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Electrodeposition of Zn-Ni alloy-A voltammetric study

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The effect of addition of citrate on the deposition of Zn-Ni alloy as well as on the alloy composition has been investigated by cyclic voltammetric technique in the context of our earlier studies on the practical aspects of Zn-Ni alloy deposits.

Key words: Zn-Ni alloy, electrodeposition, voltammetry

INTRODUCTION

During our investigations on the electrodeposition of Zn-Ni alloy, it is observed that each of the constituents in the electrolyte, as also the operating parameters, influences the composition of the alloy. In an earlier paper, the effect of H_3BO_3 on the alloy composition has been discussed using cyclic voltammetry [1]. This paper discusses the effect of citrate addition and other operating variables on the composition of the alloy.

EXPERIMENTAL

The alloy deposition was carried out using a sulphate electrolyte. The details about the experimental set up, instrumentation used, alloy analysis, X-ray and structural analysis are discussed elsewhere [1,2].

RESULTS AND DISCUSSION

From the analytical data (Table I) on electrodeposited Zn-Ni alloys, it was inferred that the deposition followed the anomalous type in which the presence of citrate ion, high Zn/Ni ratio, current densities below 4 $A.dm^{-2}$, high pH etc. increase the zinc content of the alloy. These findings are substantiated by the voltammetric studies.

When Zn/Ni ratio is 0.5 (Fig. 1) the zinc dissolution peak (P_1) is not significantly altered in presence of citrate, whereas the nickel dissolution peak P_3 and the zinc dissolution peak from the α-phase P_2 are shifted to more positive potentials with a considerable reduction in peak heights. It is known, that in presence of H_3BO_3, a weak buffer, the alloy contains inclusions of oxides and hydroxides [3] which may be responsible for the active dissolution of the porous nickel matrix left after the preferential leaching of zinc. Citrate, being a good complexant and a buffer, solubilises and prevents the above inclusion and enhances the formation of compact nickel. This results in the shift of P_3 to more positive potentials. The shift in P_2 also indicates a reduction in the amount of zinc present in the α-phase. With increasing citrate addition, the pattern remains the same, except for a progressive decrease in the peak heights, probably due to increased inhibition to alloy deposition. A similar behaviour is observed at a Zn/Ni ratio of 1 also (Fig. 2). XRD analysis of the alloy confirmed that the alloy exists in the γ-phase with a cubic structure, but has a little contribution from the α-phase also. The absence of peaks due to NiO, $Ni(OH)_2$ etc. confirm the previous observations.

TABLE–I: Variation of alloy composition with Ni/Zn ratio and current density

Ni/Zn ratio	% Ni in deposit A	% Ni in deposit B	C.D. ($A.dm^{-2}$)	% Ni in deposit A	% Ni in deposit B
3.8	25.2	22.1	1.5	28.0	24.5
2.2	20.0	18.0	3.0	25.5	21.2
1.36	18.4	12.2	4.0	21.5	18.0
0.9	10.1	5.1	5.0	16.0	19.8

A - No citrate, B - With 0.1M citrate, Electrolyte = 0.66M H_3BO_3,pH 3, 4 Adm^{-2}, R.T.,Ni/Zn ratio is varied using their sulphates. For c.d.studies Ni/Zn ratio = 2.2 citrate 0.1M. Other conditions as above.

Figure 3 shows the CV pattern obtained when cycling was effected between −0.1 to −1.3 V contrary to the above results, citrate increases the nickel content, as indicated by the increase in peak currents of P_3 and P_2. This indicates that under these conditions, the deposition of zinc is limited by mass transport and more nickel is deposited.

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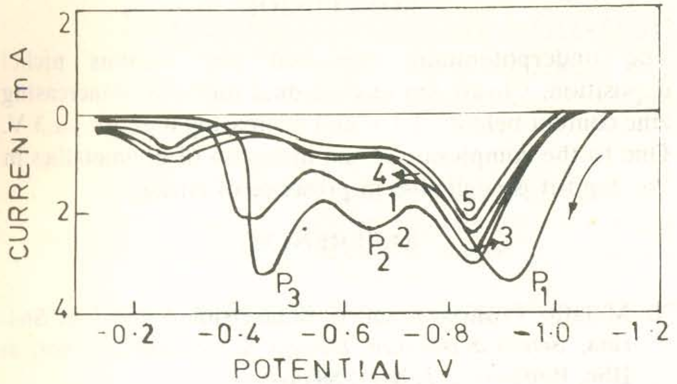

Fig. 1: Voltammogram of Zn-Ni alloy from a solution containing Zn-0.2M,Ni-0.4M (1) No H_3BO_3 (2) With 0.66M H_3BO_3 (3) With H_3BO_3 and 0.05M citrate. (4) As in 3 with citrate 0.1M (5) As in 3 with citrate 0.2 M. 10mV/sec

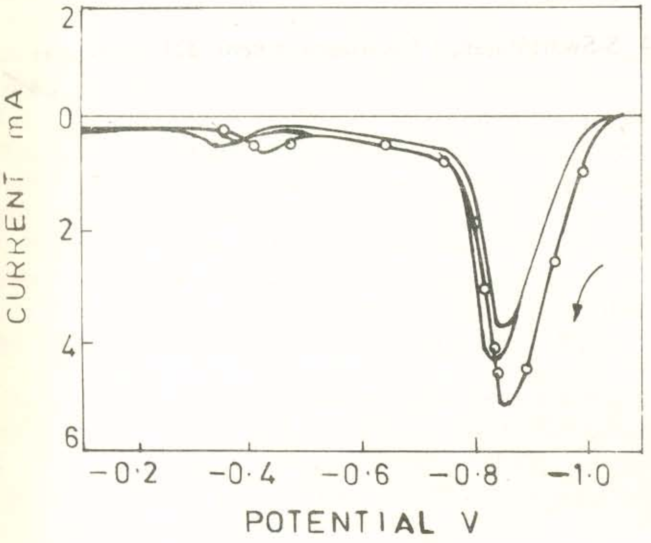

Fig. 2: Voltammogram of Zn-Ni alloy from a solution containing Zn 0.3M, Ni 0.3M (1) Plain bath (2) With H_3BO_3 (3) With H_3BO_3 and 0.1M citrate. Scan range −0.1 to −1.2 V

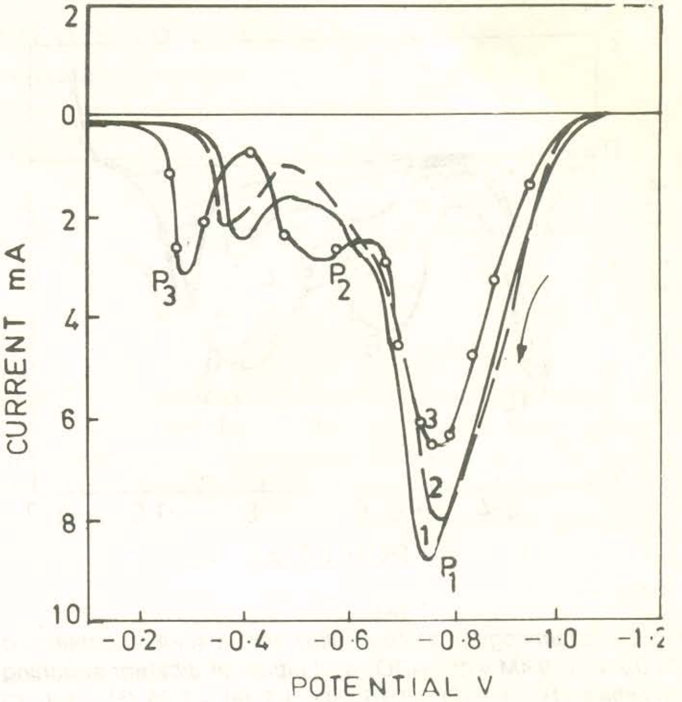

Fig. 3: Voltammogram of Zn-Ni alloy. Conditions as in Fig. 2. Scan range −0.1 to −1.3 V, 10 mV/sec

This is in accordance with the given analytical data. This effect may be due to the depolarisation observed, in the forward cycle, in presence of citrate at current densities above 4 A.dm^{-2}.

Figures 4 & 5 illustrate the role of citrate on the stripping peaks obtained when the scan range was gradually increased in the more negative direction. In the absence of citrate, deposition starts at a slightly lower potential and the peak heights are also higher upto −1.2 V. The presence of citrate increases the overpotential associated with alloy deposition. In both cases, the initial layer formed is only zinc, indicating the probability of UPD of zinc which inhibits nickel deposition by interaction with growing nickel clusters [4]. This enhances the polarisation for nickel deposition and results in anomalous deposition.

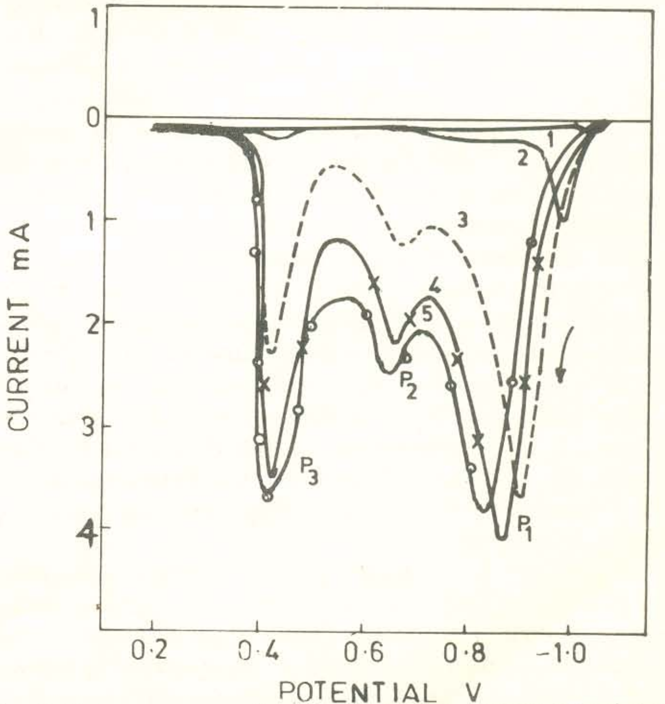

Fig. 4: Voltammogram of Zn-Ni alloy from a solution containing Zn 0.2M, Ni 0.4M with H_3BO_3 alone at varying switching potentials (V) (1) −1.08 (2) −1.1 (3) −1.16 (4) −1.18 (5) −1.2

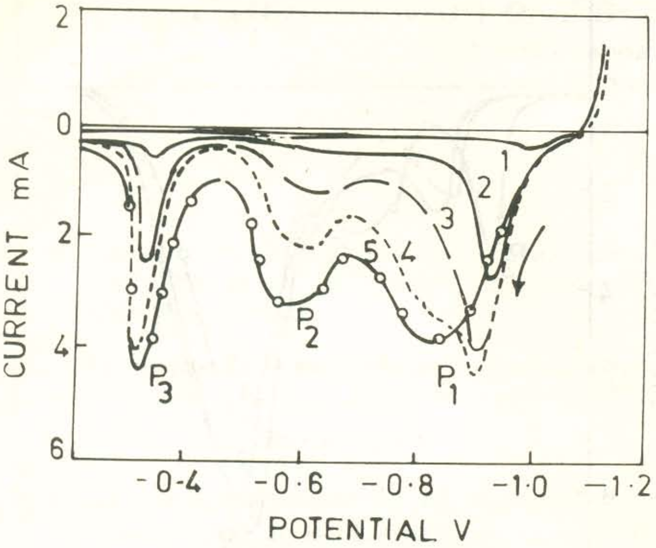

Fig. 5: Voltammogram of Zn-Ni alloy from a solution containing Zn 0.2M, Ni 0.4M with H_3BO_3 and citrate at different switching potentials (1) −1.1 (2) −1.15 (3) −1.2 (4) −1.25 (5) −1.3, 10 mV/sec

CONCLUSION

The underpotentially deposited zinc inhibits nickel deposition. Citrate ion has the dual function of increasing zinc content below −1.2 V and decreasing it above −1.3 V. Due to the complexation, the inclusion of nonmetallics in the deposit is negligible in presence of citrate.

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