A NONCYANIDE ALKALINE BATH FOR ZINC-NICKEL ALLOY DEPOSITION

Shanmugasigamani and Malathy Pushpavanam
Central Electrochemical Research Institute, Karaikudi-630 006, India.
E-mail : malathypush@yahoo.com

ABSTRACT

Zinc-nickel alloy has been proven as a highly corrosion resistant coating meant especially for automotive applications. The acid baths have the drawback of poor throwing power and high composition dispersion. On complicated structures, this property not only results in variation in appearance but also, ends up with setting up of local cells within the deposit itself due to variation in composition leading to lower service life than expected. So, these baths are mainly preferred for plating uncomplicated structures. The alkaline baths on the other hand, obviate the above problems, yielding deposits with uniform appearance and composition throughout the component. Due to the environmental and operational hazards posed by the conventional cyanide baths, non-cyanide baths are highly recommended and are in commercial practice abroad.

This paper deals with our experience with a non-cyanide alkaline bath for depositing smooth deposits. Special addition agent has also been identified to function as a brightener. The effect of parametric variables on the composition, current efficiency and throwing power of the deposits are dealt with.

Keywords: Alloy deposition, Hull cell experiment, throwing power, cathode efficiency, polarization, additives

INTRODUCTION

In recent years, great interest has been shown in the possibilities offered by the electro-deposition of alloys, mainly in the automotive industry. Usually the mechanical and chemical properties of metals are improved by alloying. In particular, it is known that the mechanical properties of zinc electrodeposits can be improved by alloying zinc with nickel [1,2]. Using ZnNi alloy deposits on iron also increases their corrosion resistance [3-8].

The electro-deposition of Zn-Ni alloys is classified by Brenner [9] as an anomalous co-deposition, where zinc, which is the less noble metal, is preferentially deposited. Although this phenomenon [10] has been known since 1907, the co-deposition mechanisms of zinc and nickel are not well understood [11,12]. Many studies have attempted to understand the characteristics of the deposition process [13-16]. Most of the studies are based on acid baths. The alkaline baths are development in the effort to produce non-toxic cyanide-free zinc electrolyte. Initially these baths were considered as able only to give spongy or powdery deposits and presence of additives was felt essential.

In comparison with cyanide systems, non-cyanide alkaline zinc baths have a narrower range of optimum operating zinc concentration. For instance, if the zinc metal content is around 7.5 g/L at 3 A.dm^{-2}, a bright deposit is obtained at 80 % current efficiency. However, at 5.3 g/L zinc, at the same current density, the current efficiency is already lower than

60%. Still, raising the zinc content above 17 g/L will result in dull gray deposits. Also increasing sodium hydroxide concentration increases current efficiency but causes metal buildup on sharp cornered edges. Of course additives are essential. In the first commercial alkaline non-cyanide zinc baths, it was necessary to replace the complexing effect of cyanide ions by other complexing agents like EDTA, gluconate, tartrate and triethanolamine. However, this created new effluent problems (e.g., EDTA can prevent precipitations of zinc following pH adjustments and can also delay precipitation of other metals in mixed effluents). This approach has fallen out of use, and the alkaline non-cyanide zinc baths may now be considered as zincate baths.

Experimental Techniques

Laboratory grade chemicals were used. Zinc-nickel alloy plating electrolytes of the following composition were used. The compositions and their operating conditions remain the same unless otherwise specified.

Bath composition:

ZnO	9-12g/L
NaOH	75-120 g/L
Complexant	40-120mL/L
Ni as sulphate	1-2.5 g/L
Temperature	30-60°C
Operating Conditions:	
pH	13
Current densityl	1-5 A/dm^2

The electrolytes prepared were given zinc dust pretreatment to get rid of the metallic impurities. The zinc electrolyte was treated with 3 g/L of zinc dust at pH 3 for nearly 4 hours with constant stirring. This treatment helps in removal of impurities like copper, more noble than zinc in the electrochemical series The solution was then filtered and electrolyzed at a very low current density of 0 3 A/dm^2 with steel cathode and zinc anode for a period of 2 hours to remove the other.metallic impurities also. The solution was filtered and made up to the volume. The pH of the electrolyte was corrected to the required value by using a pH meter.

The zinc-nickel solution was given only low current density electrolysis as mentioned above using zinc anodes. The solution was then filtered, made up and the pH corrected electrometrically.

For alloy plating, the above two electrolytes prepared as stock solutions with the required amount of constituents, in the same manner mentioned above, were mixed in the desired proportion and pH was then corrected electrometrically.

Pure zinc anodes of 99.9% purity were used for deposition. Stirring during deposition was effected using a magnetic stirrer and the electrolyte temperature was maintained using a water bath.

Mild steel cathodes of 2.5 x 2.5 cm^2 area were mechanically polished and degreased with trichloroethylene. The unwanted portions were suitably masked so as to exposure an area of 6.25 cm^2. The electrodes were then electrolytically cleaned in a solution containing

Sodium hydroxide	30 g/L
Sodium carbonate	30 g/L

for 3 minutes, washed, rinsed and introduced into the plating electrolyte. Experiments were conducted by varying the nickel content, metal ion ratio, complexant, carrier additive and the brightener

Hull Cell Studies:

Hull cell studies were made using a 267 mL cell at current I= 1 A and duration t=10 min.[10]. Suitably pretreated mild steel cathode panels and plating grade zinc anodes were used. The operating current density range were brightness of the deposits etc. was taken as the main criteria for optimizing the conditions using Hull cell studies. Thickness on the Hull cell patterns was measured using X-ray fluorescence spectroscopy (XRF, CMI, XRX series USA) after dividing the panel into five equal segments to determine the throwing power.

Cathode Current Efficiency:

In the case of alloy deposition, the cathode current efficiency was calculated using the following formula

$$\text{Cathode efficiency} = \frac{P_1W}{Q_1It} + \frac{P_2W}{Q_2It} \quad \text{where}$$

P1 and P2 are the percentage metal content o: zinc and nickel respectively in the deposit, W is the weight of alloy deposited, Q1 and Q_2 are the electrochemical equivalents of zinc and nickel respectively. It is the total coulombs passed for depositing the alloy.

From the total mass of deposit obtained. the rate of deposition of the deposits per unit time and the thickness of the deposit were calculated knowing the density of the deposits. Experiments were conducted by varying the concentration of bath constituents and the operating conditions.

Throwing Power:

The most generally used cell to determine throwing power of an electrolyte is that of Harning and Blum. This is a rectangular container with two cathodes of sheet metal of equal area, which fill the entire cross section of the cell. A perforated anode is placed at a distance from one cathode which is five times as great as that from the other cathode. With this geometrical arrangement, five times as much metal should be deposited on the nearer than on the remoter cathode because the electrolyte resistances in the two sections are 1:5. This ratio is modified by the polarization and the possible difference in current efficiency. The throwing power S is calculated by means, of the formula

$$S = \frac{K - M_n/M_f}{5\, M_n/M_f \;-2} \times 100$$

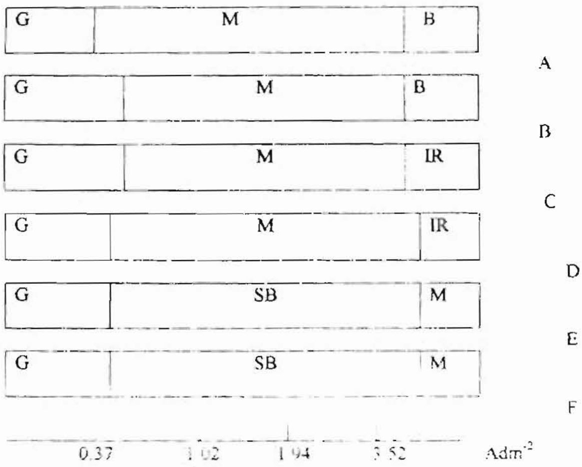

Fig. 1 - Hull patterns showing the effect of Nickel concentrations. Ni g/L; (A) 2 (B)3 (C)4 (D)5 (E)7 (F)10.

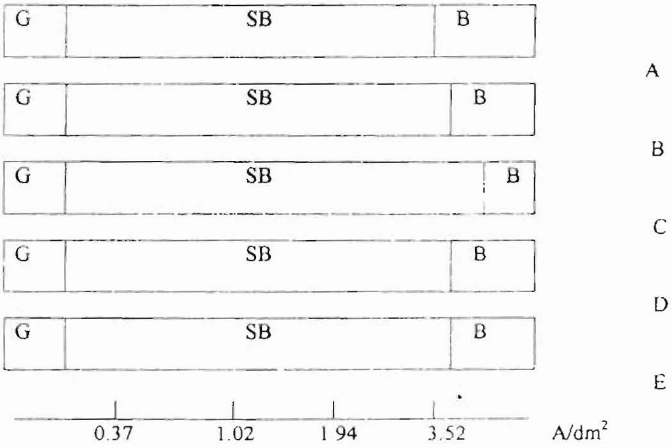

Fig. 2 - Hull patterns showing the effect of PVA concentrations at 7.5 g/L Ni. PVA g/L; (A)2 (B) 2.2 (C) 2.4 (D) 2.6 (E) 2.8

Galvanostatic Polarisation Studies :

The effect of different additives or. the cathode polarization was galvanostatically evaluated using a steel cathode, platinum anode and a saturated calomel (SCE) reference electrode [16] in a three-necked H-type cell. Constant current was applied in small increments using a controlled power supply unit and corresponding potentials were recorded after giving sufficient time to reach the steady state.

Results And Discussion

The above alkaline non-cyanide zinc bath was selected for depositing zinc-nickel alloy and was found to yield deposits with the required nickel content. Being an alkaline bath, a suitable complexing additive becomes essential in order to solublise nickel in the bath.

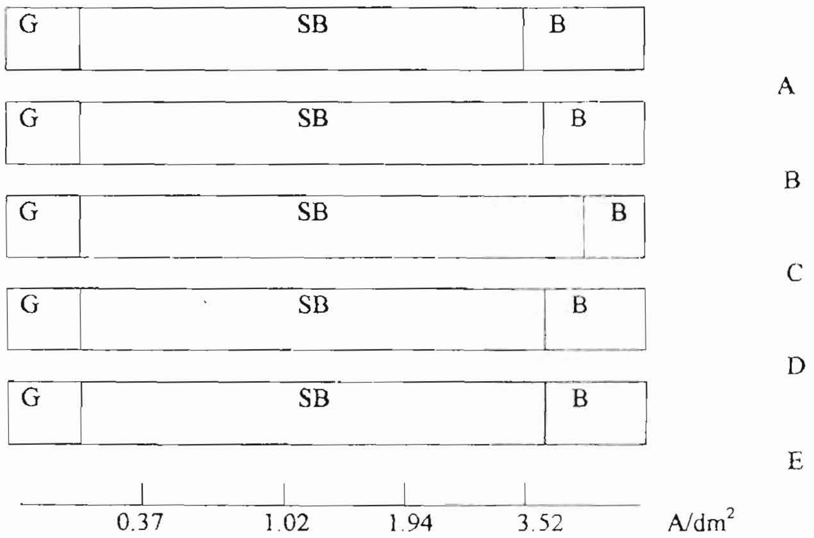

Fig. 3 - Hull patterns showing the effect of PIP concentration with PVA at 7.5 g/L Ni. Concentrations of PIP g/L; (A) 4 (B) 6 (C) 8 (D) 1 (E) 1.2

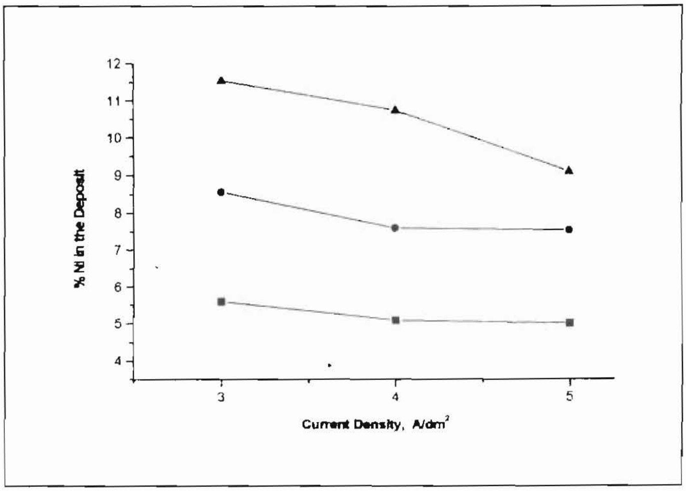

Fig. 4 - Effect of curent density on the nickel percent in the deposit; Nickel content in the bath g/L: (■) 4 (●) 5 (▼) 7.5

Triethanoamine has been already reported to be the best complexing additive in our previous work on zinc-cobalt alloy deposition. However, in order to get the high corrosion resistance claimed, the required nickel content of the deposit needs to be more than an order of magnitude higher than the cobalt content of the zinc-cobalt deposit. Hence, the nickel content in the solution also must be higher and the amount of complexant needed to complex nickel should also be higher. The operating conditions for this bath need optimization to produce the alloy with the desired composition along with good appearance.

As discussed above, deposition from an alkaline non-cyanide bath can yield only mossy non-coherent deposits due to the fast reaction kinetics. Addition of polyvinyl alcohol is widely used as a primary additive to get over this problem However, the optimum concentrations of the primary and the secondary additive need to be suitably modified in

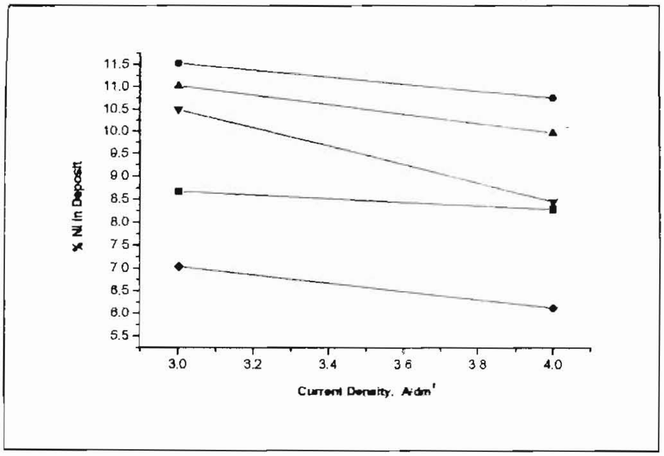

Fig. 5 - Effect of current density on the nickel percent in the deposit at different complexant concentrations, ml/L; (■) 1.5 (●) 2.5 (▲) 3 (▼) 3.5 (◆) 4

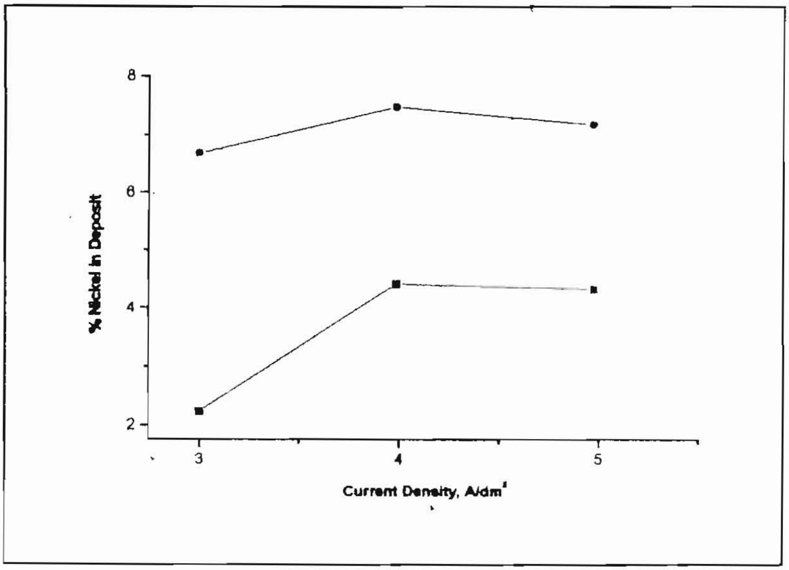

Fig. 6 - Effect of current density on the nickel percent in the deposit in presence of additives, Bath containing nickel g/L : (■) 4; (●) 5 Ni

order to get bright alloy deposit containing 10- 12% nickel from this bath.

The bath optimization was done initially with Hull cell experiments. Figs. 1-3 show Hull cell patterns of the alloy deposits from solution containing varying nickel contents and having, 85 ml/L of complexing additive and 2.g/L of PVA. Solutions with lower amounts of complexants were highly unstable and nickel started precipitating either during deposition or on storage indicating that nickel complexation is incomplete. Still higher amounts led to cessation of deposition.

The deposits obtained were matt gray in appearance up to 5.5g/L nickel in solution and above 7.5 g/L they were semi-bright (Fig.1). The operating current density was identified as 0.54A/ dm^2.

Fig.2 shows the effect of PVA concentration on the nature of deposits. As the concentration

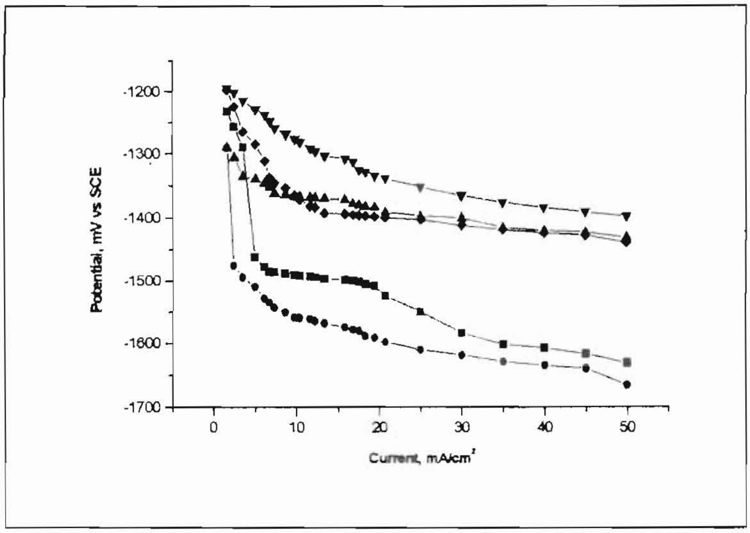

Fig. 7 - Polarization curves for zinc, and zinc- nickel alloy deposition (■) plain zinc bath (●) zinc+PVA (▼) zinc + PVA + 5g/LNi (▼) zinc+PVA + 7.5g/LNi (◆) zinc + PVA + 7.5g/LNi+PIP

of PVA increased from 2 to 2.6 g/L. the operating current density extended from 3.5 A/dm^2 - 4.2 A/dm^2 and further increase in its, concentration, decreased the range. As shown in Fig.3, piperonal (PZP) works synergistically in presence of PVA to produce bright deposits. The semi brightness became mirror bright when the concentration of PIP was increased from 0.4 to 1 g/L associated with broadening of the operation current density However, further increase caused reduction in the current density range though the brightness was retained.

Deposits obtained on 6.25 cm^2 panels are examined for their nickel content using XRF Fig.4 shows that the nickel content increased marginally with increase in its concentration in the solution. But, the percent nickel is nearly 10% or that present in the solution. The figure also shows that with increase in current density at all concentrations tried, the nickel content showed a slight decrease.

Fig. 5 shows the effect of complexing agent on the nickel content of the alloy deposit. Increasing complexant addition reduces nickel content of the deposit indicating that nickel

Table 1 - Effect of Bath Operating Temperature on the Nickel Content of the Deposit

Ni content in the bath	Current Density	Ni in deposit (%)	
(g/1)	(A/dm2)	30°C	60°C
5	3	8.57	9.1
5	4	7.61	8.45
7.5	3	11.SS	17.9
7.5	4	10.75	-15.22

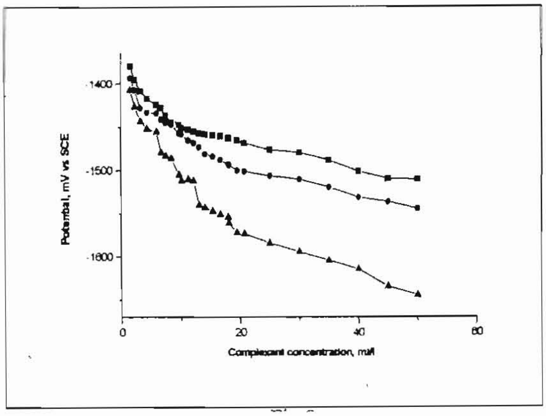

Fig. 8 - Polarization curves for zinc - nickel alloy deposition in presence of complexant 7.5 g/L Ni + TEA Concn. mL/L: (■) 1 (●) 1.6 (▲) 2.6

Table 2 - Effect Of Stirring on the Nickel Content of the Deposit

Ni Content in the bath (g/L)	Current Density (A/dm²)	Ni in deposit (%)	
		without strirring	With strirring
5.0	3.0	8.57	4.78
5.0	4.0	7.61	5.0
7.5	3.0	11.55	8.60
7.5	4.0	10.75	7.24

Table 3 - Throwing Power of Alloy Plating

Ni Content in the bath (g/L)	Throwing Power (%)	
	3 A/dm²	4 A/dm²
5.0	70.40	51.50
7.5	73.90	57.90

becomes more strongly bound to the complexant as its concentration increases. Fig 6 shows that in presence of additives the nickel content generally decreases but with increase in current density from 3-4 A/dm² shows a sight increase.

Table 1-2 shows the effect of increasing the bath operating temperature and solution stirring on the nickel content of the alloy deposit and the cathode efficiency. Table 3 shows the throwing power values obtained for alloy deposition. It is observed that throwing power decreases with current density and increases with increase in nickel content of the bath. The cathode efficiency for the alloy deposition was found to vary from 45-64% depending on the alloy composition.
From the cathodic polarization curves shown in Figure 7, it is observed that the deposition of Zn starts at about -1.4 V vs. SCE and presence of PVA increases it to -1.45 V due to complexation, which helps in reducing the fast reaction kinetics. Also, the polarization

curve of the alloy deposition lies between the polarization curves for the deposition of Zn and Ni. The deposition of Zn take place with higher nucleation over potential and grows at high potential. The Zn-Ni co-deposited at moderate overpotential; the deposition of Ni is strongly inhibited by the presence of Zn. while the deposition of Zn is induced by the presence of Ni^{2+}.

Addition of 4 g/L nickel in the form of its complex shows a tremendous shift in the deposition potential towards positive potentials of around 1.25V and with 7.5 g/L addition it reaches -1.15. It indicates that with increasing addition of nickel, the polarization curves get shifted more towards that of nickel indicating increased nickel co-deposition.. The negative shift noticed in presence of the piperonal is due to the specific adsorption of the additive on the electrode surface influencing the grain structure and appearance.

Fig. 8 shows the effect of increasing the TEA concentration on the polarization behaviour of the alloy deposition. With increasing concentration, the curves shift towards negative potentials enabling more of zinc co-deposition since nickel ions are strongly bound by the complexing agent.

CONCLUSION

A non-cyanide alkaline bright zinc-nickel alloy deposit formulation has been developed to produce deposits similar to those from cyanide baths with respect to brightness and throwing power. The new bath also has the additional advantage of being eco-friendly in that it uses only easily disposable organics.

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