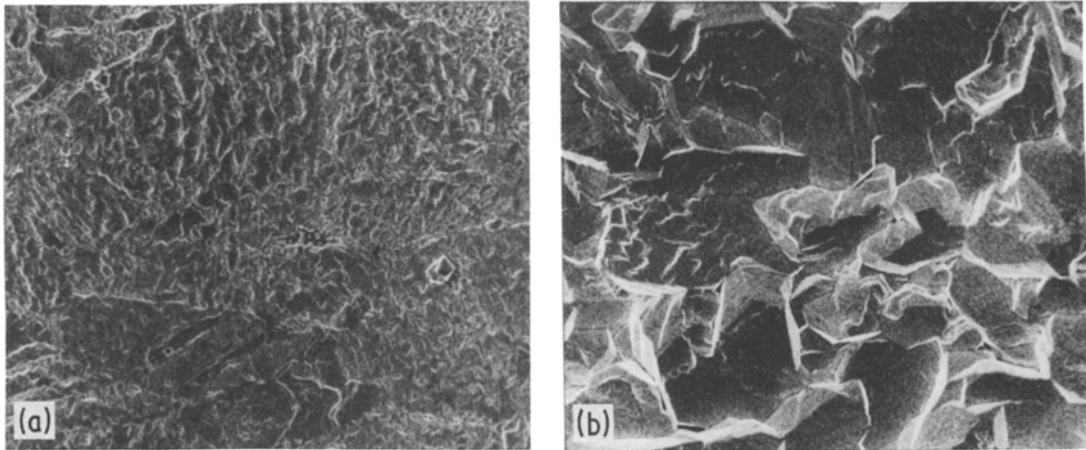


Fig. 5. Electronmicrographs of cadmium from Bath II at $t = 3$ (a) and $t = 25$ min (b); $i = 1.665 \text{ A dm}^{-2}$, $\text{pH} = 3.58$ and magnification $\times 1200$.

bigger grains are more stable thermodynamically, and if the system has enough time, it will reach its most stable state [20]. This phenomenon would result from redissolution and recrystallization of the deposits, through the formation of local cells between them [21].

The non-acidified Bath II ($\text{pH} 5.35$) produces a highly dispersed, friable deposit lacking a metallic appearance (Fig. 6a). It is thought that the deposit consists of basic compounds of cadmium which are formed favourably. This is because gelatin solutions are dissolved by acids and coagulated by neutral salts; consequently, the formation of thicker membrane-like gelatin films is expected in the acid-free Bath II. These films cause hinderance of the migration and discharge of Cd^{2+} ions com-

pared with H^+ ions and thus lead to raising of the pH in the cathode layer above the initial value ($\text{pH} 5.35$). On lowering the pH of Bath II by the addition of $0.4 \text{ mol HCl l}^{-1}$ ($\text{pH} 1.92$) a coherent accumulation of metallic cadmium crystallites is formed (Fig. 6b).

3.4. Microhardness

The effect of the variables: bath composition, i , t and pH on the microhardness of the as-plated cadmium was examined and the results are given in Tables 2–5, respectively.

Table 2 shows that the microhardness of cadmium electroplates from Bath I increases by the addition of gelatin (Solution 9) or melamine

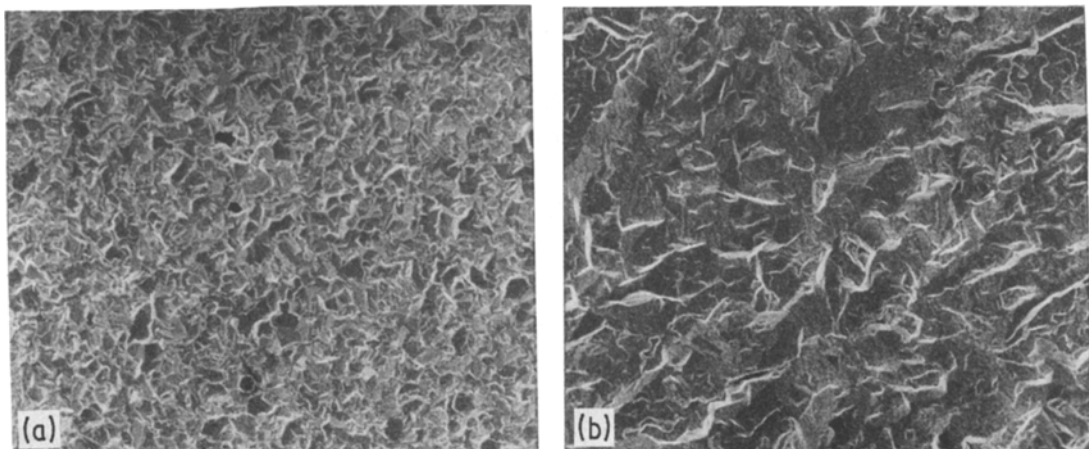


Fig. 6. Electronmicrographs of cadmium from Bath II without HCl (a) and with 0.4 M HCl (b); $i = 1.665 \text{ A dm}^{-2}$, $t = 10$ min and magnification $\times 1200$.

(Solution 10) and reaches its maximum in the presence of a combination of the two additives (Bath II). These results are in good agreement with the morphological changes created by gelatin and melamine (Fig. 3) and confirm that the microhardness is a structure sensitive property [10, 14].

On increasing the plating current density within the narrow range $1.665\text{--}1.995\text{ A dm}^{-2}$, there is a negligible increase in the microhardness of cadmium electroplates from Bath II (Table 3). At the lower current density range, $0.165\text{--}0.660\text{ A dm}^{-2}$, the substrate was not completely covered and the thickness of the cadmium plates was not suitable for hardness measurements (Fig. 4a).

The microhardness of cadmium electroplates from Bath II increases slightly by increasing the plating time within the range 10–25 min (Table 4). This feature may be attributed to increasing the thermodynamic stability of the cadmium plates with increasing crystal size (Fig. 5) via a redissolution–recrystallization mechanism as discussed above in Section 3.3. [20, 21].

The lowering of the pH of Bath II by the inclusion of 0.4M HCl leads to increased microhardness of the cadmium electroplates (Table 5). A similar feature is observed for cadmium electroplating from an acidic chloride bath [10]. The microhardness of the cadmium deposit from the acid-free Bath II (pH 5.35) could not be measured since it was loose and friable.

4. Conclusions

The addition of gelatin and melamine to the acidic bromide bath results in increasing cathode polarization of cadmium deposition. This beneficial effect leads to suppression of crystal growth, promotion of nucleation density and a negligible decrease of current efficiency. Practically, the additive-containing Bath II yields finer grained, more coherent, brighter and harder cadmium plates than the additive-free Bath I.

Bath II can be easily controlled and the optimum operating conditions for obtaining

satisfactory cadmium plates at 25°C are: $i = 0.6\text{--}1.6\text{ A dm}^{-2}$; $t = 10\text{--}15\text{ min}$ and $\text{pH} = 3.6\text{--}1.9$. Under such conditions Bath II is characterized by a high current efficiency ($\geq 97.3\%$) and by the production of bright cadmium plates of good hardness ($\geq 146\text{ kgf mm}^{-2}$). The maximum brightness and hardness (161 kgf mm^{-2}) are achieved at the lowest pH of 1.9.

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