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Electrodeposition of Cd–Ni alloys from acetate baths using a superimposed alternating current

A. M. ABD EL-HALIM, S. S. ABD EL REHIM, S. M. ABD EL WAHAAB,
E. A. ABD EL MEGUID

Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

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The electrodeposition of Cd–Ni alloys from some selected acetate baths has been investigated. The influences of the proportions of Ni^{2+} and Cd^{2+} ions in the bath, the operating current density and superimposed alternating current on the electrodeposited alloys have been examined. The study includes the effect of these variables on the cathodic polarization curves, current efficiency, chemical composition and surface morphology of the alloys. Under all conditions the electrodeposition process is of the anomalous type. An explanation of this phenomenon with the help of a comparison between the experimental and the calculated polarization curves is given. X-ray diffraction studies show that the nickel-rich alloys consist of Ni and β(Cd–Ni) phases, while the cadmium-rich alloys contain Cd, β(Cd–Ni) and Ni phases. The optimum bath composition and operating conditions for the electrodeposition of sound, smooth and bright Cd–Ni alloys have been identified.

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1. Introduction

In recent years interest in electrodeposited Cd–Ni alloys has increased rapidly. This is mainly due to their numerous applications such as decorative finishing of metals, protection of jet-engine parts from corrosion, manufacture of electrical contacts and in battery applications. The electrodeposition of Cd–Ni alloys has been investigated from acidic sulphate [1], sulphate–chloride [2, 3], sulphamate [4] and acetate [5] baths as well as from an alkaline bath [6]. Most of these investigations have shown that the electrodeposition process is of the anomalous type and that the appearance of the alloy depends on the percentage of each metal in the deposit. However, those alloys high in cadmium were grey, smooth and soft. Those low in cadmium were bright, but brittle and stressed. Deposits of intermediate composition were non-uniform, spongy and poorly adherent.

The improvement of the properties of electrodeposited Cd–Ni alloys is of great importance and requires intensive investigations. Therefore, in our laboratory, systematic studies of the electrodeposition of individual nickel [7] and cadmium [8] metals from optimized acetate baths under the influence of superimposed a.c. have been made. The present paper describes a further study of the electrodeposition of Cd–Ni alloys in an attempt to improve their characteristics.

2. Experimental details

The deposition baths were freshly prepared in distilled water using AR grade chemicals (BDH). The symbols, numbers and compositions of these baths are given in Table 1. The experimental set-up for the electrodeposition process, whether in the absence or in the presence of superimposed a.c., has been described elsewhere [8]. All deposition experiments were carried out at 25 ± 1° C with the help of an air thermostat. In each run a copper sheet cathode was placed midway between two plane-parallel platinum anodes; all electrodes were of the same geometrical area (2.5 × 3.0 cm).

The cathodic potentials were measured relative to the saturated calomel electrode (SCE) using a potentiometer type EIL 23 AUK. The composition of each electrodeposited alloy was determined by means of an atomic absorption spectrophotometer (Unicam SP 1900). The mor-

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Table 1. Composition of cadmium, nickel and Cd–Ni alloy electrodeposition baths (pH = 5.4)

Bath	*Amount of the following compounds in bath*						
	$Cd(CH_3COO)_2 2H_2O$ ($mol\,l^{-1}$)	$Ni(CH_3COO)_2 4H_2O$ ($mol\,l^{-1}$)	H_3BO_3 ($mol\,l^{-1}$)	CH_3COOH ($mol\,l^{-1}$)	CH_3COONa ($mol\,l^{-1}$)	*Gelatin* ($g\,l^{-1}$)	*TSA*[a] ($g\,l^{-1}$)
Cd 1	0.010	–	0.3	0.2	0.1	1.0	1.0
Cd 2	0.400	–	0.3	0.2	0.1	1.0	1.0
Ni 1	–	0.150	0.3	0.2	0.1	1.0	1.0
Ni 2	–	0.250	0.3	0.2	0.1	1.0	1.0
(Cd–Ni)1	0.001	0.150	0.3	0.2	0.1	1.0	1.0
(Cd–Ni)2	0.005	0.150	0.3	0.2	0.1	1.0	1.0
(Cd–Ni)3	0.010	0.150	0.3	0.2	0.1	1.0	1.0
(Cd–Ni)4	0.010	0.250	0.3	0.2	0.1	1.0	1.0
(Cd–Ni)5	0.400	0.100	0.3	0.2	0.1	1.0	1.0

[a] TSA, toluene-4-sulphonic acid.

phology of the as-formed deposits was examined with a scanning electron microscope (JEOL Model JSM-T 20). X-ray diffraction analysis was carried out using a Siemens X-ray diffractometer D 500, with a copper target and nickel filter.

3. Results and discussion

3.1. *Polarization curves*

Cathodic polarization curves were obtained for the electrodeposition of Cd–Ni alloys from baths (Cd–Ni) 1 to 5. The curves exhibit the same general features and the position of each curve is controlled by the total metal content in the bath.

Fig. 1 (solid curves) shows that the polarization curve for the alloy deposition from bath (Cd–Ni)4 lies in between the polarization curves of the parent metals from baths Ni 2 and Cd 1. The latter baths have the same composition as the alloy bath except for the absence of the other depositable metal ions. Such a feature is common in many alloy plating baths [9, 10]. The observed low current efficiency of the Cd–Ni alloy deposition, which is discussed in a later section, indicates that the experimental polarization curve of the alloy includes a partial current due to the simultaneous discharge of H^+ ions. The polarization curves for the metals and hydrogen in co-deposition were calculated using the procedure recommended by previous investigators [9], and are shown as dotted curves in

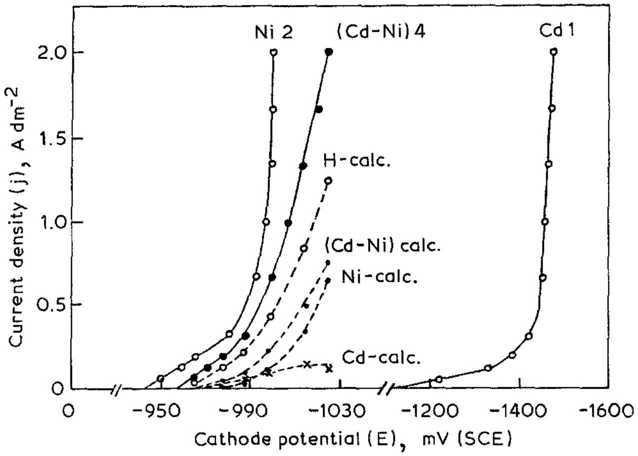

Fig. 1. Experimental polarization curves (——) for electrodeposition from Ni 2, (Cd–Ni)4 and Cd 1 baths and calculated polarization curves (– – –).

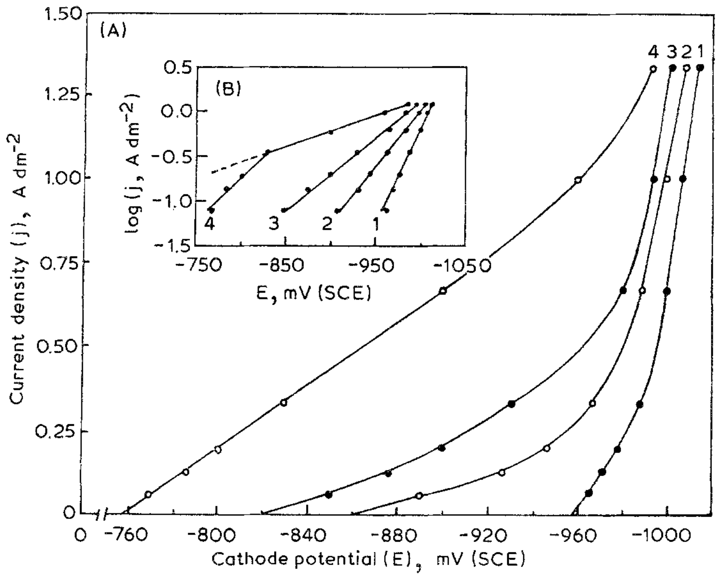

Fig. 2. Effect of superimposed a.c. density ($j_\sim$), a.c. frequency 50 Hz, on polarization curves for Cd–Ni alloy electrodeposition from bath (Cd–Ni)4. (1) d.c. only; (2) $j_\sim = 0.20\,\mathrm{A\,dm^{-3}}$; (3) $j_\sim = 0.50\,\mathrm{A\,dm^{-3}}$; (4) $j_\sim = 1.33\,\mathrm{A\,dm^{-2}}$. (A) Linear scale; (B) logarithmic scale.

Fig. 1. The data show that co-deposition has shifted the potentials of cadmium deposition to less negative values and the potentials of nickel deposition in the more negative direction. This indicates that nickel assumes a higher overpotential in co-deposition than in individual deposition and the opposite is true with respect to cadmium.

If an a.c. is superimposed, bath (Cd–Ni)4 is the most suitable for depositing an alloy characterized by the best adherence, soundness and brightness. Consequently, this bath was selected in order to examine the influence of superimposed sinusoidal a.c. on the electrodeposition of Cd–Ni alloys. The data obtained indicate that a superimposed a.c. results in a shifting of the polarization curve to less negative potentials. Moreover, the higher the a.c. density (Fig. 2) and the lower the a.c. frequency (Fig. 3) the greater is the depolarizing effect, particularly at low direct current densities. Similar results were reported for nickel [7] and cadmium [8] in their respective acetate baths.

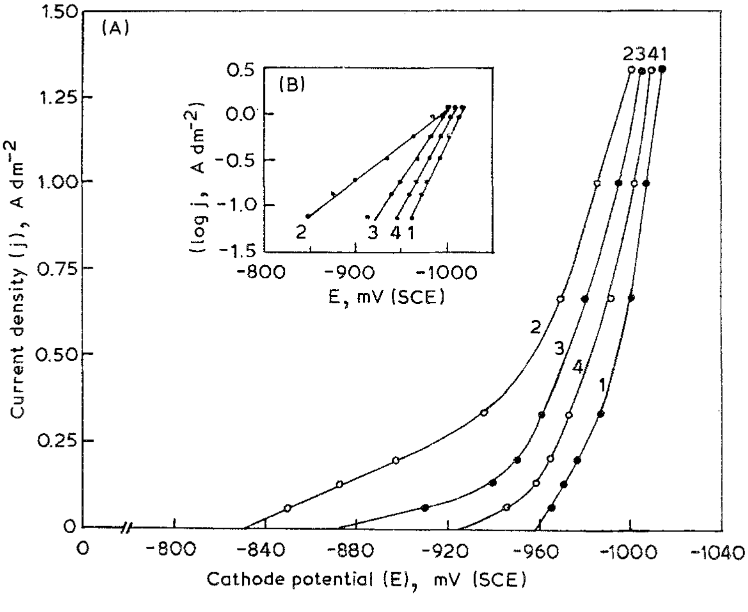

Fig. 3. Effect of superimposed a.c. frequency (ω), a.c. density $0.66\,\mathrm{A\,dm^{-2}}$, on polarization curves for Cd–Ni alloy electrodeposition from bath (Cd–Ni)4. (1) d.c. only; (2) $\omega = 50\,\mathrm{Hz}$; (3) $\omega = 250\,\mathrm{Hz}$; (4) $\omega = 1000\,\mathrm{Hz}$. (A) Linear scale; (B) logarithmic scale.

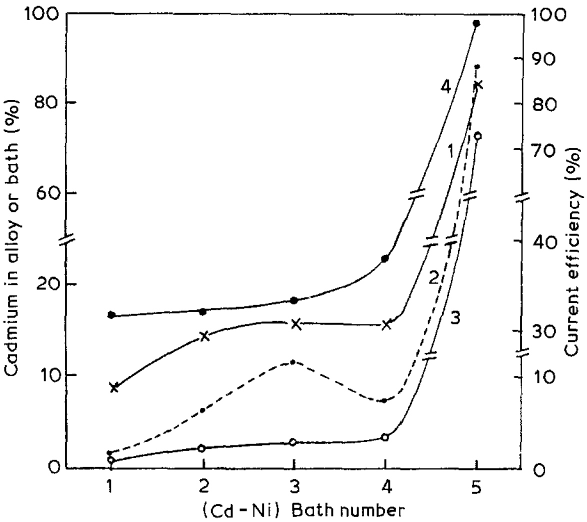

Fig. 4. Effect of the composition of (Cd–Ni) baths on the metal-percentage of cadmium in the alloy (curve 1), the partial current efficiency of cadmium (curve 3) and the current efficiency of the alloy (curve 4); curve 2 represents the composition reference of cadmium in the baths. Current density (j) = 2 A dm^{-2}; duration (t) = 10 min.

3.2. *Alloy composition*

The composition of Cd–Ni alloys deposited from baths (Cd–Ni)1 to 5, at a current density of 2 A dm^{-2} and a duration of 10 min, were determined. Inspection of Fig. 4 (curve 1) reveals that Cd–Ni alloys containing 10–85% cadmium could be obtained from the baths examined. A feature worthy of attention is that the percentages of cadmium in the alloy deposits (curve 1) lie above its composition reference curve that represents the metal-percentages of cadmium in the baths (curve 2). This indicates that the less noble metal (cadmium) deposits preferentially and, therefore, the co-deposition of cadmium and nickel belongs to the anomalous type [11]. This phenomenon was observed during the electrodeposition of Cd–Ni alloys from various baths [2, 3, 5], but no reasonable explanation has yet been given. However, the phenomenon can be explained by reference to the polarization curves, because the deposition potentials and overpotentials govern the composition of the alloy by controlling the relative concentrations of the depositable metal ions at the cathode–solution interface. The discussion on the polarization curves in Section 3.1. shows that cadmium in co-deposition is accompanied by a considerable decrease in the overpotential. In contrast, nickel in co-deposition is accompanied by an increased overpotential. Therefore, it can be concluded that these changes in the overpotentials enhance the electrodeposition of cadmium and retard the electrodeposition of nickel, giving rise to an anomalous co-deposition.

Fig. 5 (curve 1) shows that the percentage of cadmium in the alloy formed in bath (Cd–Ni)4 decreases with increasing deposition current density and approaches the metal-percentage of cadmium in the bath (line AB). This trend of composition with current density is characteristic of an alloy plating system under diffusion control [11]. This result is in agreement with the observed shift of the calculated polarization

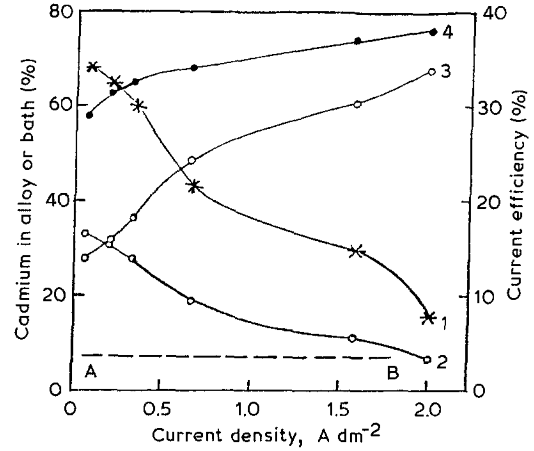

Fig. 5. Effect of current density on the metal-percentage of cadmium in the alloy (curve 1), the partial current efficiencies of cadmium (curve 2) and nickel (curve 3) and the current efficiency of the alloy (curve 4) electrodeposited from bath (Cd–Ni)4. AB represents the composition reference line of cadmium in the bath.

curve of cadmium to considerably more negative values than for nickel with increasing current density (Fig. 1). However, both features could be attributed to a relatively greater depletion of the preferentially depositable Cd^{2+} ions in the cathode film. This causes the deposition at sufficiently high current densities to be under diffusion control and the metal-percentage in the deposit tends to approach that in the bath.

The effects of the superimposed a.c. of variable density and of variable frequency on the composition of Cd–Ni alloys deposited from bath (Cd–Ni)4 are illustrated in Figs 6 and 7, respectively. Curves 1 indicated that the percentage of cadmium in the alloy increases slightly with increasing superimposed a.c. density (Fig. 6) and with lowering of its frequency (Fig. 7). These results may be explained by the depolarizing effect of the superimposed a.c. (Figs. 2, 3) and the consequent enhancement of electrodeposition of the less noble metal (cadmium) in the alloy.

3.3. *Current efficiency*

The percentage cathodic current efficiency (f) of Cd–Ni alloy electrodeposition from baths (Cd–Ni)1 to 5, as well as the partial current efficiencies of cadmium and nickel in co-deposition, were examined and the results are represented graphically in Fig. 4. However, it is observed that f of the alloy (curve 4) increases with increasing total metal content in the bath employed. In addition, the partial f of cadmium (curve 3) in co-deposition increases with increase of its metal ion content in the deposition bath (curve 2). It may be seen that the f of the alloy (38%) obtained with the (Cd–Ni)4 bath is relatively lower than f observed for the electrodeposition of nickel individually (78.5%) from a bath of similar composition and under identical operating conditions [7]. This indicates that the presence of Cd^{2+} ions at a low concentration in the alloy deposition bath hinders the discharge of Ni^{2+} ions. This conclusion is in agreement with the fact that the polarization curve for the alloy deposition lies at more negative potentials than the corresponding curve for individual nickel deposition (Fig. 1).

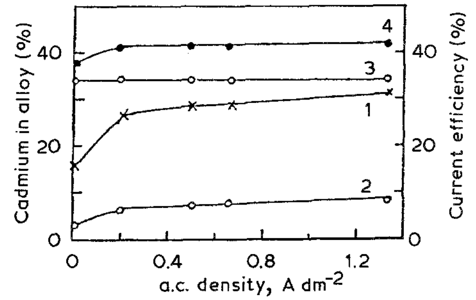

Fig. 6. Effect of superimposed a.c. density ($j_{\sim}$), a.c. frequency 50 Hz. The legends of curves 1 to 4 are the same as in Fig. 5; $j = 2\,A\,dm^{-2}$; $t = 10\,min$.

Fig. 5 shows that the f of the alloy deposition (curve 4) from bath (Cd–Ni)4 increases slightly on increasing the deposition current density. On the other hand, the partial f of nickel (curve 3) increases at the expense of the partial f of cadmium (curve 2). The latter results may be ascribed to the greater depletion of the more readily depositable Cd^{2+} ions in the cathode film with increasing current density, as discussed in Section 3.2.

Inspection of Figs 6 and 7 reveal that a superimposed a.c. causes a slight increase of both the f of the alloy (curve 4) deposited from bath (Cd–Ni)4 and the partial f of cadmium (curve 2) in co-deposition, whereas the partial f of nickel (curve 3) remains almost constant. Moreover, the increase in f is more marked at the highest a.c. density used (Fig. 6) and the lowest a.c. frequency (Fig. 7). These results may be attributed to the corresponding depolarizing effects of the a.c. (Figs 2, 3) which enable the Cd^{2+} ions to discharge at more noble potentials in co-deposition than in individual deposition.

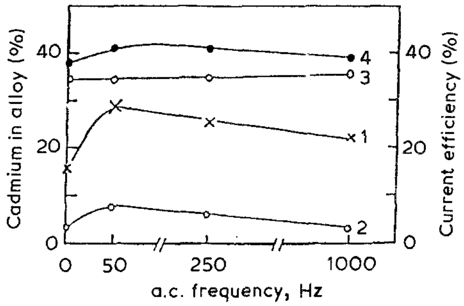

Fig. 7. Effect of superimposed a.c. frequency (ω), a.c. density $0.66\,A\,dm^{-2}$. The legends of curves 1 to 4 are the same as in Fig. 5; $j = 2\,A\,dm^{-2}$; $t = 10\,min$.

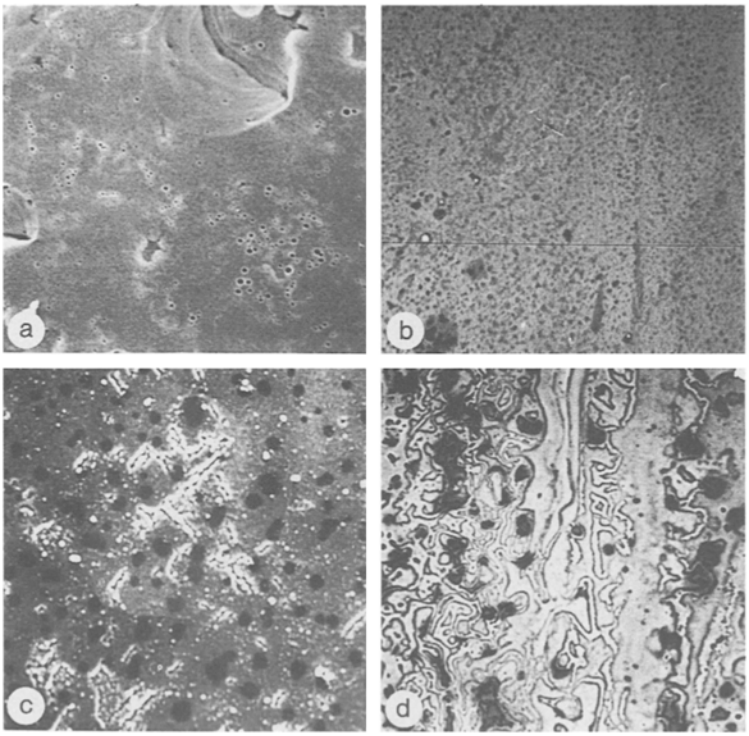

Fig. 8. Electron micrographs of nickel from (a) bath Ni 1, and Cd–Ni alloys from (b) bath (Cd–Ni)1, (c) bath (Cd–Ni)2, (d) bath (Cd–Ni)3. $j = 2\,\mathrm{A\,dm^{-2}}$; $t = 10\,\mathrm{min}$. × 620.

3.4. *Surface morphology*

The effects of bath composition and superimposed a.c. on the surface morphology of the as-deposited Cd–Ni alloys were examined, and some of the electron micrographs taken are shown in Figs 8–10.

As can be seen in Fig. 8a the nickel plate deposited from bath Ni 1 consists of flat layers including some pores and a few shapeless excrescences. The presence of a minor concentration of Cd^{2+} ions in bath (Cd–Ni)1 leads to the formation of fine-grained and more levelled texture showing some small pores (Fig. 8b). On increasing the concentration of Cd^{2+} ions in bath (Cd–Ni)2, an increase in the size of the pores accompanied by the appearance of bud-like excrescences is observed (Fig. 8c). A further increase in the concentration of Cd^{2+} ions in bath (Cd–Ni)3 results in non-continuous, intensively irregular out-growths (Fig. 8d).

Inspection of Figs 8d and 9a reveals that the electrodeposited alloys from baths (Cd–Ni)3 and 4, respectively, have almost the same morphological characteristics. A marked feature of great importance is that superimposed a.c. suppresses the irregular out-growth of the alloy obtained from bath (Cd–Ni)4 giving rise to a more levelled and finer-grained plate (Fig. 9b). Furthermore, the morphological modifications exerted by the superimposed a.c. increase on increasing the a.c. density (Fig. 9b, c) and lowering its frequency (Fig. 9c, d). It must be mentioned that the favourable effects of the a.c. on the morphology is also accompanied by a slight increase in the percentage of cadmium in the alloy (Figs 6, 7).

On the other hand, the morphological features of the cadmium-rich alloy electrodeposited from bath (Cd–Ni)5 are more or less similar to those of pure cadmium deposited from bath Cd 2. Moreover, the alloy deposit (Fig. 10a) is characterized by a finer texture and better coverage of the cathode when compared with the individual cadmium deposit (Fig. 10b).

3.5. *X-ray diffractometry*

X-ray diffraction studies were carried out on the Cd–Ni alloys deposited from the baths under

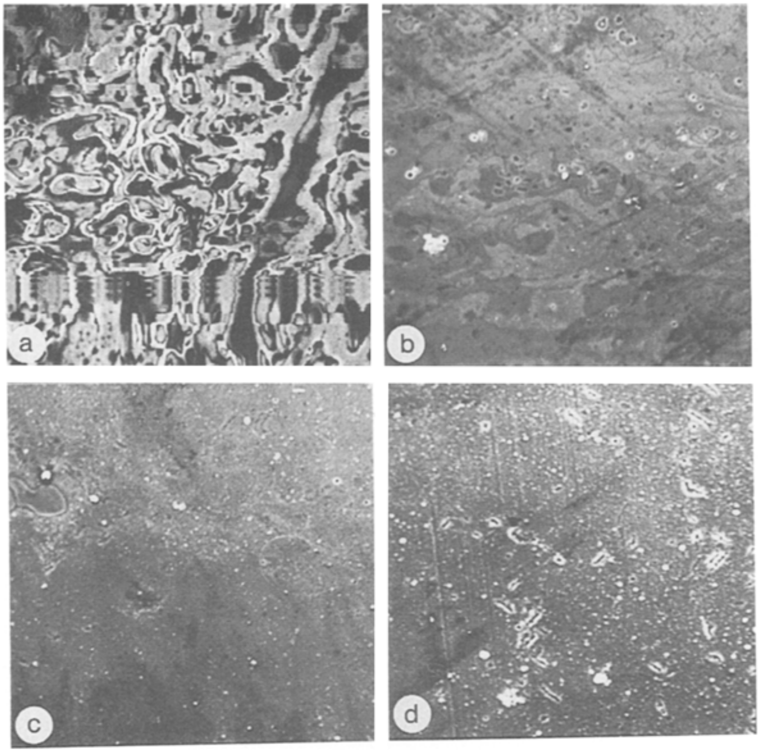

Fig. 9. Electron micrographs of Cd–Ni alloys from bath (Cd–Ni)4 under the influence of superimposed a.c. (a) d.c. only; (b) $j_\sim = 0.20\,\mathrm{A\,dm^{-2}}$, $\omega = 50\,\mathrm{Hz}$; (c) $j_\sim = 0.66\,\mathrm{A\,dm^{-3}}$, $\omega = 50\,\mathrm{Hz}$; (d) $j_\sim = 0.66\,\mathrm{A\,dm^{-2}}$, $\omega = 1000\,\mathrm{Hz}$. $j = 2\,\mathrm{A\,dm^{-2}}$; $t = 10\,\mathrm{min}$. × 620.

test, at a current density of $2\,\mathrm{A\,dm^{-2}}$ and a duration of 10 min. Some examples of the results are given in Table 2. The data show that the nickel-rich alloys obtained from baths (Cd–Ni)1 to 4, represented by Sample I, are composed mainly of a mixture of the face-centred cubic (fcc) Ni phase with a minor quantity of the body-centred cubic (bcc) β(Cd–Ni) phase. However, a small increase in the observed lattice parameter (a) of nickel than its standard value, as a result of the alloy formation, could be detected. In contrast, the cadmium-rich alloy (Sample II) consists of larger proportions of the bcc β(Cd–Ni) and the hexagonal close-packed (hcp) Cd phases in addition to a minor quantity of the fcc Ni phase. Moreover, the lattice parameters (a) of both cadmium and nickel increase with the formation of the alloy. These changes in the lattice parameters could be ascribed to the formation of solid solutions [9]. In general, similar results have been reported previously [12].

4. Conclusions

Electrodeposition of Cd–Ni alloys having 15–90% nickel was achieved from the acetate

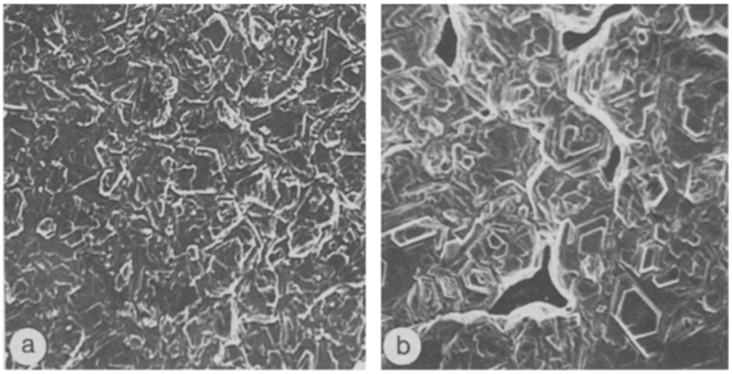

Fig. 10. Electron micrographs of (a) Cd–Ni alloy from bath (Cd–Ni)5 and (b) cadmium from bath Cd 2. $j = 2\,\mathrm{A\,dm^{-2}}$; $t = 10\,\mathrm{min}$. × 620.

Table 2. X-ray diffraction data for the electrodeposited Cd–Ni alloys. Sample I deposited from bath (Cd–Ni)3 and contains 84% nickel. Sample II deposited from bath (Cd–Ni)5 and contains 84% cadmium.

Sample	*Observed*		I/I_0	*Phase*	*Crystal symmetry*	hkl	*Lattice parameters (Å)*			
							Average		*Standard*	
	2θ	*d (Å)*					*a*	*c*	*a*	*c*
I	44.6	2.029	8	Ni	fcc	111	3.553	–	3.523	–
	45.3	1.999	13	β(Cd–Ni)	bcc	–	–	–	–	–
	50.5	1.801	100	Ni	fcc	200				
	64.9	1.435	6	β(Cd–Ni)	bcc	–				
	76.8	1.241	5	Ni	fcc	220				
	100.8	0.999	5	β(Cd–Ni)	bcc	–				
II	28.8	3.090	22	β(Cd–Ni)	bcc	–	–	–	–	–
	31.9	2.721	100	β(Cd–Ni)	bcc	–				
	34.9	2.658	10	Cd	hcp	100	3.069	5.612	2.979	5.618
	38.4	2.341	6	Cd	hcp	101				
	50.6	1.802	18	Ni	fcc	200	3.604	–	3.523	–
	60.6	1.403	80	Cd	hcp	004				

baths studied. The observed anomalous type of electrodeposition of the alloy could be explained by changes in the opposite sense of the overpotentials of cadmium and nickel in co-deposition. When a superimposed a.c. is applied, bath (Cd–Ni)4 appeared to be the most suitable for deposition of sound, smooth and bright alloy over the current density range 0.6–3.0 A dm^{-2}. Superimposed a.c., depending on its density and frequency, exerted a depolarizing effect during electrodeposition. This in turn provided a method of controlling the alloy composition and current efficiency to some extent and could improve the quality of the deposit to a great extent especially at the optimum a.c. condition ($j_\sim = 1.3\,\mathrm{A\,dm^{-2}}$ and $\omega = 50\,\mathrm{Hz}$).

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