JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 697–701

Electrodeposition of nickel-cobalt-zinc alloys from a borate bath

R. K. SHUKLA, S. K. JHA, S. C. SRIVASTAVA

Department of Chemistry, University of Lucknow, Lucknow, India

Received 6 January 1981

The electrodeposition has been studied of nickel–cobalt–zinc alloys from a borate bath containing nickel sulphate (120–140 g dm^{-3}), cobalt sulphate (30–46 g dm^{-3}), zinc sulphate (144–168 g dm^{-3}), boric acid (30 g dm^{-3}) and ammonium chloride (2 g dm^{-3}). The operating conditions were: current density, 2.0–5.0 A dm^{-2}; temperature, 30–40°C and pH, 2.4 to 5.4. Light grey, semibright, stressed films have been obtained. However, the deposits consist partially of black powder when the concentration of the various components is increased. The brightness is found to increase with decreasing temperature and pH of the solution. The total cathode efficiency increases when the pH and temperature of the solution decrease, whereas at any particular pH and temperature it first decreases, reaches a minimum and then increases with increasing current density.

---

1. Introduction

The electrodeposition of ternary alloys containing nickel as one component from aqueous media using different bath compositions has become of importance in recent years due to the fact that the alloys increase the possibility of satisfying a wide variety of practical requirements in modern technology for special items which cannot be manufactured from pure metals. A survey of the literature indicates that the deposition of these alloys has been carried out mainly from sulphate/chloride solutions using different complexing agents [1–5]. The deposition of triple alloys of nickel in fluoride [6], fluoroborate [7, 8], cyanide [9], and acetate [10] baths has also been reported. Recently the use of borate baths [11–17] has attracted much attention for the electrodeposition of these alloys. A few of the alloys are reported to exhibit magnetic properties [17] which have important engineering applications. The present work was therefore undertaken to explore the possibility of obtaining a three-component nickel–cobalt–zinc alloy from a borate bath under various electroplating conditions.

2. Experimental procedure

The electrolytic cell used was that of Mandelcorn *et al.* [18] and Schaus [19], assembled from a 3 mm thick Perspex sheet joined by chloroform. The cathode was made from bright stainless steel panels (5 cm by 2 cm) which were sealed on a rectangular Perspex sheet of similar size with Araldite to avoid uncertainties of surface area. Platinum wire was used as an anode.

The bath consisted of sulphates of the three metals together with 30 g dm^{-3} boric acid for buffering and 2 g dm^{-3} ammonium chloride to give bright deposits. The films deposited at the cathode were washed with distilled water and dried. They were then peeled off carefully, weighed and then dissolved in sulphuric acid and analysed for nickel, cobalt and zinc. Nickel was estimated gravimetrically as dimethylglyoxime complex. Cobalt was estimated colorimetrically and zinc was determined as zinc ammonium phosphate.

The electrodeposition was carried out for 20 minutes using 225 cm^3 of fresh solution and the deposit composition, cathode efficiency and cathode potential were determined at different current densities. The densest, most uniform grey deposits were obtained under the following conditions: current density, 2.0–5.0 A dm^{-2}; pH, 2.4–5.4; temperature, 30–40° C.

The cathode current efficiency for alloy deposition was calculated under various conditions, on the basis of the chemical analysis by the usual method for alloys [20]. The pH of the solution was measured with a glass electrode and

0021–891X/81/060697–05$02.50/0

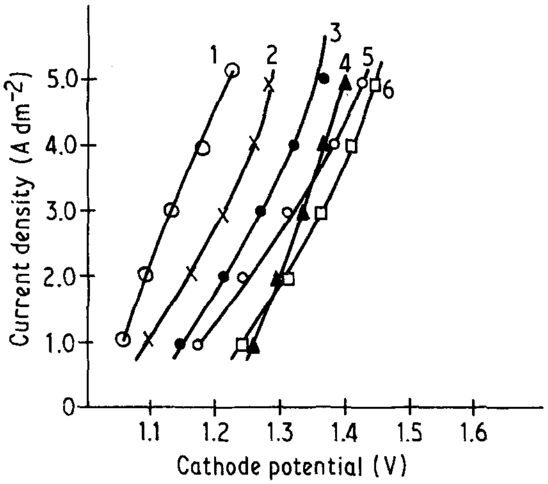

Fig. 1. Cathode potential curves for nickel, cobalt, zinc and their binary alloys. Bath conditions: boric acid 30 g dm^{-3}, ammonium chloride 2 g dm^{-3}, temperature 30° C, pH 3.8. 1, Nickel sulphate 120 g dm^{-3}; 2, cobalt sulphate 30 g dm^{-3}; 3, zinc sulphate 144 g dm^{-3}; 4, zinc–nickel: zinc sulphate 144 g dm^{-3}, nickel sulphate 120 g dm^{-3}; 5, zinc–cobalt: zinc sulphate 144 g dm^{-3}, cobalt sulphate 30 g dm^{-3}; 6, nickel–cobalt, nickel sulphate 120 g dm^{-3}, cobalt sulphate 30 g dm^{-3}.

Table 1. Effect of pH on deposit composition at 35° C and 4.0 A dm^{-2} current density

	Metal in deposit (%)		
pH	*Nickel*	*Cobalt*	*Zinc*
2.4	5.46	1.3	93.24
3.8	5.96	1.5	92.54
4.5	6.29	1.9	91.81
5.4	7.63	2.9	89.47

Bath composition (g dm^{-3}): nickel sulphate, 120; cobalt sulphate, 30; zinc sulphate, 144; boric acid, 30; ammonium chloride, 2.

was adjusted with hydrochloric acid and sodium acetate. The electrode potentials were measured against the standard calomel electrode to an accuracy of ± 0.00002 V. The recorded data correspond to the hydrogen scale. The electroplates were examined to define their morphology.

3. Experimental results

Fig. 1 represents the cathode potential–current density curves for nickel, cobalt, zinc and binary alloys of nickel–zinc, nickel–cobalt and cobalt–zinc. The relative position of the curves shows the possibility of ternary alloy formation. The effects of variables on alloy deposition are given in Tables 1–3.

The electrodeposits were stressed, light grey, semibright, thin films which had a tendency to peel off on drying. The bath was stable under various experimental conditions but on prolonged electrolysis it was difficult to control its composition.

3.1. *Alloy composition*

It was observed that the thin films deposited in the composition range 3.92–13.35% nickel, 0.6–3.8% cobalt, 84.95–95.48% zinc under various electroplating conditions. At low current densities the deposits consisted partially of black powder but

Table 2. Effect of temperature and current density on deposit composition at a pH of 3.8

	Temperature (° C)	*Current density* (A dm^{-2})				
		2.0	3.0	4.0	4.5	5.0
Nickel in deposit (%)	30	5.28	5.76	6.35	7.92	10.32
	35	5.08	5.46	5.96	7.36	9.75
	40	4.96	5.25	5.74	7.06	9.65
Cobalt in deposit (%)	30	0.9	1.5	2.1	2.3	2.5
	35	0.9	1.1	1.5	1.6	1.8
	40	0.9	1.1	1.3	1.4	1.6
Zinc in deposit (%)	30	93.82	92.50	91.54	89.78	87.37
	35	94.02	93.44	92.54	91.04	88.45
	40	94.14	93.64	92.96	91.54	88.75

Bath composition: same as given in Table 1.

Table 3. Effect of metal concentration in the bath on deposit composition at 35° C, pH 3.8 and current density 4.0 A dm^{-2}

Concentration of metal in bath (g dm^{-3})	*Metal in deposit (%)*			*Bath composition* (g dm^{-3})
	Nickel	*Cobalt*	*Zinc*	
Nickel				
120	5.96	1.5	92.54	Cobalt sulphate, 30; zinc sulphate, 144; boric acid, 30; ammonium chloride, 2
128	6.24	1.5	92.26	
136	6.62	1.4	91.98	
144	7.15	1.3	91.55	
Cobalt				
30	5.96	1.5	92.54	Nickel sulphate, 120; zinc sulphate, 144; boric acid, 30; ammonium chloride, 2
38	5.84	2.0	92.16	
42	5.78	2.2	92.02	
46	5.55	2.5	91.95	
Zinc				
144	5.96	1.5	92.54	Nickel sulphate, 120; cobalt sulphate, 30; boric acid, 30; ammonium chloride, 2
152	5.45	1.4	93.15	
160	5.25	1.2	93.55	
168	4.76	1.0	94.24	

Table 4. Deposit morphology

Sample	*Bath composition*	(g dm^{-3})	*Current density* (A dm^{-2})	*Temperature* (° C)	*pH*	*Nature of the deposit*
1	Nickel sulphate, Cobalt sulphate, Zinc sulphate, Boric acid, Ammonium chloride,	120 30 144 30 2	5.0	30	3.4	Even, fine-grain, grey deposit having grain size slightly bigger than in Sample 2
2	As 1		5.0	35	3.4	Fairly smooth, blackish grey, even grain deposit
3	As 1		4.0	35	3.4	Blackish grey, uneven deposit of largest grain size
4	As 1		5.0	35	2.4	Bright grey, fine-grain, uneven deposit
5	Nickel sulphate, Cobalt sulphate, Zinc sulphate, Boric acid, Ammonium chloride,	128 30 144 30 2	4.0	35	3.4	Localized light grey, coarsely crystalline and even deposit
6	Nickel sulphate, Cobalt sulphate, Zinc sulphate, Boric acid, Ammonium chloride,	120 38 144 30 2	4.0	35	3.4	Whitish grey, uneven crystalline deposit
7	Nickel sulphate, Cobalt sulphate, Zinc sulphate, Boric acid, Ammonium chloride,	120 30 152 30 2	4.0	35	3.4	Bright grey, uneven deposit having comparatively smaller grain size than Sample 3

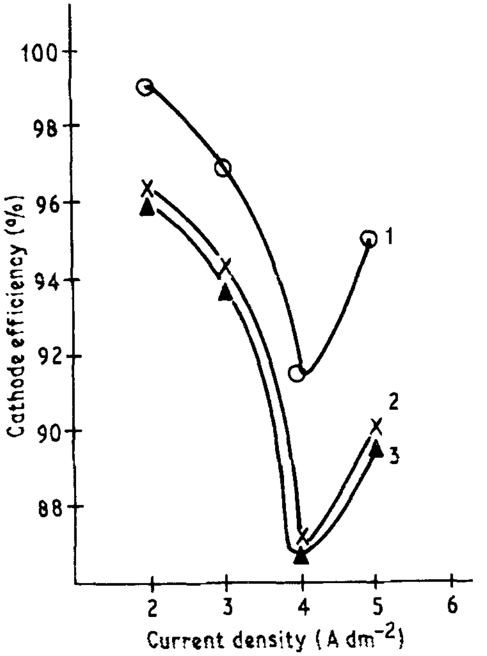

Fig. 2. Effect of temperature on cathode efficiency. Bath: nickel sulphate 120 g dm^{-3}; cobalt sulphate 30 g dm^{-3}; zinc sulphate 144 g dm^{-3}; boric acid 30 g dm^{-3}; ammonium chloride 2 g dm^{-3}; pH 3.8. 1, 30° C; 2, 35° C; 3, 40° C.

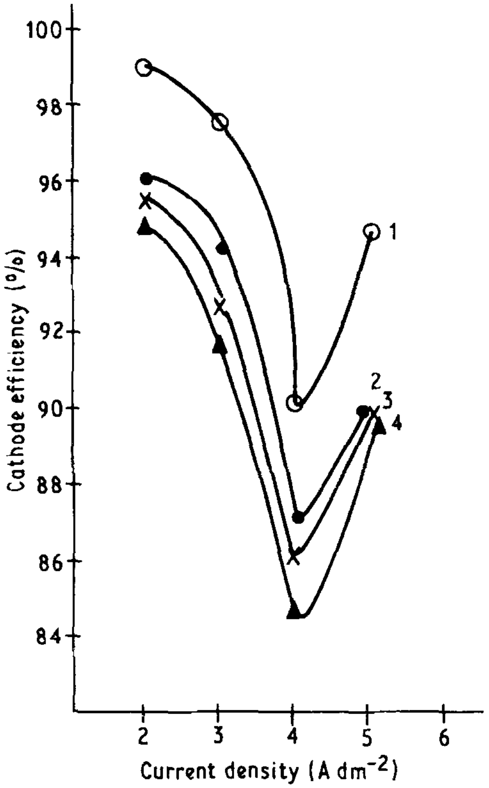

Fig. 3. Effect of pH on cathode efficiency. Bath composition as given in Fig. 2; temperature 35° C. 1, pH 2.4; 2, pH 3.8; 3, pH 4.5; 4, pH 5.4.

with increasing current density thin, bright, grey films were obtained. However, uniform, thin, semi-bright films were usually obtained at comparatively low pH and temperature, whereas by increasing the concentration of the various components the deposits again became partially powdery and black. They appeared to be brighter at the low pH values and at low temperatures. The percentage of all the metals in the deposits was found to be always greater than in the bath. Furthermore it is seen (Tables 1–3) that the percentage of nickel and cobalt increases with increasing current density, concentration of the metal and pH of the solution, but decreases with increasing temperature. However, in the case of zinc the percentage increases with increasing temperature and concentration at any particular current density, whereas it decreases with increasing pH and current density. This may be due to the fact that the incorporation of nickel and cobalt in the alloy is less at higher temperature while that of zinc is less at comparatively higher pH and current density.

3.2. *Cathode efficiency*

The cathode efficiency was always found to be less than 100% because of the simultaneous discharge of hydrogen ions with the metallic ions. The cathode efficiencies for single-metal deposition are: cobalt, 0.63–3.72%; nickel, 4.15–13.26%; zinc, 74.46–93.22%. That of the alloy under similar conditions was 84.17–99.20%. The total efficiency increases with decreasing temperature and pH of the solution, as shown in Figs. 2 and 3. It is significant to note that at any given pH and temperature the efficiency decreases first, reaches a minimum and then increases with increasing current density.

3.3. *Morphology*

The morphological studies of the alloy plates are summarized in Table 4. It seems that bright grey, uneven, fine-grain deposits are favoured by decreasing the pH of the solution, whereas decreasing the temperature gives even, fine-grain, grey deposits. Their smoothness has been found to increase with increasing current density.

Acknowledgement

The authors are grateful to the Council of Scientific and Industrial Research, New Delhi, for supporting this work by a Grant-in-Aid.

References

[1] R. Sivakumar and T. L. Ramachar, *Metall. Finish.* **18** (1972) 65.
[2] M. Sarojamma and T. L. Ramachar, *Galvanotechnik* **63** (1972) 751.
[3] V. B. Singh and P. K. Tikoo, *J. Appl. Electrochem.* 8 (1978) 41.
[4] K. Matsuoka, Japanese Patent 7902608 (C1, C 25D3/56) (1979).
[5] B. P. Vorob'ev and P. M. Shilov, *Tekhnol. Organ. Proizvod.* 4 (1975) 48.
[6] G. Dunkic and S. Djordjevic, *Hem. Ind.* **31** (1977) 395.
[7] S. Djordjevic and G. Dunkic, *ibid* **29** (1975) 59.
[8] Y. M. Faruq and K. I. Vasu, *J. Electrochem. Soc. India* **18** (1969) 181.
[9] S. Arimura and T. Inada, Japanese Patent 7646 528 (C1, C 25D3/56 (1976).
[10] V. B. Singh, *J. Appl. Electrochem.* 9 (1979) 285.
[11] A. N. Yagubets and V. N. Sherstkina, *Elektron. Obrab. Mater.* 5 (1974) 31 (Russian).
[12] G. A. Volyanuk and E. V. Guseva, *Z. Prikl. Khim. (Leningrad)* 48 (1975) 648.
[13] W. Machu, *Metalloberfläche* **30** (1976) 460.
[14] V. Racinskas and V. Charlusiene, USSR Patent 370 274 (C1. C 23b) (1973). (From *Otkryt. Izobret. Prom. Obraztsy Tovarnye Znaki* **50** (1973) 86.
[15] L. V. Orlovskaya, V. Racinskas and O. Dzilbute, *Issled. Obl. Osazhdeniya Metal. Mater. Respub. Konf. Elektrokhim. Litov, SSR,* **16** (1978) pp. 175–9.
[16] V. V. Povetkin, *Elektrokhim.* **15** (1979) 761
[17] S. V. Afanaslev, *Spraw. Elektrotekh. Mater. Vtoroe Pererab. Izd.* 3 (1976) 45.
[18] I. Mandelcorn, W. B. McConnel, W. Gavvin and C. A. Winkler, *J. Electrochem. Soc.* **84** (1952) 99.
[19] O. Schaus, PhD thesis, McGill University (1954).
[20] F. A. Lowenheim (editor), 'Modern Electroplating', 2nd edn, John Wiley, New York (1963) p. 470.