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, δ and γ phases. The morphology of Zn-Ni alloy deposits shows uniform and finer grained structure.

1. 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 mechanical properties. The electrodeposition 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 the characteristics of the deposition process of Zn-Ni alloy. It is 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 suitable composition and plating conditions for obtaining good quality Zn-Ni alloy deposit with 10 - 15% Ni and to study properties, structure and morphology of 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 in the Experimental section. The bath solution was prepared using distilled water and laboratory grade chemicals. The bath solution was purified as described in the Experimental section. The bath solution was prepared using distilled water and laboratory grade chemicals. The bath solution was purified as described in the Experimental section.

The pH of the bath was adjusted to 5.5 by using phosphoric acid. The bath was stirred by a magnetic stirrer. The bath was purged with nitrogen to remove oxygen. The bath was heated to 328 K and maintained at this temperature throughout the study. The bath solution was analyzed by atomic absorption spectrometry.

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 Ferrozyl 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 with respect to SCE by using scanning potentiostat. The phase structure of the Zn-Ni alloy deposits was examined by X-ray powder diffraction (Filter CuKα, 30 kV, 20 mA, 4000 counts). The surface morphology of the alloy deposits was examined under Scanning electron microscope (Model JED-1500).

3. Results and Discussion

3.1 Composition

Fig. 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 potential 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.

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 | 0.2 M |
| ZnSO₄·7H₂O | 0.1 M |
| NiSO₄·7H₂O | 0.1 M |
| Triethanolamine /Diethanolamine / Monoethanolamine | 0.1 M |
| Saccharin | 2 g/L |
| [NiH₄]SO₄ | 40 g/L |
| H₂BO₃ | 30 g/L |
| Sodium laurylsulphate | 0.2 g/L |
| Temperature | 55°C |
| pH | 5.5 |
| Current density | 10 A.dm⁻² |
| Stirring | normal |

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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. Fig. 2 shows the variation of alloy composition with bath composition containing fixed concentration of ethanamines. Under these conditions zinc gets deposited more preferentially than nickel. A bath having higher percentage of nickel (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.

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 Fig. 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 increases 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.

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 | 0.05-0.4 M | 2.5-80 A.dm⁻² |
|-------------|---------------------------------|------------|---------------|
|             | NA                              | MEA        | 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         |

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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 4 μm 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).

3.2 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 2-12 μm thickness on steel panels 13 × 3 sq. inch. A filter paper soaked in 1% potassium ferricyanide solution 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 > 4 μm. The microhardness 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 with respect to 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).

3.3 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. Fig. 5 shows 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; (γ) Hexagonal, (α) 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: α, δ and γ. Thus, electrodeposited Zn-Ni alloys have intermetallic phases over a wide range of composition: α (89-100% Zn), γ (15.5-84.5% Zn), δ (75.5-89% Zn) and α (0-62.5% Zn). The surface morphology of Zn-Al alloy deposits was examined by scanning electron microscopy. Fig. 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.

4. Conclusion

Electrodeposition of Zn-Ni alloy having 10-15% Ni from an acid sulphate bath containing ethanolamines follows an 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 presence of α, γ, δ and 7 phases. The morphology of Zn-Ni alloy deposits shows uniform and finer grained structure.

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