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Electrodeposition of Zinc-Nickel Alloy

Visalakshi Ravindran and V S Muralidharan*

Central Electrochemical Research Institute, Karaikudi 630 001

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Studies on the electrodeposition of zinc-iron group alloys are of academic and technological interest. The anomalous codeposition and enhanced corrosion protection of zinc-nickel alloy deposits make the search for newer plating bath formulations. Zinc and nickel were codeposited from sulphamate bath and 82 per cent zinc was obtained in the deposit. The suphamate bath developed offered 100 per cent current efficiency with 24 per cent throwing power.

Keywords: Electrodeposition, Zinc, Nickel, Zinc-Nickel alloy

Introduction

Studies on the development of zinc-transition metal electrodeposits are of technological and academic interest. The codeposition of iron group metals with zinc or with each other exhibit anamolous behaviour; the retardation of the more noble metal by zinc[1]. Zinc-nickel coatings offer enhanced corrosion protection to steel than cadmium[2]. Zinc-nickel electrodepostion from various bath formulations was attempted[3,4]. Sulphate baths in the pH range 1.5 to 2.5 and pH 4 with addition of boric acid and *p*-toluene sulphonic acid were used. Sulphate-sulphamate combinations produced a wide range of zinc-nickel deposits. Chloride baths with $SrSO_4$ gave bright deposits[5]. Boric acid added acetate baths offered > 15 per cent of nickel. The present investigation deals with the sulphamate bath developed to obtain 12-18 per cent by weight of nickel.

Experimental Procedure

Cold-rolled steel plates (10 × 7.5 × 0.05 cm) were degreased with trichloroethylene and alkaline electrocleaned cathodically for 2 min in a solution composed of 35 g/L NaOH, and 25 g/L Na_2CO_3 at 70° C; they were washed in running water, and then dipped for 10s in 5 per cent H_2SO_4 solutions. Finally, thorough washing and drying were carried out. A Hull Celi was employed to assess and optimize the conditions for the production of good deposits. A cell current of 1 A was used for 10 min. A regulate power supply was used as direct current source and calibrated ammeter along with the cell constituted th electrical circuit.

For current efficiency experiments th electrodeposition assembly comprised o electrolytically pure zinc or nickel anodes and stee cathodes of equal size (5 x 4 x 0.025 cm) immersed i a 800 mL solution in a 1 L wide-mouthed glas vessel. The solution was agitated and when necessar heated, using a heater-cum-magnetic stirrer. Fo current efficiency determination, each specimen wa weighed before and after plating and the weight of th deposits was found from the difference.

$$\text{Current efficiency (per cent)} = \frac{\text{Weight of the metal deposited}}{\text{Theoretical weight obtained from Faraday's law}} \times 100, \quad \ldots(1)$$

The current efficiency of the alloy is calculated as:

$$\text{Current efficiency, per cent} = \frac{M \times 100}{e_{\text{alloy}} \times Q}, \quad \ldots(2)$$

where M is the mass of the alloy deposit, e_{alloy} the electrochemical equivalent of the alloy and Q the quantity of electricity passed (As).

The electrochemical equivalent of the alloy wa calculated as:

* Author for correspondence
varagur@yahoo.com

$$= \frac{e_{Ni} \times e_{Zn}}{(e_{Ni} f_{Zn}) + (e_{Zn} f_{Ni})} \quad \ldots (3)$$

where e_{Ni} and e_{Ni} are the electrochemical valents of the constituent metals; f_{Ni} and f_{Zn} are fractions in the deposits. The density of the alloy calculated by taking into consideration the ion of the constituent metals. The electrodeposits removed chemically by immersion in 1:1 HNO_3 the resulting solutions containing zinc and nickel analyzed. The amount of nickel in the deposit calculated from the difference in the mass of the sit and that of the zinc determined. Zinc content e solution was analyzed, both volumetrically and tomic Absorption Spectrometry.

Throwing power is the ability of the plating tion to deposit uniformly allover the cathode ace and is measured as the ratio of the weight of deposit obtained on the cathode placed near the far from the anode.

For determining the throwing power, a Haring Blum Cell was used. A rectangular cell with two t metal cathodes measuring 9 x 0. 1 cm, filling entire cross-section at both ends and a perforated de of the same area was used. The anode was placed between the cathodes so that its distance from one of the cathodes was 1/5 of its distance from the other.

$$\text{Throwing power (per cent)} = \frac{K-C}{K+C-2} \times 100, \quad \ldots(4)$$

where C is the metal distribution ratio between the nearer cathode and the farther; K is the ratio of the distances respectively, of the farther and nearer cathodes from the anode.

Zinc sulphamate was prepared by dissolving zinc oxide in sulphamic acid (99 per cent purity). The nickel sulphamate (99 per cent purity) was supplied by LOBA Chemie, India. The chemicals used in the preparation of the plating bath were of AR quality.

Result and Discussions

(a) Zinc and Nickel Deposition

Zinc was deposited on mild steel from sulphamate bath at 30° C, using a zinc anode. The current efficiencies were found to increase with *p*H and current density (Table 1). The current efficiency was found to decrease with current density when

ble1--- Influence of pH and current density on the current efficiencies of zinc and nickel from their respective sulphamate baths current efficiency, per cent

Current density	Zinc deposition at 30°C-50°C		Nickel deposition
A/dm^2	pH 3	pH 4	pH 5.5
1	—	—	100.0
2	96.8	98.8	100.0
3	97.5	98.7	99.0
4	97.8	98.4	98.5
5	98.6	99.2	98.0
6	—	—	96.0
7	—	—	92.0

nc bath composition	: Zinc oxide	: 133.9 g/L
	Sulphamic acid	: 81.1 g/L
	Boric acid	: 10.0 g/L
ickel bath composition	: Nickel sulphamate	: 250.0 g/L
	$NiCl_2$	25.0 g/L
	NaF	4.0 g/L
	Beta naphthalene sulphonate 0.345 g/L	

nickel was deposited at 50 °C from sulphamate-chloride bath using Ni anodes. As it was possible to deposit zinc and nickel from sulphamate bath at pH 5.5, detailed investigations were done.

(b) Alloy Deposition

(i) Cathodic Polarization

The variation of mild steel cathode potentials at different current densities in sulphamate baths of zinc and nickel individually are given in Figure 1. The individual cathodic polarization curves do not intersect even at high cathodic potentials. The polarization curves obtained in the alloy plating bath were found to lie between the two individual polarization curves.

(ii) Nature of the Deposit

Well known brighteners and leveling agents were used to improve the quality of the deposit. Boric acid, ß-naphthol and sodium lauryl sulphate (SLS) at various combinations were tried. Table 2 summarizes the nature of the deposits obtained in the presence of various additives. Grey, uniform, semi-bright deposits were seen only in the presence of boric acid, SLS and ß-naphthol.

(iii) Current Efficiencies

The amount of nickel deposited in the alloy was found to vary with temperatures and current densities (Figure 2) and a maximum of 38 to 40 per cent nickel was obtained at 50° C. The current density variations

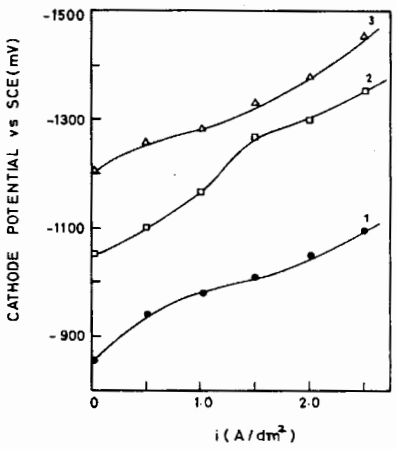

Figure 1— Variation of cathode potentials with current densities in sulphamate baths of zinc-nickel and zinc-nickel alloy at 50 °C -O-O-O- Ni bath -Δ-Δ-Δ- n bath -□-□-□- Zn-Ni bath

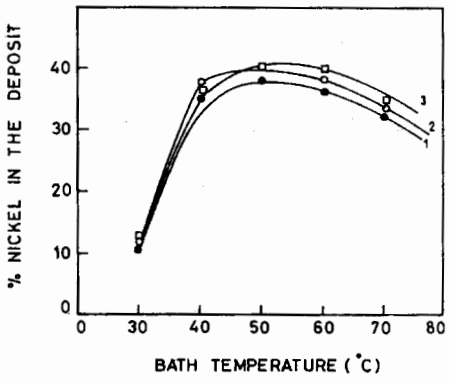

Figure 2 — Influence of temperature on the amount of nickel in the alloy -O-O-O- 1 A/dm² -Δ-Δ-Δ- 2 A/dm² -□-□-□- 3 A/dm²

Table 2 —Effect of addition of addition agents on the nature of the Zn-Ni deposit

Addition agents		Nature of the deposit
No addition agent		Bright, pitted
Boric acid – 50 g/L		Semibright, less pitting
0.345 g/L - β - naphthol		Semibright, uniform, milky, less pitting
0.865 g/L sodium lauryl sulphate (SLS)		White and black patches, but levelled
0.345 g/L β - naphthol + 0.865 g/L SLS		Milky, but with patches
Boric acid 50 g/L+ β - naphthol 0.345 g/L		Semibright, with pits at random
Boric acid 50 g/L+ 0.865 g/L SLS		Milky, uniform grey
Boric acid 50 g/L + 0.865 g/L SLS+ 0.345 g/L β - naphthol		Grey, uniform, semibright
Bath :	Zinc sulphamate	: 128.6 g/L
	Nickel sulphamate	: 125.05 g/L
	PH	: 5.5
	Temperature	: 50°C
	Current density Stirring	: 1 A/dm²

or markedly influence the current efficiencies of zinc and nickel deposition in the alloy (Table 3). high zinc content in the alloy is anomalous sition, is due to the formation of zinc hydroxides e interface. X-ray diffraction and microhardness obtained on zinc-nickel deposits revealed the sion of $Zn(OH)_2$ and the existence of a less noble Zn_{22} phase which hindered the deposition of el[6]. Factors which affected the hydrogen tion and OH^- ion precipitation influenced the position and the properties of the deposit. A ease in pH generally causes a decrease in iency and improvement in appearance. SLS and phthol might have been adsorbed on the OH ion ed surface and prevented hydrogen evolution.

Boric acid used in Ni-Fe deposition earlier[7,8] did show any evidence of buffering. Nickel plexed with boric acid might have adsorbed on $Zn(OH)_2$ surface, favouring the enrichment of zinc h caused a grey appearance. Figure 3 presents the t of NH_4Cl addition in the bath on the current iency of the alloy deposition and the weight per in the deposit. Introduction of NH_4Cl caused the ation of $ZnCl_2$ and $ZnCl_2.3\ NH_4Cl$ in the sit[1]. To get zinc-rich deposit (Table 4) 60 g/l Cl was found to be optimum. To have an mum zinc weight percentage (13-18 per cent) the with 128.6 g/L sulphamate and 125.05 g/L nickel hamate is found to be suitable.

(iv) Throwing Power

The Throwing power of the optimized bath was evaluated using zinc and nickel anodes of purity 99.99 per cent. The maximum throwing power was observed at 1.5 A/dm^2. When zinc anode was used,the throwing power of the bath varied from – 0.5 to 24 in the current density range of 0.5-1.5 A/dm^2. After 1.5 A/dm^2 there was a decrease in the throwing power from 24 to 9.6.When nickel anode was used, the

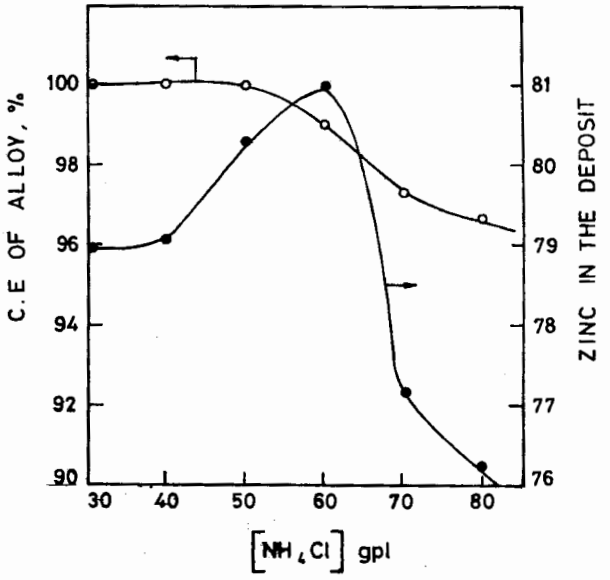

Figure 3 — Effect of NH_4Cl on the current efficiency of alloy deposition and the weight per cent of zinc in the deposit

Table 3 — Influence of the current density on the current efficiencies of Zn-Ni alloy Obtained from sulphamate bath

Current density A/dm^2	Current efficiency, per cent		
	Zinc-nickel Alloy	Zinc	Nickel
0.5	99.02	60.96	38.16
1.0	96.77	59.49	37.98
1.5	98.29	60.43	37.86
2.0	97.16	60.00	37.16
2.5	97.90	60.19	37.70

h composition and conditions:

h:	Zinc sulphamate	:	128.6 g/L (0.5*M*)
	Nickel sulphamate	:	125.05 g/L (0.5*M*)
	Boric acid	:	50.0 g/L
	β - naphthol	:	0.345 g/L
	Sodium lauryl sulphate	:	0.865 g/L
	Temperature Stirring	:	50°C

Table 4 — Effect of 60 g/L NH_4Cl on the weight percentage of zinc in the deposit

Composition of the bath		Per cent zinc	
		Without NH_4Cl in solution	With NH_4Cl in solution
Zinc sulphamate	231.57 g/L	71	81
Nickel sulphmate	25.01 g/L		
Zinc sulphamate	192.97 g/L	77	88
Nickel sulphmate	62.52 g/L		
Zinc sulphamate	128.65 g/L	65	82
Nickel sulphmate	125.05 g/L		
Zinc sulphamate	64,32 g/L	78	90
Nickel sulphmate	187.56 g/L		
Zinc sulphamate	25.73 g/L	68	80
Nickel sulphmate	225.08 g/L		
Other bath constituents:			
Boric acid	: 50 g/L		
SLS	: 0.865 g/L		
β-naphthol	: 0.345 g/L		

throwing power of the bath varied from -0.5 to 17.0, in the current density range of 0.5 to 1.5 A/dm^2. After 1.5 A/dm^2, there was a decrease in the throwing power from 17.0 to 6.8.

(v) Bath Analysis

The electrodepostion was carried out using zinc anodes and the amounts of zinc and nickel contents in the optimized bath were analysed using Atomic Absorption Spectroscopy. The nickel content was found to gradually reduce with time, while the zinc content increased up to 1h and thereafter decreased. This was due to the passivation of zinc anodes with prolonged electrolysis.

Conclusions

The optimized bath cimposition for alloy deposition is zinc sulphamate 128g/L; nickel sulphamate 125.05g/L; boric acid 50 g/L; ß- naphthol 0.345 g/L; Sodium lauryl sulphate 0.864 g/L; NH_4Cl 60g/L; temperature 50°C with stirring. The bath offered a current density of nearly 100 per cent with a throwing power of 24 per cent and 82 per cent zinc in the deposit.

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