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Physico-Chemical Properties of Zn-Ni Alloy from an Alkaline Sulphate Bath Containing Triethanolamine and Mercaptopyridine

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ABSTRACT

The composition, properties and morphology of electrodeposited Zn-Ni alloy from an alkaline sulphate bath containing triethanolamine (TEA) and mercaptopyridine (MPY) have been investigated. A bath solution containing 3.5% wt. Ni content produced an alloy deposit with 12.5% wt. Ni (more noble metal) indicating preferential deposition of nickel (i.e. Regular co-deposition process). With increase in current density and the concentration of TEA, the percentage of nickel in the alloy deposit decreased. An increase in temperature, thickness and the concentration of MPY increases the percentage of nickel (more noble) in the Zn-Ni alloy deposit. CCE was decreased with current density, increased with temperature and stirring of the bath solution. Static potentials of Zn-Ni alloy were less noble to nickel and more noble to zinc. Hardness of the alloy increased with an increase in %Ni in an alloy. Fine grained deposits were observed morphologically.

1. Introduction

In the past couple of years, many attempts have been made on developing a high corrosion resistance steel especially for an automotive body panels [1,2]. Electrodeposition of Zn-Ni alloys containing 10-15% wt. Ni have received greater attention, because these alloys provide improved corrosion resistance to steel than conventional zinc and cadmium coatings [3]. Zn-Ni alloy containing 10-15% wt. shows an excellent corrosion resistance. The Zn-Ni alloys have been deposited from various types of baths like sulphate [4,5], chloride [6,7], sulphamate [8,9], pyrophosphate [10-12], ammonical [13,14], cyanide [15-18] and alkaline sulphate [19-21] baths.

The literature survey reveals the absence of comprehensive work on the electrodeposition of Zn-Ni alloy from an alkaline sulphate bath triethanolamine (TEA) and mercaptopyridine (MPY). The aim of the present investigation is to develop the optimum plating bath with suitable composition and plating conditions for obtaining good quality Zn-Ni alloy deposit with 10-15% wt. Ni and to study composition, properties and morphology of electrodeposited Zn-Ni alloy deposit.

2. Experimental Methods

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

Electrodeposition was carried out galvanostaticaly from 250 mL bath solution by using 1 cm² mild steel as cathode and 2 cm² zinc as anode at 323 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 (Varian spectra model AA 30). The cathodic current efficiencies and deposition rates were calculated in a conventional manner. The thickness of the alloy deposit was measured by Elicometer (Model 250 FN, England). The ductility alloy deposit and adhesion of the alloy deposit to the base metal (steel) was tested by a bending test. The porosity of the alloy deposit was determined by Ferroxyl test. Static potentials of zinc and Zn-Ni alloy deposits dipped in 3.5% NaCl were measured with respect to saturated calomel electrode. Tensile strength of the alloy deposit (10 μm thick) was determined by a tensile strength testing machine (Tensiometer). Hardness of alloy deposits was determined on Vickers scale (load 50 g). Adhesion of the paint on Zn-Ni alloy deposit was evaluated by cross hatching method. Corrosion testing of zinc and zinc-iron alloy plated steel panels by accelerated neutral salt spray method was examined for 96 hours as per ASTM B117 specification in 5% NaCl at 35±2 °C. Surface morphology of alloy deposits were examined under scanning electron microscope (Model JEOL-JSM-840A).

Table 1 Bath composition and operating conditions for electroplating of Zn-Ni alloy from an alkaline sulphate bath containing TEA and MPY

Bath composition	Optimum composition and conditions
Total metal content	0.2 M
$ZnSO_4.7H_2O$	0.196 M
$NiSO_4.7H_2O$	0.004 M
TEA	40 mL/L
MPY	0.01 M
Na_2SO_4	50 g/L
NaOH	100 g/L
Saccharin	2 g/L
pH	14
Current density	15 Adm^{-2}
Temperature	55 °C
Agitation	Normal

3. Results and Discussion

3.1 Composition

In order study the zinc to nickel ratio in the plating bath on alloy composition, zinc to iron ratio was varied from 96.4 to 99.5 in the bath at 55 °C, thickness ~ 4 μm for three different current densities (10, 20 and 35 mA/cm²). Fig. 1 indicates the variation of alloy composition with bath composition. In the graph, the line AB is the composition reference line (CRL), which represents the zinc to nickel ratio in the bath, which is equal to zinc to nickel ratio in the alloy deposit. A bath solution containing 3.5% wt. Ni content produced an alloy deposit with 12.5% wt. Ni (more noble

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metal) indicating preferential deposition of nickel i.e. the curves in the graph for the percentage of nickel in the alloy deposit are well above the CRL line AB. This shows that the alloy deposition is of regular co-deposition type.

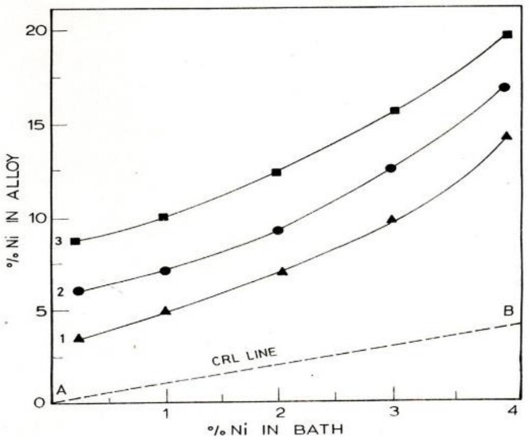

Fig. 1 Dependence of alloy composition on bath composition. Bath composition: Total metal 0.2 M, $[Zn^{2+}]$ 0.192 to 0.198 M, $[Ni^{2+}]$ 0.002 -0.008 M, TEA 40 mL/L, MPY 0.01 M, Na_2SO_4 50 g/L, NaOH 100 g/L, Saccharin 2 g/L, temperature 55 °C current density 10-35 mA / cm^2, thickness ~ 2 μm, pH > 14, stirred condition. Curve 1. 35 mA/cm^2; Curve 2. 20 mA/cm^2; Curve 3. 10 mA/cm^2

Fig. 2 shows the dependency of the alloy composition on current density from the baths having various zinc to nickel ion ratios (Zn: Ni 97:3, 98:2 and 99:1). With increase in current density, the percentage of nickel in the alloy deposit decreased. At higher current densities (more than 25 mA/cm^2), the percentage of nickel in the alloy deposit attained a steady value, this shows a steady rates of discharge of nickel ions at the cathode at higher current densities.

An increase in temperature increases the percentage of nickel (more noble) in the Zn-Ni alloy deposit (Table 2). This is because an increase in temperature might increase the preferentially depositing metal (nickel) ion concentration in the cathode diffusion layer, confirming the Zn-Ni alloy deposition to be of regular type.

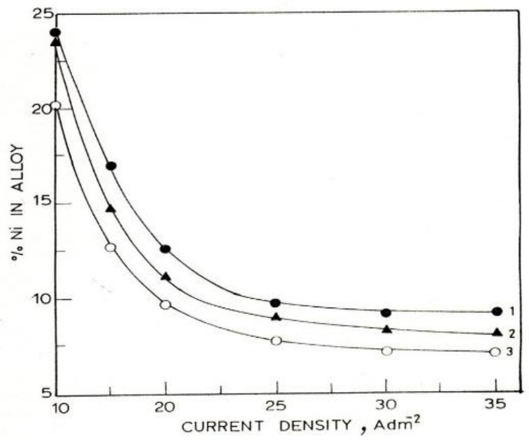

Fig. 2 Dependency of the alloy composition on current density. Bath composition: Total metal 0.2 M, $[Zn^{2+}]$ 0.194-0.198 M, $[Ni^{2+}]$ 0.002-0.006 M, TEA 40 mL/L, MPY 0.01 M, Na_2SO_4 50 g/L, NaOH 100 g/L, Saccharin 2 g/L, temperature 55 °C current density 10-35 mA/cm^2, thickness ~ 2 μm, pH 14, stirred condition. Curve 1: 97:3 Zn:Ni; Curve 2: 98:2 Zn:Ni and Curve 3: 99:1 Zn:Ni.

Table 2 Effect of temperature on composition Zn-Ni alloy from an alkaline sulphate bath

Temperature (°C)	%Ni in Zn-Ni alloy		
	99/1 Zn/Ni	98/2 Zn/Ni	97/3 Zn/Ni
25	10.03	11.92	14.54
35	12.77	13.82	16.70
45	13.23	14.56	18.11
55	15.06	17.66	21.01
65	17.24	22.35	24.23
75	21.46	25.89	29.26
Stirring	-	Normal	

Experiments were carried out at 15 mA/cm^2, 55 °C, pH 14, thickness ~ 4 μm from the baths having various concentrations of TEA and MPY. Fig. 3 illustrates the dependence of alloy composition with the concentrations of TEA and MPY. An increase in the concentration of MPY, the percentage of nickel in the alloy deposit increases to a steady value at higher concentration. In the case of TEA, an increase in the concentration of TEA, up to 20 mL/L decreased the percentage of nickel in the alloy deposit and finally attained a steady value.

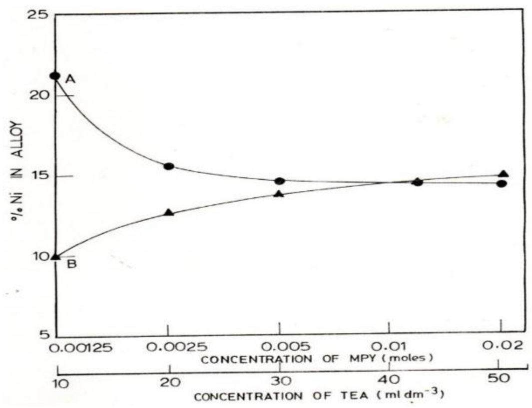

Fig. 3 Dependence of the % of Nickel in the Zn-Ni alloy deposits on the concentrations of TEA and MPY in the plating bath solution

The dependence of alloy composition with the thickness alloy deposit is shown in Fig. 4. Increase in the thickness of the alloy deposit increased the percentage of nickel in the alloy deposit. The cathodic current efficiencies were calculated for Zn-Ni alloy deposition under each set of conditions. The dependency of CCE on current density is shown in Fig. 5. With an increase in current density, the CCE was found to decrease, stirring and increase in bath temperature increased the CCE.

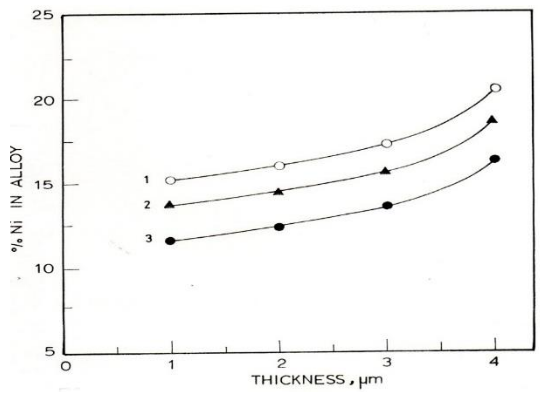

Fig. 4 Dependence of alloy composition on thickness of the alloy deposit. Curve 1. 97:3 Zn:Ni; Curve 2. 98:2 Zn:Ni; and Curve 3. 99:1 Zn:Ni.

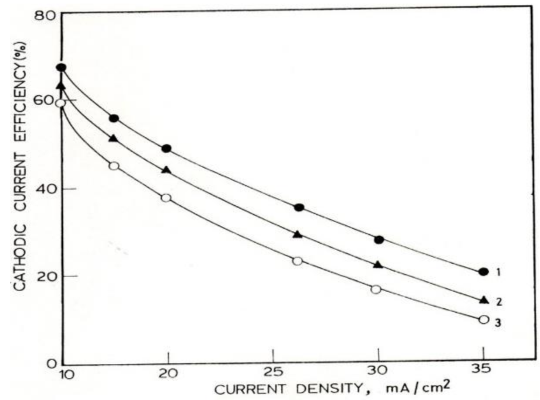

Fig. 5 Dependency of cathodic current efficiency on the current density. Curve 1. 97:3 Zn:Ni; Curve 2. 989:2 Zn:Ni; and Curve 3. 99:1 Zn:Ni.

3.2 Properties

The adhesion of alloy deposits to the base metal was tested by a bending test. Alloy deposits did not show any visual cracks even after 180° bending. This shows good adhesion of Zn-Ni alloy deposits to the substrate. Ferroxyl test was conducted for Zn-Ni alloy coated on steel. Alloy deposits with sufficient thickness (> 6 μm) were free from pores. Micro hardness of alloy deposits was determined on Vickers scale (load 50 g). Hardness of the alloy increases with an increase in the amount of nickel in the deposit (Table 3).

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Static potentials of zinc and zinc-nickel alloys were measured in 3.5% NaCl solution with respect to SCE. Table 3 lists the static potential values for zinc and Zn-Ni alloy (Fig. 6). Static potentials of Zn-Ni alloys were found to be nobler to zinc. This indicates corrosion resistant characteristics of Zn-Ni alloy. The surface morphology of alloy deposits having different percentage of nickel were examined under scanning electron microscope. The fine grained alloy deposits were observed morphologically (Fig. 7).

Table 3 Effect of percentage of nickel on hardness of alloy and on static potentials

%wt. Ni in Zn-Ni alloy	Hardness in V.H.N. (load – 50 g)	Static potentials in mV Vs SCE measured in 3.5% NaCl
0	98	-1120
5	282	-1070
10	307	-1035
15	339	-1021
20	365	-1008
25	398	-998
Mild steel	--	-630

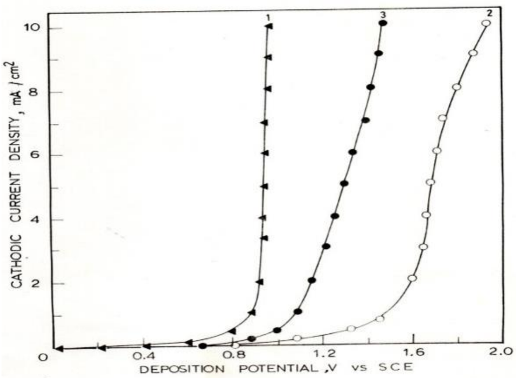

Fig. 6 Cathodic polarization curves for the deposition of zinc, nickel and Zn-Ni. Alloy from on alkaline sulphate bath. All solutions contained triethanolamine 40 mL/L, mercaptopyridine 0.01 M, Na_2SO_4 50 g/L, Saccharin 2 g/L, temperature 55 °C, Stirred condition. Curve 1. Deposition of Nickel alone, Curve 2. Deposition of Zinc alone, and Curve 3. Deposition of Zink-Nickel alloy. The bath solution contained same concentration of nickel and zinc as those in the individual baths

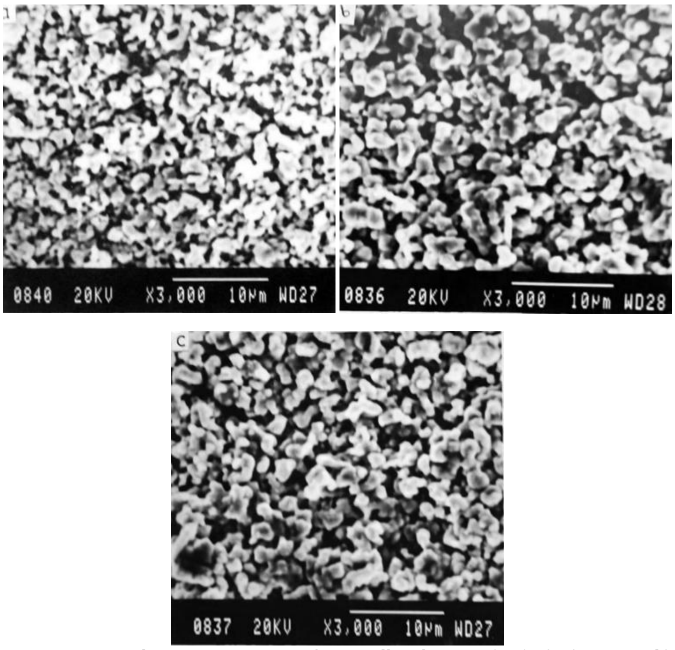

Fig. 7 Scanning electron microscopy of Zn-Ni alloy deposits (X3500). a) 10% Ni, b) 15% Ni and c) 20 %Ni.

4. Conclusion

Electrodeposition of Zn-Ni alloy from an alkaline sulphate bath containing triethanolamine (TEA) and mercaptopyridine (MPY) regular co-deposition. A bath solution containing 3.5% wt. Ni content produced an alloy deposit with 12.5% wt. Ni (more noble metal) indicating preferential deposition of nickel. With increase in current density, the percentage of nickel in the alloy deposit decreased. An increase in temperature, increases the percentage of nickel in the Zn-Ni alloy deposit. CCE was decreased with current density, increased with temperature and with stirring of the bath solution. Static potentials of Zn-Ni alloy were less noble to nickel and more noble to zinc. Hardness of the alloy increased with an increase in % Ni in an alloy. Fine grained deposits were observed morphologically.

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