Physico-chemical properties of Zn-Ni alloy deposits from an acid sulphate bath containing ethanolamines

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Abstract

The composition, properties, structure and morphology of electrodeposited Zn-Ni alloy deposits obtained from an acid sulphate bath have been investigated. A bath having higher percentage of nickel (50%) produced an alloy deposit with low percentage of nickel (12%), the percentage of nickel in the alloy deposit increases with current density up to 40 A.dm^{-2}, with further increase in current density, the percentage of nickel shows a downward trend, increase in temperature of the plating bath increases the percentage of nickel in the alloy deposit. The hardness of the alloy deposits increases with increase in nickel content in the alloy, the phase structure of alloy deposit shows the presence of α,η, δ and γ phases. The morphology of Zn-Ni alloy deposits shows uniform and finer grained structure.

Keywords

Ethanolamines, elctrodeposition, Zn-Ni alloy, current density, cathodic current efficiency, deposition rate, X-ray powder diffraction, scanning electron microscope.

Introduction

Electrodeposited zinc alloys find an extensive use as a viable substitute for zinc and cadmium metals in the corrosion protection of steel. Among zinc alloys, Zn-Ni alloy containing 10-15%Ni showed high degree of corrosion resistance and mechanicalproperties. The elctrodeposition of Zn-Ni alloy is of anomalous co-deposition

type as proposed by Brenner [1], *i.e.* under most conditions, less noble metal (zinc) deposits preferentially than more noble metal (nickel). The Zn-Ni alloys have been deposited from various types of baths like sulphate [2-5],sulphamate [6, 7], chloride [8, 9], sulphate-chloride [10], pyrophosphate [11], ammonical [12] and non-cyanide baths [13-17].

Many studies have been carried out to understand thecharacteristics of the deposition process of Zn–Ni alloy. Itis found that the characteristics of the deposited alloy coating depend on the current density, pH, bath composition, additives and temperature etc., Zinc-Nickel alloy deposition from a complex bath containing more than one organic additive has led to the production of alloy with a low percentage of nickel. Nitrogen containing organic compounds, especially amines is used in plating baths for Zn-Ni alloy deposition. Review of the literature reveals the absence of comprehensive work on the electrodeposition of Zn-Ni alloy from acid sulphate bath containing ethanolamines.

The purpose of the present investigation is to develop the optimum plating bath with suitablecomposition and plating conditionsfor obtaining good quality Zn-Nialloy deposit with 10 - 15 % Ni and to study properties, structure and morphology of Zn-Nialloy deposit.

Experimental

The plating bath solution was prepared using distilled water and laboratory grade chemicals. The bath solution was purified as described earlier [18]. The optimum bath composition and plating conditions used in the present study are given in Table 1.

Electrodeposition was carried out galvanostatically from 250 ml bath solution by using 1 cm^2 stainless steel as cathode and 2 cm^2zinc as anode at 328 K under stirred conditions. The panel so plated was weighted and stripped in 20% HNO_3, made up to 100 ml in a standard flask, the zinc and nickel contents in the test solution was analyzed by atomic adsorption spectrometry.

Table 1: Optimum bath composition and plating conditions for electrodeposition of Zn-Ni alloy containing 10-15% Ni

Bath component	Optimum composition & conditions
Total metal content	0.2M
$ZnSO_4.7H_2O$	0.1M
$NiSO_4.7H_2O$	0.1M
Triethanolamine / Diethanolamine/ Monoethanolamine	0.1 M
Saccharin	2 g/l
$[NH_4]_2SO_4$	40 g/l
H_3BO_3	30 g/l
Sodium laurylsulphate	0.2 g/l
Temperature	55 ^{o}C
pH	5.5
Current density	10 A.dm^{-2}
Stirring	normal

The adhesion of the alloy deposits to the base metal (Steel) was tested by a standard bending test. The porosity of the alloy deposit was determined by the Ferroxyl test. The micro-hardness of the alloy deposits was determined on Vickers scale. Deposition potentials of zinc, nickel and Zn-Fe alloy deposits dipped in 3.5% NaCl were measured w.r.t SCE by using scanning potentionstat.

The phase structure of the Zn-Ni alloy deposits were examined by X-ray powder diffraction (Filter CuK$_{\alpha l}$, 30kV, 20 mA, 4000 counts).The surface morphology of the alloy deposits was examined under Scanning electron microscope (Model JEOL-JSM-840A).

Results and discussion

Composition

Figure. 1 shows the cathodic polarization curves for Zn-Ni alloy deposition as well as individual metal deposition. Curve 1 is the current density potential curve for deposition of Ni alone, the deposition potential of nickel was around -0.84 V. Curve 2 is for zinc deposition alone,the deposition potential of zinc was around -1.03 V and Curve 3 is for Zn-Ni alloy deposition from the same bath solution. The deposition potential of alloy was around-1.15 V. The position of potential of alloy deposition curve is shown to be more negative to both nickel and zinc. This clearly indicates the reason for preferential deposition of zinc *i.e.* anomalous co-deposition.
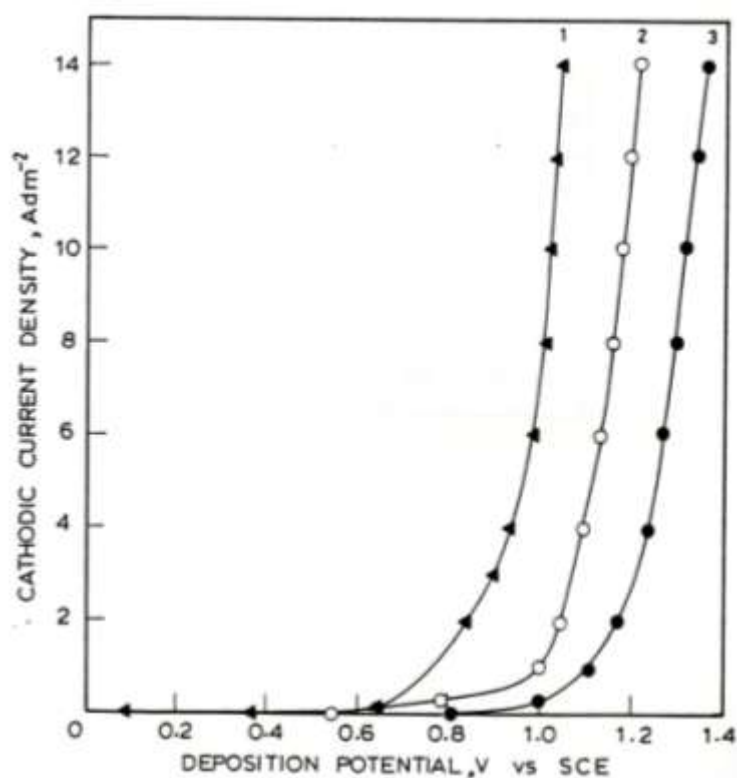

Fig. 1 Cathodic polarization curves for the deposition of nickel, zinc and Zn-Ni alloy from an acid sulphatebath.Curve 1. Deposition of nickel, Curve 2.Deposition of zinc, Curve 3. Deposition of alloy

To study the effect of metal ion ratio in the bath on the alloy composition, zinc to nickel ratio in the bath was varied from 20:80 to 60:40. Figure. 2 shows the variation of alloy composition with bath composition containing fixed concentration of ethanolamines. Under these conditions zinc gets deposited more preferentially than nickel. A bath having higher percentage ofnickel (50%) produced an alloy deposit with low percentage (12%) of nickel, it is due to preferential deposition of zinc than nickel (anomalous co-deposition). This is attributed to the formation of zinc hydroxide film at the cathode surface which suppresses the deposition of nickel.
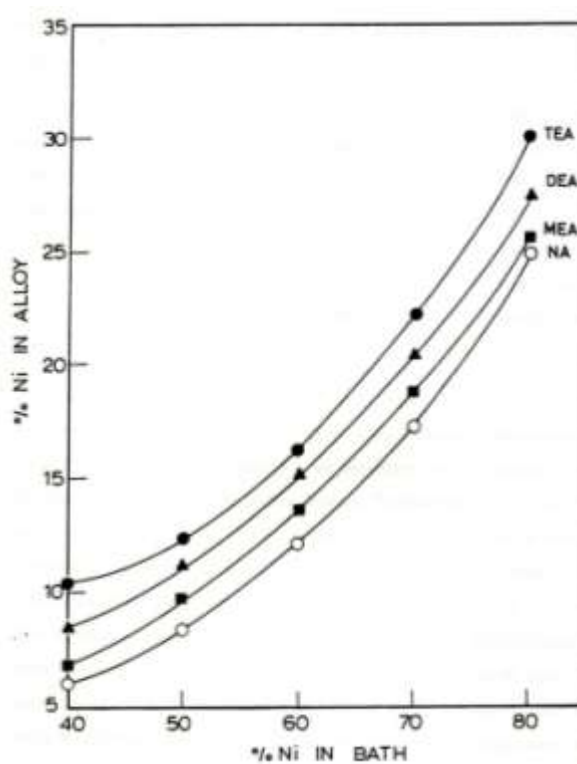
Fig. 2 Dependence of % Ni in alloy on the % Ni in the bath.Bath composition and operating conditions as in Table 1 $[Zn^{2+}] = 0.04$ -0.12 M, $[Ni^{2+}] = 0.16$ -0.08 M.

In order to study the effect of current density on the composition of Zn-Ni alloy experiments were carried out at various current densities (5-80 A.dm^{-2}) using bath solutions containing constant molar ratio of Zn/Ni (50/50) and 0.1 M of mono-, di- and tri-ethanolamines at 328 K. The variation in the composition of the deposited alloy with

current density is shown in Figure.3. The percentage of nickel in the alloy deposit increases with current density up to 40 A.dm^{-2}. With further increase in current density, the cathode potential becomes more negative and hence the percentage of nickel shows a downward trend. This decrease in percentage of nickel with increase in current density clearly indicates diffusion controlled nature of Zn-Ni alloy deposition. Increase in temperature of the plating bath increased the percentage of nickel in the alloy deposit. This is probably due to the decrease in the polarization potential of nickel (more noble metal) during alloy deposition.
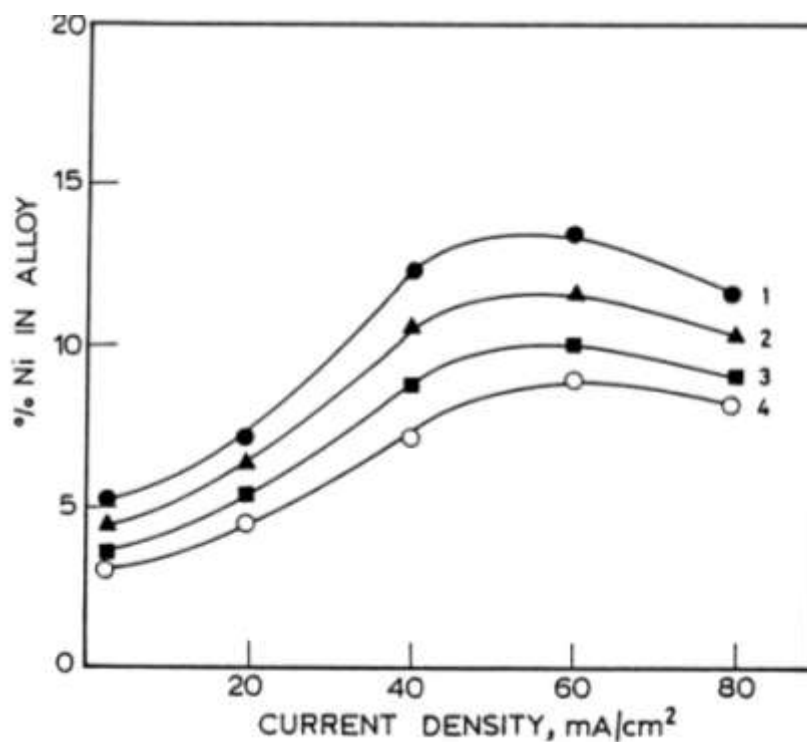

Fig. 3 Dependency of alloy composition on current density.Bath composition and operating conditions as in Table 1. Current density range 2.5-80 A.dm^{-2}. Curve 1: TEA, Curve 2: DEA, Curve 3: MEA, Curve 4: NA.

Figure.4showsthe dependence of the percentage of nickel in the alloy on the concentration of ethanolamines in the bath. The percentage of nickel in the alloy deposit is increased with increase in concentration of ethanolamines, attained a maximum value at 0.2M and then decreases slightly with further increase in the concentration of ethanolamines (>0.2M). The formation of a loose complex with metal ions always

facilitates the deposition process. In the present system, the nickel complex formed with different ethanolamine (0.2M) used may be active at the cathode, which stimulate the electrochemical discharge of nickel at higher rate. At the concentration >0.25M, the nickel may form strong complex that may retard the deposition of nickel, which leads to a decrease in the percentage of nickel in the alloy deposit at higher ethanolamine concentration.
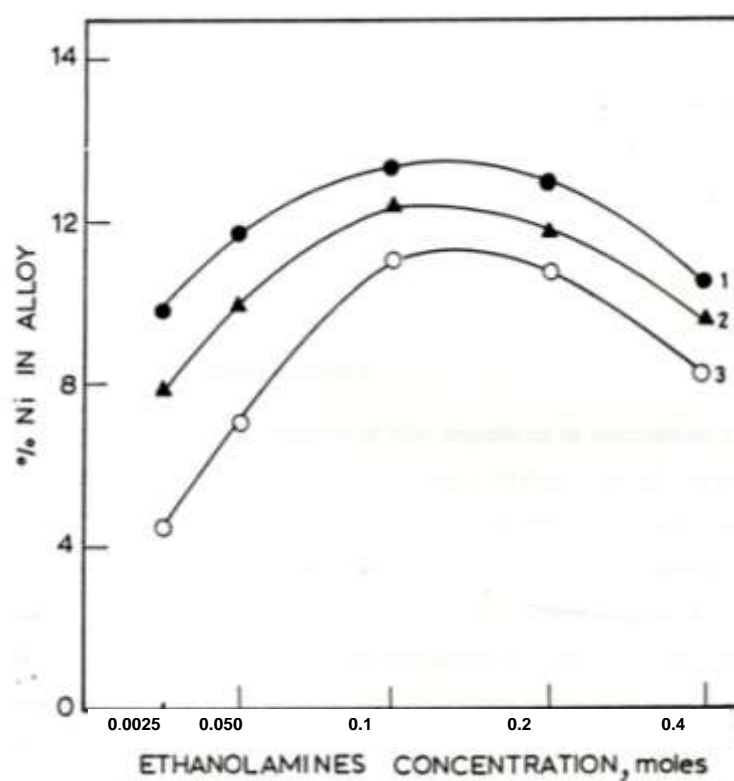

Fig. 4 Dependency of alloy composition on the concentration of ethanolamines. Bath composition and operating conditions as in Table 1.Ethanolamines concentration 0.05-0.4 M. Curve 1: TEA, Curve 2: DEA, Curve 3: MEA, Curve 4: NA.

The effect of stirring on the alloy composition was studied by carrying out experiments under stirred as well as unstirred conditions. The percentage of nickel in the alloy deposit was found to be high under stirred conditions compared to those obtained under unstirred conditions (Table 2). A significant increase in the percentage of nickel in the alloy deposit with stirring of the bath clearly indicates that deposition is under diffusion control.

Table 2: Effect of stirring on CCE

Parameter	CCE in media containing 0.1 M of			
	NA	MEA	DEA	TEA
With stirring				
% Ni	7.51	8.52	10.50	12.33
CCE	97.89	78.07	63.26	56.11
Without Stirring				
% Ni	6.33	7.67	9.48	11.14
CCE	88.17	73.66	60.59	54.02

The variation of alloy composition with its thickness is studied. The percentage of nickel in the deposit increased up to 4 μm. With further increase in deposit thickness, the percentage of nickel in the alloy deposit showed a downward trend. Beyond 4μm thickness, the cathode diffusion layer may not supply enough of nickel ions to the cathode surface and hence the decrease in the percentage of nickel in the alloy deposit.

The cathodic current efficiencies (CCE) were calculated for the Zn-Ni alloy deposition under each set of experimental condition. With increase in current density the CCE increased and attains a steady value. The CCE from bath containing no additives was found to be maximum compared in baths containing ethanolamines. With increase in temperature, CCE increased up to 55 °C, beyond this temperature, the CCE decreased (Table 3).

Table 3: Effect of temperature on CCE

Temperature (^{o}C)	CCE in media containing			
	NA	MEA	DEA	TEA
25	19.10	17.87	15.12	9.56
35	76.56	61.11	61.96	48.82
55	87.89	78.07	63.26	56.11
75	71.67	58.67	52.17	52.01

Properties

The adhesion of Zn-Ni alloy deposit to the base metal (steel) was tested by a standard bending test. Alloy samples coated to different thickness (2-12 μm) on steel (1 × 4 sq. inch) were subjected to bending tests. The alloy coatings did not develop any visual cracks even after 180° bending. This shows a good adhesion of the alloy deposits to be steel surface.Porosity tests were carried out on alloy coated to 2-12μm thickness on steel panels 13 × 3 sq. inch). A filter paper soaked in 1% potassium ferricyanidesolution was placed on alloy coated steel panels. The number of blue spots appearing on the filter paper with time was a measure of porosity of the deposit. The alloy deposits were pore free at thickness > 4μm.Themicrohardness of Zn-Ni alloy (10 μm thick deposit) specimens was determined. The hardness of the alloy deposits increased with increase in nickel content in the alloy. The static potential values of zinc and zinc-nickel alloy were measured w.r.t. SCE in 3.5%NaCl solution. The potentials of Zn-Ni alloy were found to be less noble to steel and more noble to zinc. This clearly shows that Zn-Ni alloy coatings protect steel more efficiently than zinc coatings (Table 4).

Table 4: Dependency of nickel content in the Zn-Ni alloy on microhardness and on static potentials

% Ni in alloy	Microhardness in VHN (load -50gm)	Static potential in mV vs. SCE in 3.5% NaCl
0	120	-1060
10	300	-1050
15	330	-1043
20	370	-1028
25	450	-1010

Structure and morphology

The phase structure of electrodeposited Zn-Ni alloy from an acid sulphate bath containing ethanolamines was studied by X-ray powder diffraction. Figure. 5shows the relationship between the phase structure and the percentage of nickel in the alloy deposit. The phase diagram of Zn-Ni alloy reveals the presence of intermetallic phases:(η) Hexagonal, (δ) F.C.C, (γ) B.C.C and (α) B.C.C. Low zinc containing alloy shows a solid solution of zinc in nickel, *i.e.,* α-phase, whereas zinc rich alloy deposits showed intermetallic phases:η,$\delta$and γ. Thus, electrodeposited Zn-Ni alloys have intermetallic phases over a wide range of composition: η (89-100% Zn), γ (13.5-84.5% Zn), δ (75.5-89% Zn) and α (0-62.5% Zn).The surface morphology of Zn-Ni alloy deposits was examined under scanning electron microscope. Figure 6 shows the morphology of Zn-Ni alloy deposits obtained at 40 A.dm^{-2} from an acid sulphate bath containing various ethanolamines. The morphology of Zn-Ni alloy deposits shows uniform and finer grained structure.
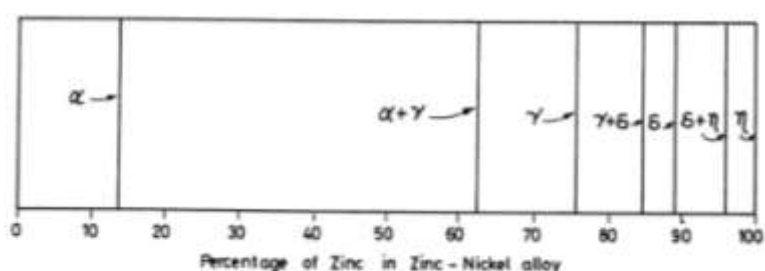

Fig. 5 Relationship between phase structure and percentage of zinc in the Zn-Ni alloy deposit.
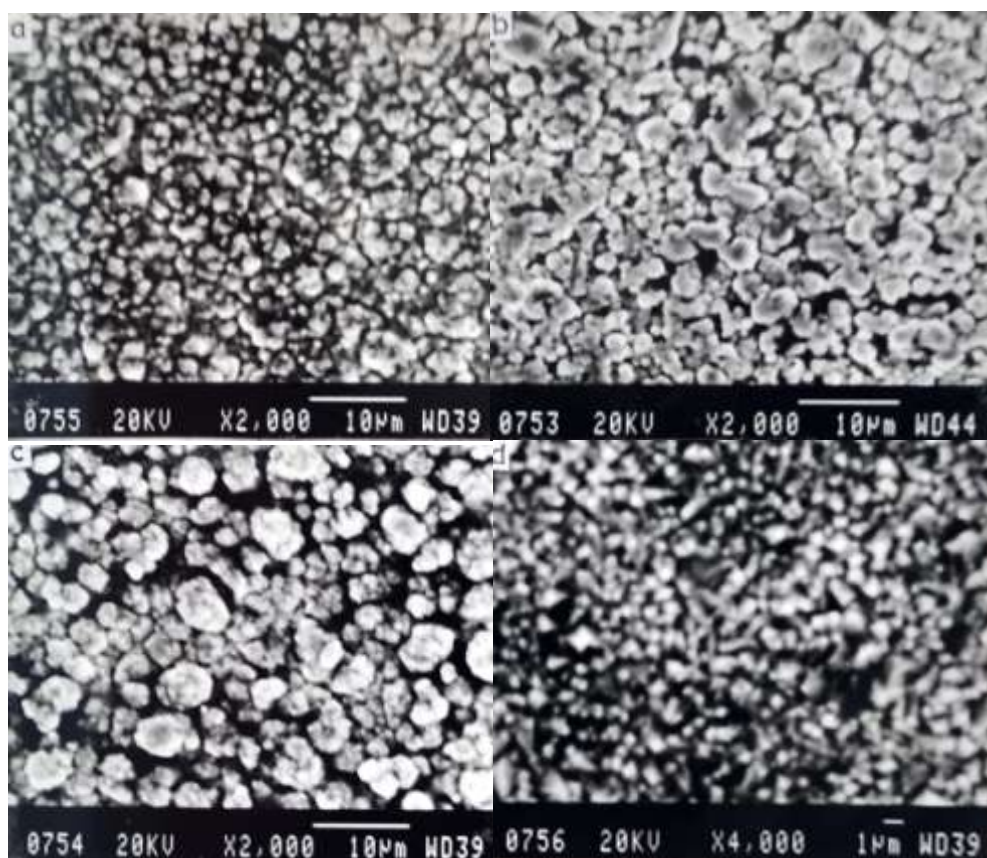
Fig. 6 scanning electron micrographs of Zn-Ni alloy deposits obtained from an acid sulphate bath containing various ethanolamines.

a. Bath with NA, cd 40 A.dm^{-2} b. Bath with MEA, cd 40 A.dm^{-2}

c. Bath with DEA, cd 40 A.dm^{-2} d. Bath with TEA, cd 40 A.dm^{-2}

Conclusion

Electrodeposition of Zn-Ni alloy having 10-15% Ni from an acid sulphate bath containing ethanolamines follows anomalous co-deposition. The deposition potential of alloy is less noble to both zinc and nickel deposition. A bath having high nickel content (50%) produces an alloy with low nickel content (12%). Increase in current density, temperature and stirring increases the percentage of nickel in the alloy deposit. With increase in thickness of the alloy deposit, the percentage of nickel increases, reaches a maximum and then decreases with further increase in thickness. The cathodic current efficiency is dependent on current density, temperature and stirring of the bath. Hardness of the alloy increases with increase in nickel content of the alloy,the phase structure of alloy deposit shows the presenceof α,η,δ and γ phases. The morphology of Zn-Ni alloy deposits shows uniform and finer grained structure.

Acknowledgement

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