



## Electrodeposition of Zn-Ni alloy from an alkaline sulphate bath containing triethanolamine and mercaptopyridine

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### Abstract

Electrodeposition of Zn-Ni alloy from non-cyanide alkaline sulphate bath containing triethanolamine (TEA) and mercaptopyridine (MPY) under optimized plating conditions such as bath pH, temperature current density and metal ion ratio in the bath produced an alloy deposit with the desired composition of 10-15 % wt. of nickel, alloy of this composition showed good adhesion, high hardness pore free, smooth, uniform and finer grained. Deposition potentials of Zn-Ni alloy lie between the potentials of individual metals. Increase in temperature density decreased the nickel content in the alloy deposit, which with increase in temperature and thickness of the alloy deposit increased nickel content in the alloy deposit. Alloy deposition followed a regular type of co-deposition.

### Keywords

Electrodeposition, Zinc-Nickel alloy, Cathodic Current Efficiency, Scanning Electron Microscope, Triethanolamine.

### Introduction

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 coatings. The zinc-nickel alloys have been deposited from various types of baths such as sulphate [1,2], chlorides [3,4], sulphamate [5,6], pyrophosphates [7-9], ammonical [10-12] and cyanide [13-16] baths.

Alkaline Zn-Ni alloy system has proved to be functional substituted for zinc and cadmium electrodeposits. Compared to cadmium, alkaline zinc-nickel alloy system not only



offers greater resistance to corrosion but also reduces the health hazards caused involving cadmium since, it is toxic. There are only a few reports cited in the literature on the electrodeposition of Zn-Ni alloy from an alkaline sulphate baths. The main disadvantages of alkaline sulphate baths is the loss of ammonia at high operating temperature, which makes the process difficult to operate and control the plating conditions. The problems encountered in the effluent treatment of alkaline baths containing cyanide is another limitation. In order to overcome these problems, it was felt to develop a non-cyanide and ammonia free alkaline sulphate bath for the electrodeposition of Zn-Ni alloy, which is easy to operate with no effluent problems. Therefore, we tried to develop alkaline sulphate bath containing triethanolamine (TEA) as a complexing agent and mercaptopyridine (MPY) as a brightener for the electrodeposition of Zn-Ni alloy. The results obtained are reported in this paper.

## **Materials and Methods**

The plating bath solutions were prepared by using distilled water and laboratory grade chemicals. The bath solution was purified as described elsewhere. Table 1 lists the bath composition and operating conditions used for plating.

Hull cell experiments were carried out in a standard 267 ml cell for 5 minutes at 1A cell current. The test results were utilized to optimize the plating conditions. Electrodeposition was carried out galvanostatically at 55<sup>0</sup>C under stirred conditions. The percentage of Zinc and Nickel content in the alloy deposit was determined by plating on the stainless steel cathode having the area 1 cm<sup>2</sup>. The panel so plated was weighed, then stripped in 20 per cent HNO<sub>3</sub> and made up to 100 ml in a standard flask. The zinc and nickel concentrations in the solution were determined by atomic absorption spectrometry.

During plating, deposition potentials were recorded with respect to saturated calomel electrode using scanning potentiostat (model CL-95, Elico, India). The cathodic current efficiencies (CCE), deposition rates were calculated in the conventional manner. The thickness of the alloy deposit was determined by using Elicometer (model 256 FN, UK). The adhesion of Zn-Ni alloy deposits to the base metal (steel) was tested by standard bending test. The porosity of alloy deposit was determined by ferroxyl test., microhardness of the alloy deposits containing various nickel contents were determined on Vickers scale with a 50 g – load (Zwick 32122, Germany). Scanning electronic microscope (model JEOL-JSM, 840A) was used to examine the surface morphology of the alloy deposits coated on a polished copper substrate.



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

Bath composition	Range studied	Optimum composition and conditions
Total metal content	0.2 M	0.2 M
ZnSO <sub>4</sub> . 7 H <sub>2</sub> O	0.192-0.198 M	0.196 M
NiSO <sub>4</sub> . 7 H <sub>2</sub> O	0.002-0.008 M	0.004 M
TEA	10-60 ml/l	40 ml/l
MPY	0.0025-0.04 M	0.01 M
Na <sub>2</sub> SO <sub>4</sub>	20-100 g/l	50 g/l
NaOH	20-160 g/l	100 g/l
Saccharin	1-8 g/l	2 g/l
pH	-	> 14
Current density	5-35 Adm <sup>-2</sup>	15 Adm <sup>-2</sup>
Temperature	25-75 °C	55 °C
Agitation	-	Normal

## Results and discussion

### Effect of metal ion ratio

In order study the zinc to nickel ratio in the plating bath on alloy composition, zinc to iron ratio in the bath was varied from 96.4 to 99.5 at 55<sup>0</sup> C, constant thickness ~ 4 µm for three different current densities (10, 20 and 35 mA/cm<sup>2</sup>). Figure 1 shows 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 with less nickel content (12.4 per cent) indicating that more noble metal (nickel) depositing preferentially, that is 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 deposition is of regular type with nickel as the more noble metal.

### Effect of current density

The effect of current density on alloy composition was studied by carrying out the experiments at various current densities (10-35 mA/cm<sup>2</sup>) at 55<sup>0</sup>C, thickness ~ 4 μm, pH > 14 under stirred conditions. Figure 2 illustrates the dependency of the alloy composition on current density from the baths containing various zinc to nickel 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<sup>2</sup>), 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.

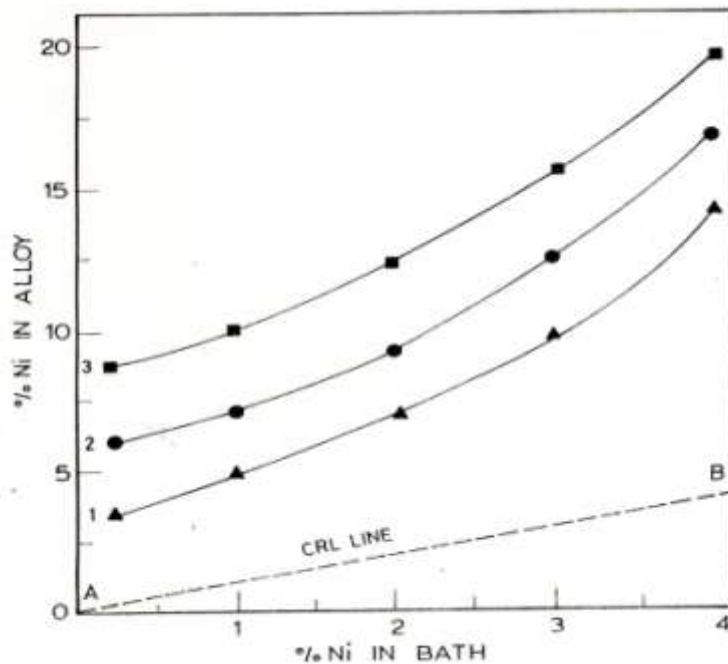


Figure 1. Dependence of alloy composition on bath composition

Bath composition: Total metal 0.2 M, [Zn<sup>2+</sup>] 0.192 to 0.198 M, [Ni<sup>2+</sup>] 0.002 -08 M, TEA 40 ml/L, MPY 0.01 M, Na<sub>2</sub>SO<sub>4</sub> 50 g / L, NaOH 100 g / L, Saccharin 2 g / L, temperature 55<sup>0</sup>C current density 10-35 mA / cm<sup>2</sup>, thickness ~ 2 μm, pH > 14, stirred condition.

Curve 1.35 mA / cm<sup>2</sup>    Curve 2.20 mA / cm<sup>2</sup>    Curve 3. 10 mA / cm<sup>2</sup>

### Effect of temperature

In order to know the effect of temperature on the composition of Zn-Ni alloy, experiments were carried out at various temperature (25-75<sup>0</sup>C) at 15 mA/cm<sup>2</sup>, thickness ~4 $\mu$ m under stirred conditions from the baths containing different zinc to nickel ion ratio. 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.

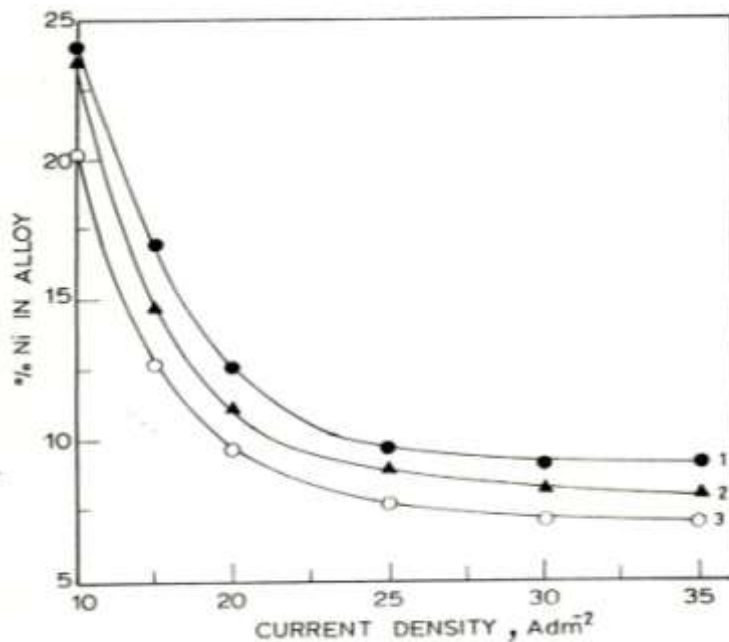


Figure 2. Variation of alloy composition with current density

Bath composition: Total metal 0.2 M, [Zn<sup>2+</sup>] 0.194-0.198 M, [Ni<sup>2+</sup>] 0.002-0.006 M, TEA 40 ml/L, MPY 0.01 M, Na<sub>2</sub>SO<sub>4</sub> 50 g / L, NaOH 100 g / L, Saccharin 2 g / L, temperature 55<sup>0</sup>C current density 10-35 mA / cm<sup>2</sup>, thickness ~ 2  $\mu$ m, pH > 14, stirred condition.

Curve 1. 97:3 Zn: Ni Curve 2. 98:2 Zn: Ni Curve 3. 99:1 Zn: Ni



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

Temperature ( <sup>0</sup> 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	

Bath composition: Total metal 0.2 M,  $[Zn^{2+}]$  0.194-0.198 M,  $[Co^{2+}]$  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, current density 15 mA /  $cm^2$ , pH > 14, thickness ~ 2  $\mu m$ , stirred condition.

#### Effect of triethanolamine (TEA) and mercaptopyridine (MPY)

Triethanolamine (TEA) was found to be suitable complexing agent for zinc and nickel, experiments were conducted at 15mA/ $cm^2$ , 55 <sup>0</sup>C, pH > 14, thickness ~ 4  $\mu m$  from the baths containing various concentrations of TEA and MPY. Figure 3 shows the dependence of alloy composition with the concentrations of TEA and MPY. 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. In the case of MPY, with an increase in its concentration, the percentage of nickel in the alloy deposit increases to a steady value at higher concentration.

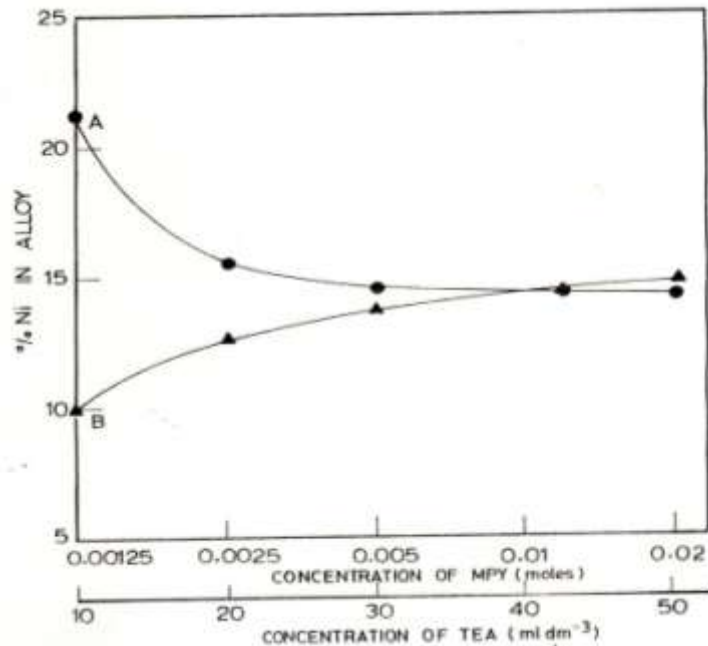


Figure 3. Variation of the % of Nickel in the Zn-Ni alloy deposits with the concentrations of TEA and MPY in the plating bath

Bath composition: Total metal 0.2 M,  $[Zn^{2+}]$  0.194M,  $[Ni^{2+}]$  0.004M, TEA 10-50 ml/L, MPY 0.00625-0.02 M,  $Na_2SO_4$  50 g / L, NaOH 100 g / L, Saccharin 2 g / L, temperature 55<sup>0</sup>C, current density 15 mA / cm<sup>2</sup>, thickness ~ 2  $\mu$ m, pH > 14, stirred condition.

### Effect of thickness

The dependence of alloy composition with the deposit thickness is shown in figure 4. Increase in the thickness of the alloy deposit increased the percentage of nickel in the alloy deposit.

### Cathodic current efficiency (CCE)

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 figure 5. With an increase in current density, the CCE was found to decrease, Stirring and increase in bath temperature increased the CCE.

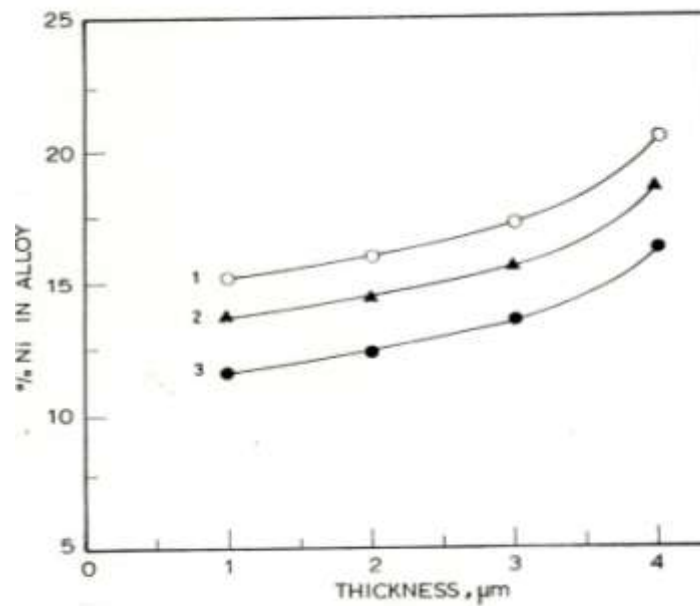


Figure 4. Dependence of alloy composition on thickness of the alloy deposit.

Bath composition: Same as in figure 2, current density 15 mA / cm<sup>2</sup>, thickness ~ 1-4 μm,

Curve 1. 97:3 Zn: Ni, Curve 2. 98:2 Zn: Ni, Curve 3. 99:1 Zn: Ni

### Cathodic polarization characteristics

Figure 6 shows the polarization characteristics of zinc, nickel and zinc-nickel alloy deposition. Curve 1 represents the deposition of nickel alone at a potential of about -0.90 V, curve 2 corresponds to zinc deposition alone, the deposition potential being -1.55 V and curve 3 is for Zn-Ni alloy deposition. The deposition was intermediate between nickel and zinc (-1.10 V) which is less noble to nickel and more noble to zinc. This current density – potential characteristics for Zn-Ni alloy deposition clearly shows the cause for regular type of co-deposition.



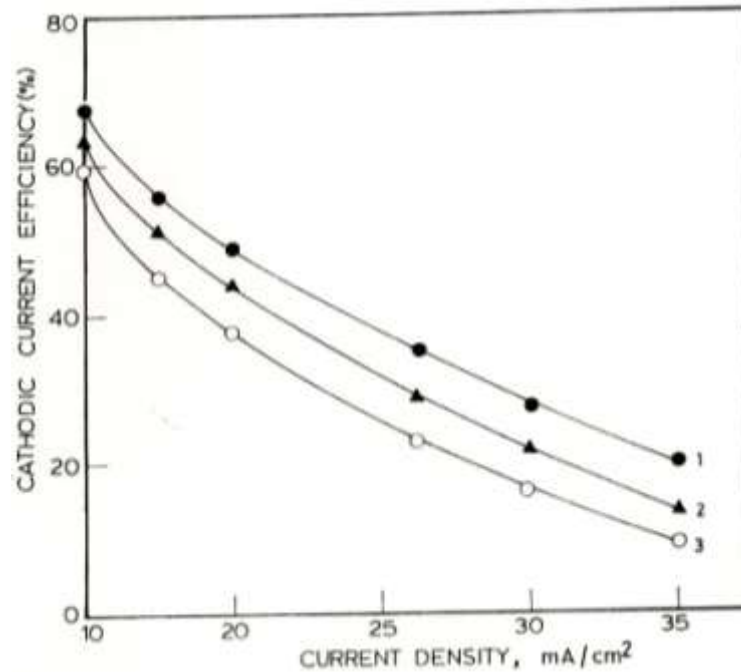


Figure 5. Dependency of cathodic current efficiency on the current density

Bath composition: Same as in figure 2

Curve 1. 97:3 Zn: Ni    Curve 2. 989:2 Zn: Ni    Curve 3. 99:1 Zn: Ni

## Properties and morphology

The adhesion of the Zn-Ni alloy deposit to the base metal (steel) was tested by a standard bending test. Zn-Ni alloy samples coated to different thickness (2-6  $\mu\text{m}$ ) on steel (1  $\times$  4 sq. inch) were subjected to bending test. The alloy coating did not develop any visual cracks even after 180<sup>o</sup> bending. This shows a good adhesion of the alloy deposit to the base metal.

Porosity tests were conducted on Zn-Ni alloy coated on steel (3  $\times$  3 Sq. inch) to a thickness of 2-6 $\mu\text{m}$ . A filter paper soaked in 1%  $\text{K}_4\text{Fe}(\text{CN})_6$  solution placed on alloy coated steel panels. Appearance of blue spots on the filter paper with time was observed. The number of blue spots appearing on the filter paper with time is a measure of porosity of the deposit. The alloy deposits were pore free at sufficient thickness (> 4  $\mu\text{m}$ ).

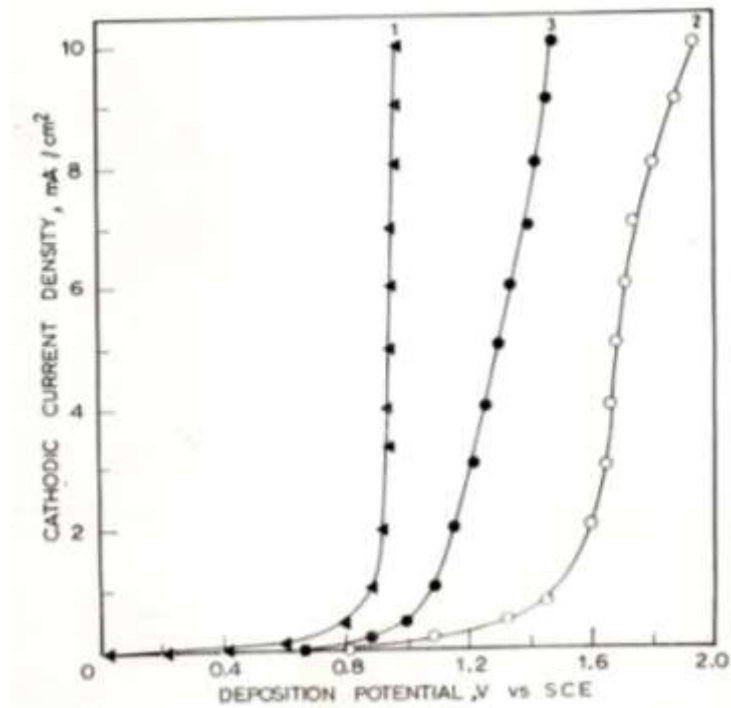


Figure 6. Cathodic polarization curves for the deposition of Zinc, Nickel and Zn-Ni alloy from an alkaline sulphate bath. All solutions contained triethanolamine 40 ml/L, mercaptopyridine 0.01 M,  $\text{Na}_2\text{SO}_4$  50 g/L, Saccharin 2 g/L, temperature  $55^\circ\text{C}$  Stirred condition. Curve 1. Deposition of Nickel alone, Curve 2. Deposition of Zinc alone, Curve 3. Deposition of Zinc-Nickel alloy. The bath solution contained the same concentration of Nickel and Zinc as those in the individual baths.

Microhardness of  $6\ \mu\text{m}$  thick Zn-Ni alloy specimens was determined on Vickers scale (load-50 gm). Hardness of the alloy deposit increased with an increase in the percentage of nickel in Zn-Ni alloy deposit (Table 3).

The static potentials of Zinc and Zinc-Nickel alloys were measured in 3.5% NaCl solution with respect to SCE. Table III lists the static potential values for zinc and Zn-Ni alloy. Static potentials of Zn-Ni alloys were found to be nobler than zinc, indicating corrosion-resistant characteristics.

The surface morphology of Zn-Ni alloy deposits containing different percentages of nickel were examined under scanning electron microscope. The morphology of the alloy deposits is shown in Figure 7.

Table 3: Effect of percentage of Nickel on hardness of Zn-Ni alloy and static potential values

%Ni in Zn-Ni alloy	Hardness in V.H.N. (load – 50 gm)	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

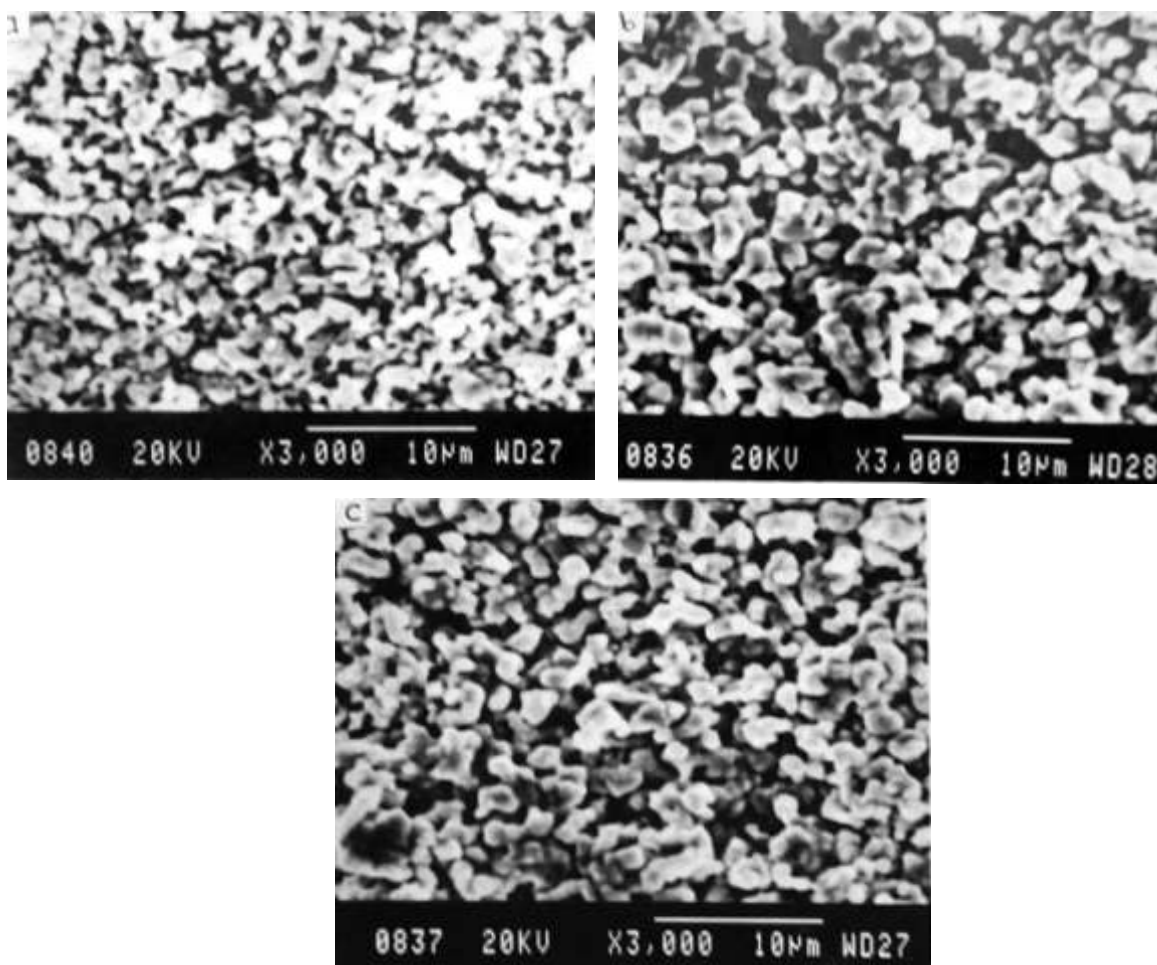


Figure 7. Scanning electron microscopy of Zn-Ni alloy deposits containing TEA and MPY (X3500) a) 10% Ni b) 15% Ni c) 20 %Ni



## Conclusion

Zn-Ni alloy containing 10-15% Ni, electrodeposited from an alkaline sulphate bath containing TEA and MPY is of regular type of co-deposition. The potential of Zn-Ni alloy deposition lies in between those of individual metals. The nickel content in the alloy deposit decreased with current density and increased with elevation in bath temperature, stirring of the bath solution and with thickness of the alloy deposit. Hardness of the alloy deposit was found to depend on nickel content of the alloy deposit. Fine grained deposits were observed morphologically.

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## References

- [1] Ramesh S. Bhat & Vinayak B. Shet, Development and characterization of Zn-Ni, Zn-Co and Zn-Ni-Co coatings, *Surface Engineering*, 6(4) (2020) 429-437.
- [2] N. Lotfi, M. Aliofkhaeizadeh, H. Rahmani, G. Barati Darband, Zinc-Nickel alloy electrodeposition: characterization, properties, multilayer's and composites, *Prot. Metals & Phy. Chem. Surf*, 54 (2018) 1102-1140.
- [3] S. Rajendran, S. Bharathi, T. Vasudevan, Electrodeposition of Zinc-Nickel alloy from a cyanide-free alkaline plating bath, *Trans. IMF*, 78(3) (2017) 129-133.
- [4] S. Mohan, V. Ravindran, B. Subramanian, G. Saravanan, Electrodeposition of zinc-nickel alloy by pulse plating using non-cyanide bath, *Trans. IMF*, 87(2) (2013) 85-89.
- [5] Satoru Ando, Electrodeposition behavior of Zn-Ni alloys produced from sulfate solutions at high current densities, *Mat. Trans*, 57(11) ((2016) 1908-1914.
- [6] Zhongbao Feng, Qingyang Li, Jinqiu Zhang, Peixia Yang, and Maozhong Anz, Electrochemical Behaviors and Properties of Zn-Ni Alloys Obtained from alkaline non-cyanide bath using 5, 5'-dimethylhydantoin as complexing agent, *J. Elect. Soc*, 162 (9) (2015) 412-422.



- [7] Roventi, electrodeposition of nickel-zinc alloy from a sulfamate bath, *Advan.Mats*,4 (2015) 21-26.
- [8] R. Katurcı, Effects of ZnO and NaOH in Zn–Ni bath, *Surf.Eng*, 31 (2015) 11-16.
- [9] K. O. Nayana,T. V. Venkatesha, Effect of ethyl vanillin on Zn-Ni alloy electrodeposition and its properties, *Bull. Mater. Sci*,37(5) (2014)1137–1146.
- [10] S.H.MosavatM.E.BahrololoomM.H.Shariat, Electrodeposition of nanocrystalline Zn–Ni alloy from alkaline glycinate bath containing saccharin as additive, *App.Surf.Sci*,257(20) (2011) 8311-8316.
- [11] Yogesha. S, Hegde.A.C,Optimization of bright zinc-nickel alloy bath for better corrosion resistance, *Trans. Inst. Met*, 63 (2010) 841–846.
- [12] L.S.Tsybulskaya,T.V.Gaevskaya,O.G.Purovskaya,Electrochemical deposition of zinc–nickel alloy coatings in a polyligand alkaline bath, *Sur.Coat.Tech*,203(2008)234-239.
- [13] M.G Hosseini, H. Ashassi-Sorkhabi and H.A.Y. Ghiasvand,Study of corrosion performance of electrodeposited nanocrystalline Zn–Ni alloy coatings,*Sur.Coat.Tech*, 59 (2012) 81-87.
- [14] S. Shanmugasigamani and M. Pushpavanam, Nanocrystalline zinc–nickel alloy deposition using pulse electrodeposition (PED) technique, *Trans.IMF*,86(2) (2008) 122-128.
- [15] V. Ravindran,V.S. Muralidharan, zinc-nickel alloy electrodeposition – influence of triethanolamine, *Port.Elect.Acta*, 25 (2007)391-399.
- [16] M. M. Abou-Krishna, F. H. Assaf & A. A. Toghan, Electrodeposition of Zn-Ni alloy from an acid sulfate bath, *J.Sol.Stat.Elect*,11 (2007) 244–252.