JOURNAL OF APPLIED ELECTROCHEMISTRY 8 (1978) 71–74

SHORT COMMUNICATION

Electrodeposition of tin-cadmium alloys from a chloride-fluoride bath

R. D. SRIVASTAVA, D. TRIPATHI, A. K. AGARWAL

Chemical Laboratories, University, Lucknow, India

Received 1 March 1977

1. Introduction

Interest in the co-deposition of tin and cadmium has developed because the alloy provides protective coatings to ferrous metals. The coatings of the alloy on iron and steel plates are found to be more corrosion resistant than the single metals. Tin–cadmium alloys have been used to protect engine parts from atmospheric, saline corrosion [1] and from the exhaust gases of jet fuels. The tin–cadmium electroplates have been reported to resist corrosion from organic acids [2].

The alloy was initially deposited from a stannate–cyanide bath [3, 4]. Since then various other baths, namely fluosilicate [5], fluoborate [6–8] and sulphate containing cetyl trimethyl ammonium bromide as addition agent [9] have been reported. Fine crystalline coatings of the alloy have been obtained from chloride baths containing ammonium chloride and glycine [10].

The co-deposition of cadmium and tin from chloride–fluoride baths was carried out by Kudryavtsev [11] who worked out in detail the conditions of co-deposition [12–15]. In the present work the composition of the electrodeposited tin–cadmium alloy has been studied as a function of bath composition, current density, pH and temperature from a chloride–fluoride bath with a view to obtaining fine-grained, bright, non-porous, adherent and elastic electroplates containing 25–30% tin with good current yield on copper and steel substrates. The effects of different additives on the quality of the electroplates have also been studied.

2. Experimental

The electrolysis was carried out in a rectangular cell. The other experimental details were the same as described earlier [16]. All the solutions were prepared from analytical grade (B.D.H.) chemicals in doubly-distilled water. The electroplates obtained on smooth stainless steel plates were washed, dried in the oven at 110° C, weighed and peeled off for the gravimetric analysis of the tin–cadmium alloy components.

The cathode current efficiencies under varying values of current density, pH and temperature were calculated using Faraday's law. The distribution of total current for the discharge of tin (II) cadmium (II) and hydrogen ions in the electrolyte at different values of pH and current-density was calculated from the knowledge of the composition of the electrodeposits and the cathode current efficiency.

Microscopic studies were carried out in order to investigate the morphology and quality of the alloys electrodeposited from the baths containing different additives.

3. Results and discussion

It was observed earlier [17] that fluoro complexes of tin shifted the cathode potential to more negative values such that cadmium was simultaneously electrodeposited. In unstirred solutions at temperatures between 15 and 30° C, aerial oxidation can be avoided by maintaining tin (II) to fluoride ion concentrations in the ratio of (1 : 4).

The cadmium content of the electrodeposit was found to increase with the cadmium concentration of the electrolyte and was found to be a maximum around the current density of $2{\cdot}0\ \mathrm{A\,dm^{-2}}$. The tin content of the electrodeposit decreased with the increase in current density, it was found to be a minimum at $\mathrm{pH} = 2{\cdot}0$, at any current density between $0{\cdot}4$ and $4{\cdot}0\ \mathrm{A\,dm^{-2}}$.

The effects of current density on cathode

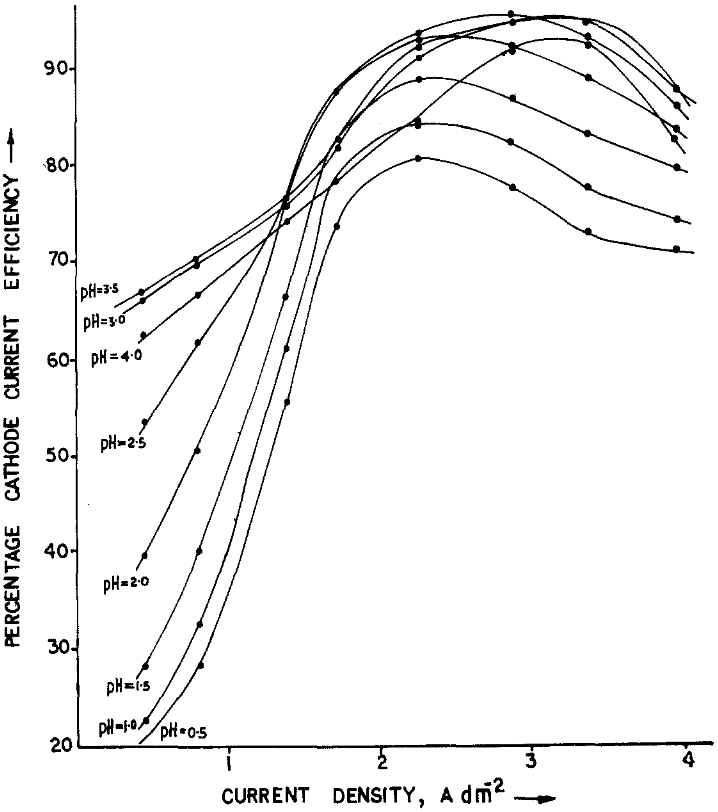

Fig. 1. Effect of current density on cathode current efficiency at different pH values. Temperature of the bath = 25° C.

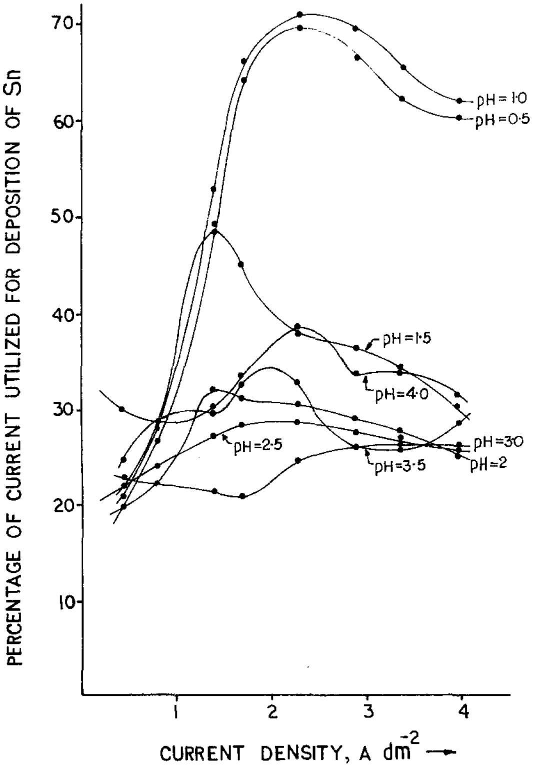

Fig. 2. Effect of current density on distribution of total current for the discharge of Sn^{2+} ions in the electrolyte at different pH values. Temperature of the bath = 25° C.

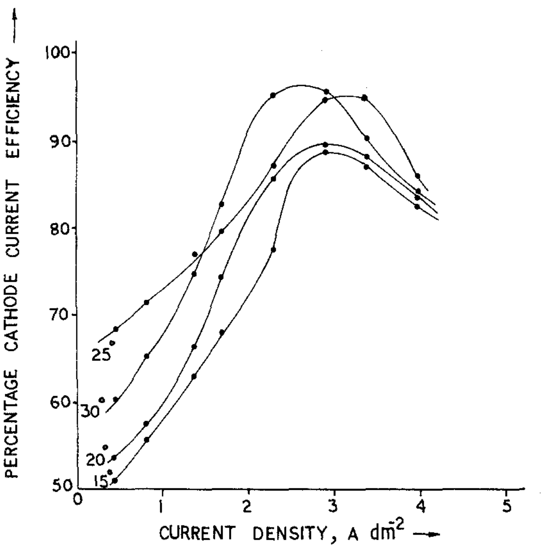

Fig. 3. Effect of current density on cathode current efficiency at different temperatures. pH of the bath = 3·0.

current efficiency and the percentage of total current utilized for the discharge of Sn(II) ions at a temperature of 25° C and at different pHs are shown in Figs. 1 and 2, and at a constant pH of 3·0 and different temperatures in Figs. 3 and 4. In general, it was noticed, that at all pH values studied the cathode current efficiency first increased with increase in the current density and then decreased slowly after attaining a maximum value depending on pH. At lower pH values, tin was deposited with a higher cathode efficiency and cadmium with a lower cathode efficiency. This resulted in a higher tin content in the alloy at lower pH values than at higher pH values.

A tin–cadmium alloy can be obtained at a high current efficiency (> 94%) at pH values 2·5–4·0 and current density 2·5–3·5 A dm^{-2} at 25° C for the bath studied. Electroplates of 25–30% Sn can be obtained between pH 2·5 and 3·5.

The effects of additives on the quality and

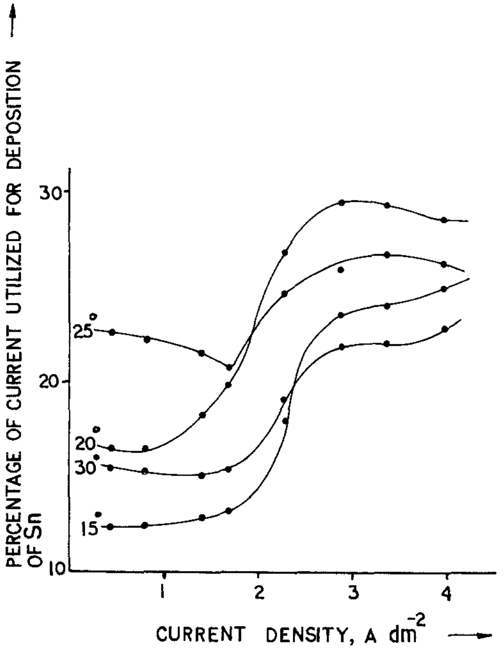

Fig. 4. Effect of current density on distribution of total current for the discharge of Sn^{2+} ions in the electrolyte at different temperatures. pH of the bath = 3·0.

Table 1. Effect of different additives on the microscopic appearance of the Sn–Cd electroplates obtained from a solution containing 0·3N $SnCl_2$*, 0·5N* $CdCl_2$ *and 1·2 N* NH_4F*. Cathode: copper; Anode: 30/70 tin–cadmium alloy at pH 3·0 and temperature 25° C.*

Number	*Additive used*	*Current density* (A dm^{-2})	*Deposition time* (min)	*Sn%*	*Nature of the electroplates*
(1)	Gelatin 1·0 g l^{-1}	1·5	10	27·5	Coarsely crystalline, bright adherent and silvery white electrodeposit.
(2)	Gelatin 1·0 g l^{-1}	3·0	5	28·9	Finer-grained than (1), bright and more adherent silvery white electroplate.
(3)	Gelatin 1·0 g l^{-1} and phenol 10 ml l^{-1}	1·5	10	26·4	Fine-grained, elastic, adherent, bright and compact silvery white electroplate.
(4)	Gelatin 1·0 g l^{-1} and phenol 10·0 ml l^{-1}	3·0	5	27·8	Very fine-grained, elastic, adherent, bright silvery white electroplate.
(5)	Gelatin 1·0 g l^{-1} and triethanolamine 2·0 ml l^{-1}	1·5	10	25·8	Coarsely crystalline, adherent bright silvery white electrodeposit.
(6)	Gelatin 1·0 g l^{-1} and triethanolamine 2·0 ml l^{-1}	3·0	5	29·6	Fine-grained, bright and adherent coating.
(7)	Gelatin 1·0 g l^{-1} and ethylenediamine 2·0 ml l^{-1}	1·5	10	28·3	Very fine-grained, bright, elastic and adherent silvery white coating.
(8)	Gelatin 1·0 g l^{-1} and ethylenediamine 2·0 ml l^{-1}	3·0	5	30·2	Fine-grained, adherent, bright silvery white electroplate.

nature of the electroplates have been studied microscopically and the results are described in Table 1. All the alloys coatings were adherent to copper. These were bright silvery white with excellent covering power having a grain-size of the order of 10^{-4} cm. The additives phenol, triethanolamine and ethylenediamine when used along with gelatin improved the quality of the deposit to a greater extent in comparison to the improvement in the deposits obtained in the presence of gelatin alone.

Acknowledgement

A. K. Agarwal thanks C.S.I.R., New Delhi for the award of a research fellowship.

References

[1] R. Martinon and R. Chevalier, *Surface* **13** (86) (1974) 17.

[2] M. S. Abdelaal, I. M. Inna and A. Zedan, *J. Appl. Electrochem.* **6** (1976) 79.

[3] K. Aotani, *J. Electrochem. Soc. Japan* **21** (1953) 21.

[4] A. E. Davies, *Bull. Inst. Metal Finishing* **6** (1956) 43.

[5] *Idem, ibid* **6** (1956) 31.

[6] B. Cohen, *Plating* **44** (1957) 963.

[7] K. Aotani, K. Nishimoto and I. Sakate, *Kinzoku Hyomen Gijutsu* **22**(8) (1971) 442.

[8] A. B. Livshits, Yu. M. Loshkarev and V. P. Fedash, *Zashch. Metal* **8**(4) (1972) 835.

[9] K. S. Indira and H. V. K. Udupa, *Prod. Finish. (London)* **25**(5) (1972) 21.

[10] E. D. Kochman and I. G. Martynova, *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* **48(12)** (1971) 104.

[11] N. T. Kudryavtsev, K. M. Tyutina and A. M. I. Fatkh, *ibid* **43**(16) (1966) 127.

[12] N. T. Kudryastev *et al., Tr. Mosk. Khim.-Tekhnol. Inst.* **67** (1970) 219.

[13] N. T. Kudryastev, K. M. Tyutina and E. N. Kubasova, *ibid* **67** (1970) 226.

[14] K. N. Tyutina, E. N. Kubasova and N. T. Kudryastev, *Zashch. Metal* **8**(3) (1972) 358.

[15] *Idem, ibid* **8**(1) (1972) 78.

[16] R. D. Srivastava, R. C. Mukerjee and D. Tripathi, *Acta Chim. Hung.* **86**(2) (1975) 163.

[17] R. D. Srivastava, D. Tripathi and R. C. Mukerjee, *J. Electrochem. Soc. Japan* **45**(1) (1977) 11.