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Electrodeposition of Nano Zinc - Nickel Alloy from Bromide Based Electrolyte

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Abstract

Zinc coatings offer sacrificial protection to iron and steel components at low cost. The basic reason for plating from an alloy bath is to produce some desired change in the electrodeposits unobtainable from the pure metal baths. Zinc-nickel alloy coatings can be obtained from two different systems, acidic and alkaline, both capable of producing deposits of exceptional corrosion resistance with the nickel content of 10-14% and 5-10% respectively. In this study, nano crystalline zinc-nickel coatings were electro-deposited on mild steel substrates from an electrolyte containing zinc bromide, nickel chloride and boric acid at pH 4. The bath and deposit characteristics such as cathode current efficiency, rate of build up, nature of deposit, anode efficiency, throwing power and micro hardness were studied. The morphology and structure were also examined by SEM and XRD.

Keywords: Electrodeposition, nano zinc-nickel, bromide based electrolyte, cathode efficiency.

Introduction

Zinc coatings by electrodeposition have found extensive use for the corrosion protection of steel components. The corrosion resistance of zinc coatings can be improved by chromate conversion coatings or/and alloying with iron group metals[1-4]. The electro-deposited Zn-Ni alloy coatings to protect steel from corrosion are found to be 3 to 4 times better than pure zinc coating by salt spray tests, although the cost is only 2 times higher. The co-deposition of Zn-Ni alloys is anomalous in nature, i.e., nickel, is hindered before the deposition of other alloy constituent[5]. Zinc-nickel alloy coatings are used for several applications like electrolysis of water by electro catalytic method and in the electronic industry in addition as the coatings to improve the corrosion resistance of automobile steel components[6-10]. Zinc-nickel alloy is a better and safe substitute for cadmium coatings[11,12]. Zinc-nickel alloy electrodeposits can be obtained from various types of baths like chloride, sulphate, sulphate-chloride and alkaline[13-26]. A search for non cyanide and eco friendly plating bath resulted in formulation of zinc-nickel electrolyte containing zinc bromide and nickel chloride, producing semi bright milky deposit. This present study presents the details of optimization of zinc-nickel alloy deposition from bromide based electrolyte; the bath and deposit characteristics.

Material and Methods

Experimental: The plating experiments were carried out using polished cold-rolled mild steel specimens subjected to the usual pretreatments like solvent degreasing, alkaline electro cleaning and 5% acid dip. High pure (99.9%) zinc was used as the anode. The optimum current density range for obtaining quality deposits was determined by Hull cell experiment using a standard 267 ml cell[27]. The Hull cell experiments were carried out at 1A cell current for 10 minutes duration at 30°C. The cathode current efficiency and rate of build up at different current densities were determined from the weight of deposit on the stainless steel cathode of 7.5x2.5 cm size. The cathode current efficiency was calculated using the relation.

$$\text{Cathode current efficiency (\%)} = \frac{M \times 100}{e_{alloy} \times Q}$$

$$\text{Rate of build up } (\mu m / hr) = \frac{M \times 10^4 \times 60}{d \times A \times t}$$

where, M - the mass of alloy deposited in g, e_{alloy} - the electrochemical equivalent of zinc-nickel alloy, Q - the quantity of electricity passed in A/sec., d - density of the alloy in g/cm^3, A - the area of the deposit in cm^2, t -the time duration in minutes.

The throwing power (TP) was measured using Haring-Blum cell[28]. A porous zinc anode was placed between two parallel steel cathodes filling the rectangular cell cross section. One of the cathodes was nearer to anode than the other. The distance ratio was 5: 1The Field's formula was used for the calculation of throwing power[29],

$$\text{Throwing power (\%)} = \frac{K - C}{(K + C - 2)} \times 100$$

where $C = C_n / C_f$ is the metal distribution ratio; C_n - the weight of the deposit at the nearer cathode, C_f - the weight of the deposit at the farther cathode, K – the ratio of the distances respectively of the farther and nearer the cathodes from the anode.

Micro hardness of electrodeposits of zinc-nickel was determined on the Vicker's scale by using LECO Tester. The micro hardness of the deposit in kg / mm^2 was determined in each case by using the formula,

$$\text{Vicker's hardness (kg / mm}^2\text{)} = \frac{1854 \times P}{d^2}$$

where P - the load applied in grams and d - diagonal of the indentation obtained in micrometers.

Scanning electron microscope (JEOL-JSM-35 LF) was used to assess the grain size, deposit nature and pores present in the deposits. The electrodeposited specimens were cut into (1 x 1) cm size, mounted suitably and examined under the microscope. The SEM photographs were taken at 20 KV with a magnification of 2000 times.

The X-ray diffraction (Philips TW 3710) was carried out using nickel-filtered Cu-Kα radiation for determining the lattice parameter, approximate grain size of the deposit. The Scherrer's equation[30] was used for the determination of grain sizes of the coating.

Results and Discussion

Bath optimization - Hull cell studies: The results of the Hull cell studies carried out in zinc - nickel alloy plating bath are presented in figures 2-4. The legends used in the Hull cell studies of zinc -nickel alloy plating are given in figure 1.

Figure -1
Legends used for Hull cell studies

Effect of concentration of nickel chloride: The effect of varying concentration of nickel chloride in zinc - nickel alloy electrolyte containing zinc bromide 160 g/l and boric acid 60 g/l at a cell current of 1A and 30^{0}C is presented in figure 2. From the figure, it may be seen that with increase in nickel chloride concentration there is an improvement in the nature of the deposit. When the concentration of nickel chloride was 175 g/l, semi bright milky deposit was obtained over a wide current density range (0.1 - 2.4 A/dm^2) with satin deposit at the high current density region above 2.4 A/dm^2. Further increase in the concentration of nickel chloride, decreased the semi bright milky region. From these studies, it may be concluded that 175 g/l of nickel chloride is the optimum concentration.

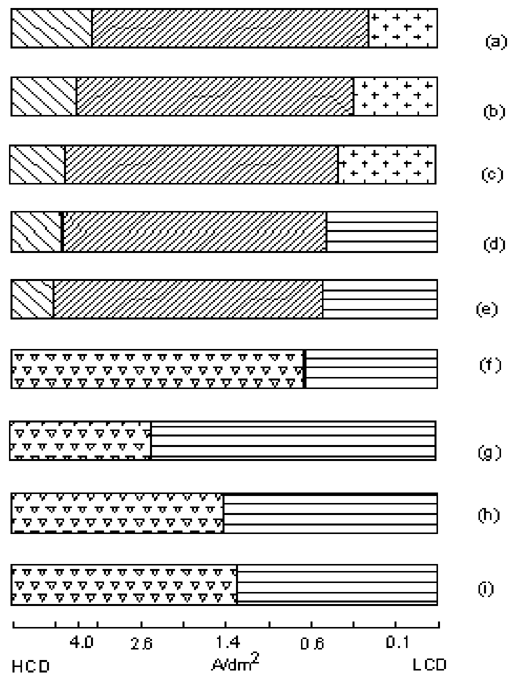

Figure - 2
Effect of change in concentration of Nickel chloride
Bath Composition and Conditions: Zinc bromide - 160g/l, Boric acid - 60g/l and Nickel chloride(g/l) (a) 25, (b) 50, (c) 75, (d) 100, (e) 125, (f) 150, (g) 175 (h) 200, (i) 225, Cell Current - 1 A, Temperature - 30° C and pH 4

Effect of concentration of zinc bromide: Figure 3 presents the effect of varying concentration of zinc bromide in a zinc-nickel alloy plating electrolyte containing nickel chloride 175 g/l and boric acid 60 g/l at a cell current of 1A and 30^{0}C. From the figure, it may be seen that increase in zinc bromide concentration improves the nature of the deposit. When the concentration of zinc bromide reached 100 g/l, semi bright milky deposit was obtained to a larger extent along with satin and bright deposits at the high current density region. It may also be seen from the figure that further increase in concentration of zinc bromide gradually decreases the current density range for semi bright milky deposit. Hence, 100 g/l of zinc bromide is the optimum concentration.

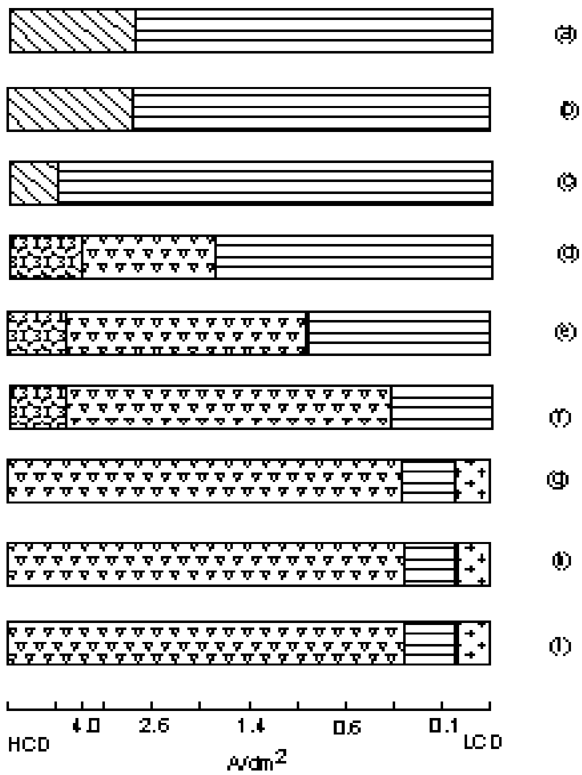

Figure - 3
Effect of change in concentration of Zinc bromide
Bath Composition and Conditions: Zinc bromide (g/l) (a) 40, (b) 60, (c) 80, (d) 100, (e) 120, (f) 140, (g) 160, (h) 180, (i) 200, Boric acid - 60g/l and Nickel chloride- 175, Cell Current - 1A, Temperature - 30° C and pH 4

Effect of concentration of boric acid: The effect of varying concentration of boric acid in the zinc-nickel alloy plating electrolyte containing zinc bromide 100g/l and nickel chloride 175 g/l at 1A cell current and 30^0C is given in figure 4. From the figure, it may be concluded that 60 g/l of boric acid is optimum to obtain semi bright milky deposit to a greater extent at low current density region (0.1-1.7 A/dm^2) with satin and bright deposit at high current density region.

From the Hull cell studies, the following bath composition was chosen for further studies: Zinc bromide = 100 g/l, Nickel chloride = 175 g/l, Boric acid = 60 g/l, pH = 4.

Bath Characterisation: Cathode current efficiency, rate of build up, anode efficiency and nature of the deposit: Table 1 presents the cathode current efficiency, rate of build up anode efficiency, and nature of the deposit of zinc-nickel alloy plating bath at 30^0C and at pH 4. The cathode current efficiency increases with current density upto1.5 A/dm^2 and then decreases. The rate of build up goes on increasing with current density. Also, it may be seen that the anode efficiency increases with current density and is always higher than the cathode efficiency. Semi bright milky and satin deposits were obtained at different current densities studied.

Throwing power: Throwing power of zinc-nickel plating bath at different current densities and at 30^0C is given in table 2.

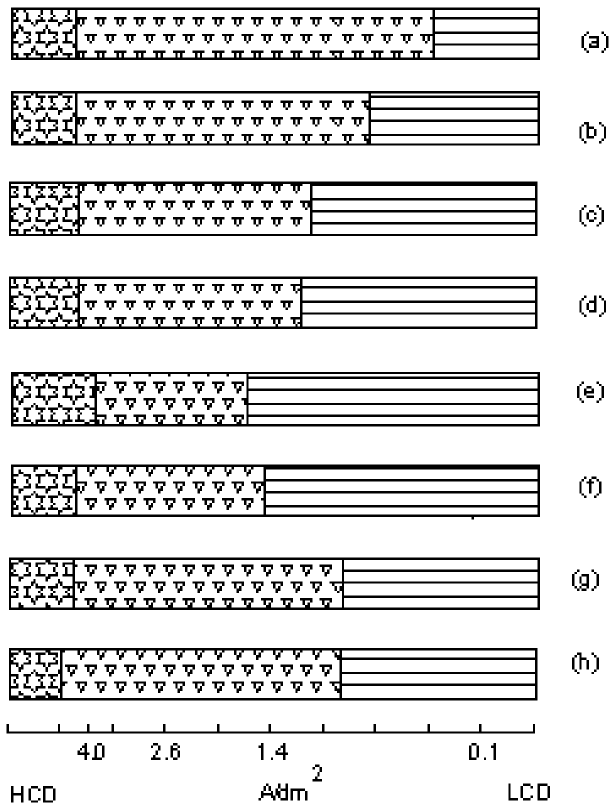

Figure - 4
Effect of change in concentration of Boric acid
Bath Composition and Conditions: Zinc bromide - 100g/l, Boric acid (g/l) (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70, (g) 80, (h) 90 and Nickel chloride - 175 g/l, Cell Current - 1A, Temperature - 30° C and pH 4

Throwing power of 14.5% was obtained at 2.0 A/dm^2. Throwing power increased up to 2.0 A/dm^2 and then decreased.

Characterization of zinc-nickel electro deposit: Micro hardness: The results of the micro hardness measurements of Zn-Ni alloy deposits of thickness 35 µm obtained from the bromide-chloride based bath at 1.0 and 2.0 A/dm^2 is given in table 3. It can be seen that a micro hardness value of 80.5 kg/mm^2 was observed for the deposit obtained at 2.0 A/dm^2.

Surface morphology of zinc-nickel alloy: When viewed at 2000 X magnification, the surface of the alloy deposit obtained at 1 A/dm^2 exhibited 10 µm sized crystallites. These crystallites completely covered the surface. An increase of current density favoured the growth of these crystallites (40-60 µm). These bigger crystallites completely covered the surface (figure 5).

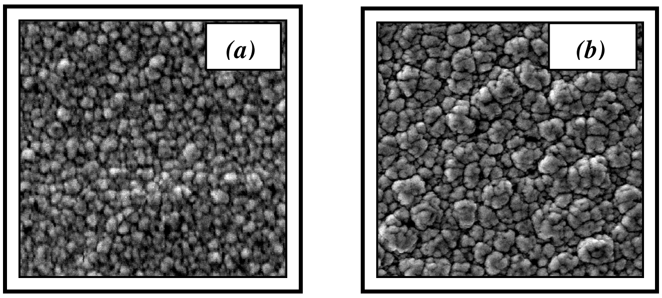

Figure - 5
SEM photographes of Zn - Ni deposits (a) 1.0 A/dm^2, (b) 2.0 A/dm^2

Structure of zinc-nickel alloy: Figure 6 presents XRD pattern obtained for the Zn-Ni alloy deposit. The reflections from the phases (0 0 2) (3 0 1), (4 3 1) (0 4 0), (1 0 4) planes of Zn $(OH)_2$ were identified. The most predominant phases due to Ni_3Zn_{22} phases of (4 1 1) (3 3 0), (6 1 1) (3 3 2), (5 5 4) planes were inferred. The intermediate phase formed in this anomalous co-deposition is Ni_3Zn_{22}, a zinc rich phase (table 4).

Crystalline size was determined from the full width at half maximum (FWHM) of the X-ray peaks using Scherrer's equation. The average size of the deposit was approximately 34 nm.

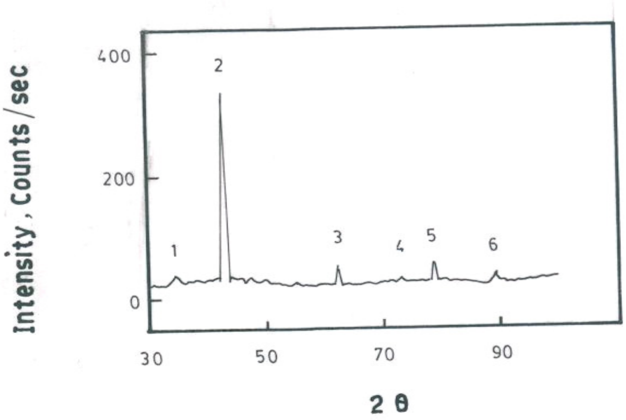

Figure - 6
XRD pattern of zinc-nickel deposit (25 µm) from bromide-chloride bath

Table - 1
Effect of current density on cathode current efficiency rate of build up, anode efficiency and nature of the deposit at temperature 30^{0}C

Bath Composition (g/l)	Current Density (A /dm^2)	Current Efficiency (%)	Rate of Build up (µm / hr)	Anode efficiency (%)	Nature of the Deposit
Zinc bromide 100	0.5	90.3	7.7	95.3	Semi bright milky
Nickel chloride 175	1.0	91.8	15.7	96.8	Semi bright milky
Boric acid 60	1.5	92.5	23.7	97.7	Semi bright milky
pH 4	2.0	88.4	30.2	98.9	Dull Satin
	2.5	86.7	37.1	99.4	Grey

Table - 2
Throwing power of Zn - Ni alloy plating bath at 30^{0}C

Bath composition (g/l)	Current Density (A/dm^2)	Throwing Power (%)
Zinc bromide 100	0.5	4.1
Nickel chloride 175	1.0	6.4
Boric acid 60	1.5	9.8
pH 4	2.0	14.5
	2.5	13.0

Table - 3
Micro hardness of Zn - Ni alloy deposits from bromide-chloride based bath

Bath composition (g/l)	Current Density (A/dm^2)	Micro hardness (kg/mm^2)
Zinc bromide 100		
Nickel chloride 175	1.0	76.3
Boric acid 60	2.0	80.5
pH 4		

Table - 4
Parameters derived from XRD pattern for Zn-Ni alloy deposit

S.No	2θ (degree)	d (A^{0})	I	I / I_0	h k l	Probable phase
1	34.6	2.590	41	12	0 0 2 3 0 1	$Zn(OH)_2$
2	42.8	2.111	345	100	4 1 1 3 3 0	Ni_3Zn_{22}
3	62.3	1.489	51	15	6 1 1 3 3 2	Ni_3Zn_{22}
4	73.1	1.293	35	10	4 3 1 0 4 0	$Zn(OH)_2$
5	78.7	1.215	57	17	1 0 4	$Zn(OH)_2$
6	89.0	1.099	40	12	5 5 4	Ni_3Zn_{22}

Conclusion

From the investigations carried out, the bath composition and operating parameters to produce good quality zinc-nickel coatings is as follows: Zinc bromide 100 g/l, Nickel chloride 175 g/l, Boric acid 60 g/l, Cathode Mild steel, Anode Pure zinc(99.9%), Current Density 0.5 -2.0 A/ dm^2 and pH 4. This bath produced semi bright milky, uniform and fine grained deposit and XRD analysis confirmed the formation of nano crystalline zinc-nickel alloy deposition.

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