

## Influence of variables on Cd-Ni-Ti alloy plating from a sulphate bath

S D Shukla & Neena Srivastava

Department of Chemistry, University of Lucknow, Lucknow 226 007, India

Received 8 February 1994; accepted 11 August 1994

Cadmium, nickel and titanium have been codeposited from a sulphate bath containing sulphates of cadmium and nickel, potassium titanium oxalate, starch and sulphuric acid under different electroplating conditions. The codeposits obtained are grey and dull. The effect of operating conditions on the contents of the individual metals in the codeposit has been studied. The throwing power of the electroplating bath has also been evaluated.

The electrodeposition of alloys of nickel and cadmium with other metals has become technologically important because of their potential applications as protective coatings.

Ternary thin films containing nickel and cadmium as major components have been electrodeposited mainly from sulphate<sup>1,2</sup> and acetate<sup>3,4</sup> baths under different operating conditions. The fluoride<sup>5</sup>, fluoroborate<sup>6</sup> and borate<sup>7</sup> baths have also been utilized to obtain satisfactory deposits. However, a very little work has been done to incorporate titanium into such ternary systems<sup>8</sup>. It is quite probable that such ternary systems are more corrosion resistant and possess better mechanical properties than those without titanium. This encouraged us to investigate the possibility of codepositing titanium with nickel and cadmium from a sulphate bath under various electrolytic conditions.

### Experimental Procedure

Thin alloy films were obtained by electrolysis of 225 mL of a solution containing sulphates of nickel and cadmium, potassium titanium oxalate, ammonium sulphate (20 g dm<sup>-3</sup>), starch (1 g dm<sup>-3</sup>) and conc. H<sub>2</sub>SO<sub>4</sub> (2 mL dm<sup>-3</sup>) in a rectangular electrolytic cell for 30 min. Details of the electrolytic cell have been given elsewhere<sup>9</sup>. The pH of the electrolytic solution was adjusted to the desired value using either 0.1 N sulphuric acid or ammonia solution. The cathode was washed with distilled water, dried and then peeled off carefully. A fixed amount (50 mg) of the alloy was dissolved in 2 N sulphuric acid in a 50 mL flask for analysing its various metal constituents. Nickel and cadmium were estimated gravimetrically using dimethylglyoxime and β-naphthaquinoline complexes, respectively, whereas titanium was estimated by standard colorimetric method<sup>10</sup>.

The deposit composition and hence the cathode current efficiency under various plating conditions were calculated by the usual method<sup>11</sup>. The cathode

potentials with and without a definite flow of current were measured to an accuracy of ±0.001 V against a saturated calomel electrode. The difference between the potentials gave the value of the cathode overpotential η.

The throwing power *N* was calculated from the resistivity ρ of the electrolyte and the Tafel slope *b* of the plot of the cathode overpotential against the logarithm of current density by using Gardam's formula<sup>12</sup>:  $N = b/2\rho$ .

### Results and Discussion

The relative position of the cathode potential-current density curves given in Fig. 1 for Ni, Cd, Ti and binary Ni-Cd, Cd-Ti and Ti-Ni alloy suggests that codeposition of these metals is feasible.

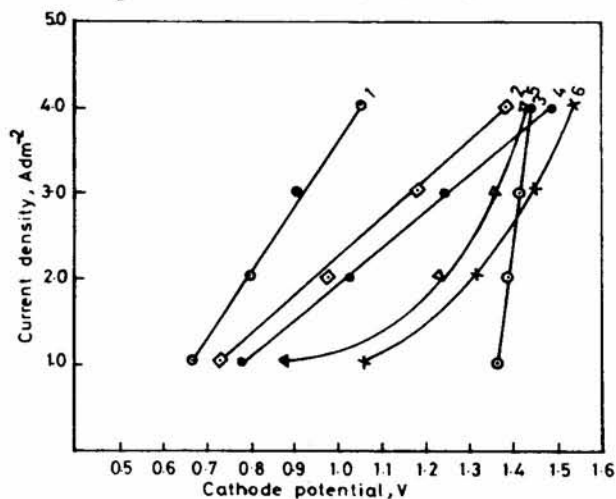


Fig. 1—Cathode potential-current density curves for Ni, Ti and Cd and their codeposits at 30°C and at a pH of 2.0 [Bath composition (g dm<sup>-3</sup>): (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 20.0; H<sub>2</sub>SO<sub>4</sub> ~ 2 mL; starch 1.0; curve 1—Ni (NiSO<sub>4</sub>·7H<sub>2</sub>O, 60.0); curve 2—Ti (potassium titanium oxalate, 2.0); curve 3—Cd (CdSO<sub>4</sub>·8H<sub>2</sub>O, 15.0); curve 4—Ni-Ti (NiSO<sub>4</sub>·7H<sub>2</sub>O, 60.0 & potassium titanium oxalate, 2.0); curve 5—Ni-Cd (NiSO<sub>4</sub>·7H<sub>2</sub>O, 60.0 & CdSO<sub>4</sub>·8H<sub>2</sub>O, 15.0); curve 6—Cd-Ti (CdSO<sub>4</sub>·8H<sub>2</sub>O, 15.0 & potassium titanium oxalate, 2.0)]

Table 1—Effect of pH, temperature and current density on the deposit composition

| pH  | Temperature<br>°C | Metal | Amount (%) of the metal in the deposit at current density (A dm <sup>-2</sup> ) of |       |       |       |
|-----|-------------------|-------|------------------------------------------------------------------------------------|-------|-------|-------|
|     |                   |       | 1.0                                                                                | 2.0   | 3.0   | 4.0   |
| 2.0 | 20                | Ni    | 1.22                                                                               | 2.89  | 3.26  | 5.71  |
|     |                   | Ti    | 0.27                                                                               | 0.41  | 0.55  | 0.63  |
|     |                   | Cd    | 98.51                                                                              | 96.70 | 96.19 | 93.66 |
| 2.0 | 25                | Ni    | 1.85                                                                               | 3.25  | 4.12  | 6.98  |
|     |                   | Ti    | 0.23                                                                               | 0.40  | 0.53  | 0.62  |
|     |                   | Cd    | 97.92                                                                              | 96.35 | 95.35 | 92.40 |
| 2.0 | 30                | Ni    | 2.61                                                                               | 3.66  | 4.88  | 9.36  |
|     |                   | Ti    | 0.23                                                                               | 0.37  | 0.49  | 0.59  |
|     |                   | Cd    | 97.16                                                                              | 95.97 | 94.63 | 90.05 |
| 2.0 | 35                | Ni    | 2.85                                                                               | 4.09  | 5.19  | 10.54 |
|     |                   | Ti    | 0.21                                                                               | 0.35  | 0.40  | 0.49  |
|     |                   | Cd    | 96.94                                                                              | 95.56 | 94.41 | 88.97 |
| 1.8 | 30                | Ni    | 0.81                                                                               | 1.22  | 3.25  | 5.69  |
|     |                   | Ti    | 0.27                                                                               | 0.49  | 0.61  | 0.68  |
|     |                   | Cd    | 98.92                                                                              | 98.29 | 96.14 | 93.63 |
| 1.9 | 30                | Ni    | 1.19                                                                               | 1.63  | 3.66  | 6.92  |
|     |                   | Ti    | 0.23                                                                               | 0.39  | 0.54  | 0.61  |
|     |                   | Cd    | 98.58                                                                              | 97.98 | 95.80 | 92.47 |
| 2.1 | 30                | Ni    | 3.15                                                                               | 4.02  | 6.51  | 14.65 |
|     |                   | Ti    | 0.15                                                                               | 0.22  | 0.35  | 0.54  |
|     |                   | Cd    | 96.70                                                                              | 95.76 | 93.14 | 84.81 |

Bath composition (g dm<sup>-3</sup>): Nickel sulphate, 60.0; potassium titanium oxalate, 2.0; cadmium sulphate, 15.0; ammonium sulphate, 20.0; starch, 1.0; & conc. H<sub>2</sub>SO<sub>4</sub> ~ 2 mL dm<sup>-3</sup>.

Deposits of compositions Ni:0.81-14.65%, Ti:0.15-0.68% and Cd:84.81-98.92% were obtained from baths of different compositions under the following conditions: current density, 1.0-4.0 A dm<sup>-2</sup>; pH, 1.80-2.10; temperature, 20-35°C and duration of deposition, 30 min. In general, uniform semibright grey coatings were obtained at low current densities. The deposits became dark grey, patchy and dull at higher current densities. Their brightness improved with increasing pH and current density, whereas it decreased with increasing temperature of the bath.

**Codeposit composition**—Tables 1 and 2 show the effects of the plating variables on the composition of the codeposit. As the current density is increased, the nickel and titanium contents of the deposits gradually increase, whereas the cadmium content decreases continuously. The percentage of nickel in the alloy rises with increasing temperature and pH of the electrolyte whereas the percentage of cadmium and titanium exhibits a reverse behaviour. Furthermore, it was observed (Table 2) that if the concentration of nickel in the bath is increased, the amount of nickel in the deposits increases, whereas the amounts of the other two constituents, namely, titanium and

Table 2—Effect of metal concentration in the bath on the deposit composition at a temperature of 30°C, pH of 2.0 and current density of 3.0 A dm<sup>-2</sup>

| Concentration of metal compound<br>gdm <sup>-3</sup> | Amount (%) of the metal in the deposit |      |       | Bath composition,<br>gdm <sup>-3</sup>                                                                                                                                                                                            |
|------------------------------------------------------|----------------------------------------|------|-------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                      | Ni                                     | Ti   | Cd    |                                                                                                                                                                                                                                   |
| Nickel sulphate                                      |                                        |      |       |                                                                                                                                                                                                                                   |
| 55.0                                                 | 3.73                                   | 0.49 | 95.78 | K <sub>2</sub> TiO(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> – 2.0,<br>CdSO <sub>4</sub> – 15.0,<br>(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> – 20.0,<br>starch – 1.0 &<br>conc. H <sub>2</sub> SO <sub>4</sub> ~ 2.0 mL |
| 60.0                                                 | 4.88                                   | 0.49 | 94.63 |                                                                                                                                                                                                                                   |
| 65.0                                                 | 5.31                                   | 0.35 | 94.34 |                                                                                                                                                                                                                                   |
| 70.0                                                 | 6.51                                   | 0.29 | 93.18 |                                                                                                                                                                                                                                   |
| —                                                    |                                        |      |       |                                                                                                                                                                                                                                   |
| Potassium titanium oxalate                           |                                        |      |       |                                                                                                                                                                                                                                   |
| 1.5                                                  | 4.13                                   | 0.38 | 95.49 | NiSO <sub>4</sub> – 60.0,<br>CdSO <sub>4</sub> – 15.0<br>(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> – 20.0,<br>starch – 1.0 &<br>conc. H <sub>2</sub> SO <sub>4</sub> ~ 2.0 mL                                               |
| 2.0                                                  | 4.88                                   | 0.49 | 94.63 |                                                                                                                                                                                                                                   |
| 2.5                                                  | 5.48                                   | 0.52 | 94.00 |                                                                                                                                                                                                                                   |
| 3.0                                                  | 5.90                                   | 0.52 | 93.58 |                                                                                                                                                                                                                                   |
| Cadmium sulphate                                     |                                        |      |       |                                                                                                                                                                                                                                   |
| 10.0                                                 | 5.85                                   | 0.51 | 93.64 | K <sub>2</sub> TiO(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> – 2.0,<br>NiSO <sub>4</sub> – 60.0,<br>(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> – 20.0,<br>starch – 1.0 &<br>conc. H <sub>2</sub> SO <sub>4</sub> ~ 2.0 mL |
| 12.5                                                 | 5.01                                   | 0.50 | 94.49 |                                                                                                                                                                                                                                   |
| 15.0                                                 | 4.88                                   | 0.49 | 94.63 |                                                                                                                                                                                                                                   |
| 17.5                                                 | 4.62                                   | 0.47 | 94.91 |                                                                                                                                                                                                                                   |

cadmium decrease. Similar is the behaviour with cadmium addition. However, when the concentration of titanium in the electrolyte is increased, the concentration of both nickel and titanium in the alloy rises slowly, whereas the concentration of cadmium shows a downward trend.

**Cathode efficiency**—The cathode current efficiency for the deposition of single metal is 1.20-12.36% for Ni; 0.29-1.85% for Ti; 29.01-77.43% for Cd and 36.18-83.39% for alloy deposition under similar conditions. The variation in the total current efficiency with temperature and pH is represented in Figs 2 and 3. It increases slowly with decrease in the pH of solution from 2.10 to 1.80 and temperature of the electrolytic bath from 35 to 20°C at a given current density. It is also observed that at any particular pH and temperature of the bath the total current efficiency decreases rapidly to begin with and then decreases slowly as the current density is raised.

**Cathode overpotential**—The variation in the cathode overpotential with current density during electrodeposition at pH values of 1.80-2.10 and temperatures of 20-35°C is summarized in Table 3. It is observed that the overpotential shifts to more negative values when the current density and the pH values of the solution are increased. With increasing current density, the diffusion of metal ions becomes insufficient to keep pace with their discharge at the cathode, with the result that more hydrogen ions get

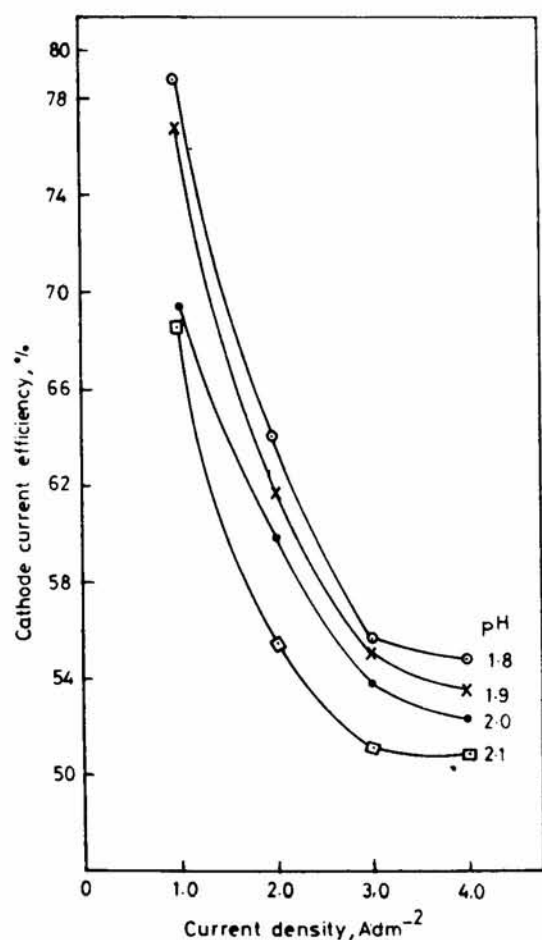


Fig. 2—Effect of pH on the cathode efficiency at 30°C [Bath composition : as given in Table I]

Table 3—Variation in cathode overpotential with pH and temperature at different current densities

| pH  | Temperature<br>°C | Rest<br>potential<br>V | Cathode overpotential $\eta$ (V)<br>at current density(Acm <sup>-2</sup> ) of |        |        |        |
|-----|-------------------|------------------------|-------------------------------------------------------------------------------|--------|--------|--------|
|     |                   |                        | 1.0                                                                           | 2.0    | 3.0    | 4.0    |
| 1.8 | 30                | -0.3185                | -0.551                                                                        | -0.742 | -0.850 | -0.926 |
| 1.9 | 30                | -0.3265                | -0.581                                                                        | -0.801 | -0.919 | -1.010 |
| 2.0 | 30                | -0.3485                | -0.671                                                                        | -0.896 | -1.018 | -1.110 |
| 2.1 | 30                | -0.3505                | -0.698                                                                        | -0.938 | -1.084 | -1.179 |
| 2.0 | 20                | -0.3875                | -0.800                                                                        | -1.054 | -1.185 | -1.308 |
| 2.0 | 25                | -0.3695                | -0.740                                                                        | -0.959 | -1.079 | -1.181 |
| 2.0 | 35                | -0.3275                | -0.615                                                                        | -0.820 | -0.932 | -1.023 |

Bath composition : as in Table I.

simultaneously discharged which makes the cathode overpotential more negative. In contrast, with increasing temperature the overpotential becomes less negative at a constant current density which may be due to a higher rate of diffusion of the depositing ion.

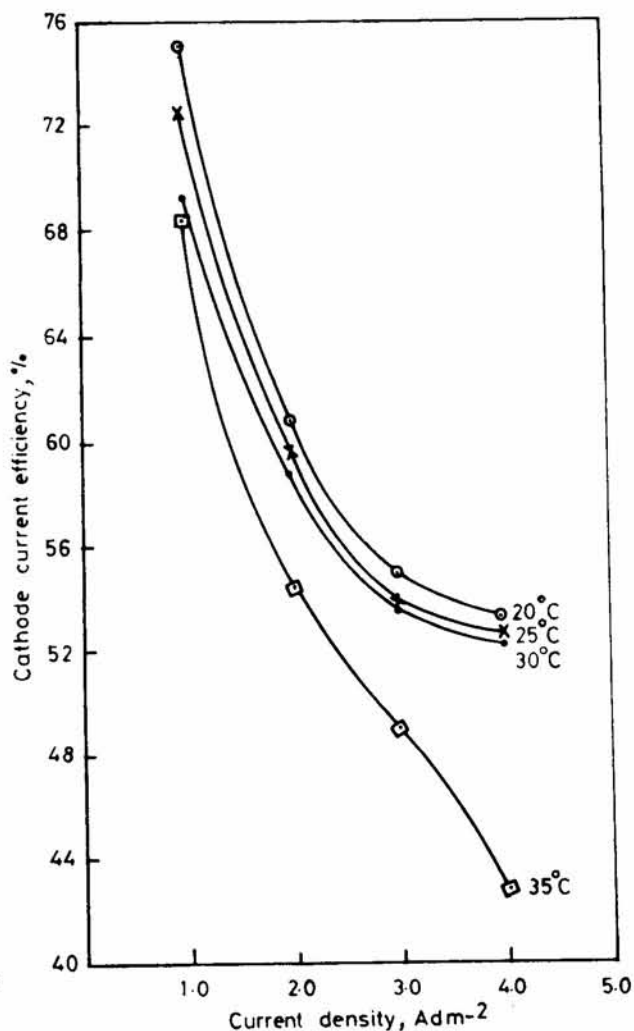


Fig. 3—Effect of temperature on the cathode efficiency at a pH of 2.0 [Bath composition : as given in Table I]

Table 4—Effect of temperature and pH on the resistivity, the Tafel slope and the throwing power of electrodeposits

| Temperature<br>°C | pH  | Resistivity<br>$\rho$ , $\Omega$ cm | Tafel slope<br>$b$ , V | Throwing<br>power<br>Acm <sup>-1</sup> |
|-------------------|-----|-------------------------------------|------------------------|----------------------------------------|
| 20                | 2.0 | 75.145                              | 0.850                  | 0.0057                                 |
| 25                | 2.0 | 34.682                              | 0.733                  | 0.0106                                 |
| 30                | 2.0 | 23.410                              | 0.733                  | 0.0157                                 |
| 35                | 2.0 | 23.121                              | 0.663                  | 0.0143                                 |
| 30                | 1.8 | 20.896                              | 0.625                  | 0.0150                                 |
| 30                | 1.9 | 22.543                              | 0.700                  | 0.0155                                 |
| 30                | 2.1 | 23.988                              | 0.800                  | 0.0167                                 |

Bath composition: as in Table I.

**Throwing power**—The cathode overpotential was found to vary linearly with the logarithm of the current density (Figs 4 and 5), thus the Tafel relationship holds. The throwing power which is a measure of the tendency of the bath to give a uniform

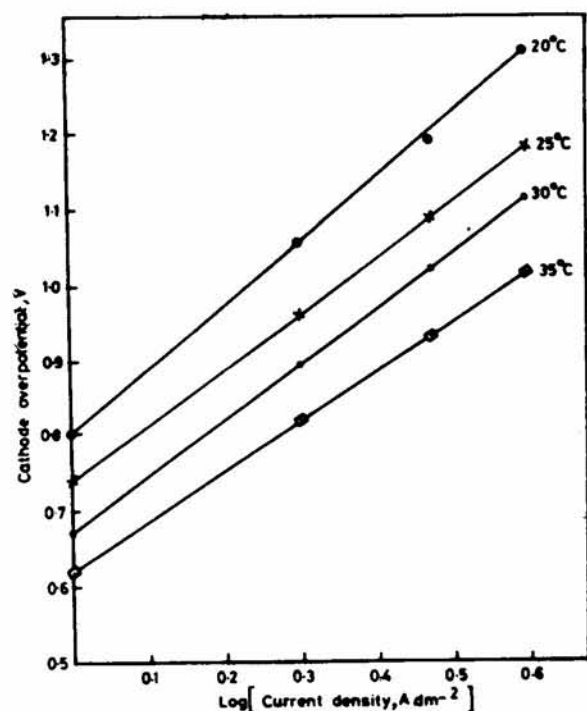


Fig. 4—Variation of cathode overpotential with logarithm of current density at various temperatures and a pH of 2.0 [Bath composition : as given in Table I]

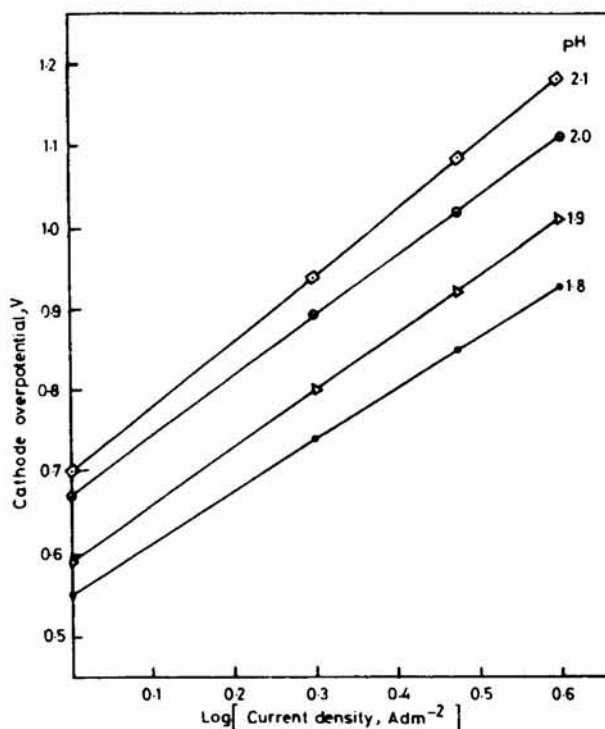


Fig. 5—Variation of cathode overpotential with logarithm of current density at different pH and 30°C [Bath composition : as given in Table I]

deposit, was calculated from the values of the Tafel slope and the resistivity and the results are listed in Table 4. Its value was found to increase with increasing temperature, however, above 30°C, the value of throwing power decreases. This indicates that 30°C and relatively high value of pH should favour more uniform deposits.

## References

- 1 Dambal R P & Ramachar T L, *Electroplat Met Finish*, 25(4) (1972) 10-18.
- 2 Siva Kumar R & Ramachar T L, *Met Finish J*, 18(206) (1972) 65-70.
- 3 Singh V B & Tikoo P K, *Electrochim Acta*, 23(4) (1978) 393-396.
- 4 Singh V B, *J Appl Electrochem*, 9(3) (1979) 285-289.
- 5 Dunkie G & Djordjevic S, *Hem Ind*, 31(8) (1977) 395-400.
- 6 Djordjevic S & Dunkie G, *Hem Ind*, 29(2) (1975) 59-65.
- 7 Srivastava S N & Srivastava S C, *Surf Technol*, 18 (1983) 107-115.
- 8 Srivastava S, Kashyap R & Srivastava S C, *Indian J Technol*, 26(5) (1988) 225.
- 9 Shukla R K, Jha S K & Srivastava S C, *J Appl Electrochem*, 11 (1981) 697-701.
- 10 Vogel A I, *A text book of quantitative inorganic analysis*, 3rd ed. (ELBS and Longmans Green and Co Ltd, London), 1961.
- 11 Lowenheim F A, ed., *Modern electroplating*, 2nd ed. (Wiley, New York), 1963, 470.
- 12 Gardam G E, *Trans Faraday Soc*, 34 (1938) 698.