

Bright zinc–nickel alloy deposition from alkaline non-cyanide bath

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Zinc–nickel alloy deposition with polyvinyl alcohol and piperonal as bath additives has been investigated. The effects of additive concentration, triethanolamine concentration and other parametric variables on the deposit and solution properties have been studied. Polarisation studies were carried out under different conditions to understand the effect of triethanolamine and the brighteners on the co-deposition. Results indicated that the additives lead to bright alloy deposition containing ~10% nickel. The deposit produced at the optimum conditions with the additives has a nanograined structure with a γ phase.

Keywords: Addition agent, Bright zinc–nickel alloy deposit, Zincate bath, Polarisation, Throwing power, Structural examination

Introduction

Zinc–nickel alloy coatings have attracted much attention because of their higher corrosion resistance and better mechanical properties in comparison with zinc and other zinc alloy coatings.^{1–15} Zn–Ni deposits provide improved corrosion protection for steels in relatively aggressive environments. It has been found that the maximum protection is obtained with the nickel content between 12 and 15%.^{1–17} Recently, several new technologies for Zn–Ni alloy have been developed and further researches for better coating and characteristics are of commercial interest.^{18–24} The processes of Zn–Ni alloy deposition can be divided into two types: acid type and alkaline type.^{25–29} The nickel content of the deposits plated from the acid bath is more sensitive to variation of cathode current density. For this reason, acid Zn–Ni coatings are recommended only for steel parts of simple shape and their industrial applications are limited. In contrast, alkaline baths can give more uniform nickel content in the coatings even on intricate shaped components. In addition, the alkaline process has several other advantages over the acid process such as less corrosion of equipment and lower production cost.^{30–32}

According to Brenner,³³ Zn–Ni deposition belongs to the anomalous type, which has been proved by Ohtsuka and Komora³⁴, with an *in situ* ellipsometry method. Recently, Benballa *et al.* have reported on nanocrystalline Zn–Ni coatings obtained from the ammonium chloride baths.³⁵ Brooks and Erb³⁶ have obtained nanocrystalline Zn–Ni coatings from a chloride based electrolyte. Although work on alkaline Zn–Ni electroplating has been carried out,^{37–39} details on bright Zn–Ni deposition from alkaline baths are scarce.⁴⁰

In the authors' previous reports, deposition of bright zinc and zinc–cobalt alloy from an alkaline non-cyanide

formulation has been dealt with.^{41,42} The present work deals with the details on bright Zn–Ni alloy deposition using the same additives namely, polyvinyl alcohol (PVA) and piperonal (PIP). The basic alkaline bath contained zinc and nickel ions, sodium hydroxide and triethanolamine (TEA). The influence of additive concentrations, TEA concentration and operating variables on the composition, structure and morphology of the deposits has been investigated.

Experimental

The solutions were freshly prepared using doubly distilled water and Analar grade chemicals. A Zn–Ni alloy plating electrolyte of the following composition was used. The compositions and their operating conditions remain the same in all experiments unless otherwise specified. Bath compositions are: Zn as ZnO (Fischer), 7.2 g L⁻¹; NaOH (Fischer), 75–120 g L⁻¹; TEA (Merck), 40–20 mL L⁻¹; Ni as sulphate (Merck), 1–7.5 g L⁻¹. Operating conditions are: temperature, 303–333 K; pH 13; current density, 1–5 A dm⁻².

The zinc solution was prepared as a concentrate and given the appropriate pretreatments to get rid of the metallic impurities.⁴³ The zinc electrolyte was treated with 3 g L⁻¹ of zinc dust for nearly 4 h with constant stirring. This treatment displaces impurities like copper, and other metals more noble than zinc from the solution. The solution was then filtered and electrolysed at a very low current density of 0.3 A dm⁻² with a steel cathode and zinc anode for a period of 2 h to remove the other metallic impurities remaining. The solution was filtered and made up to the volume. Similarly, a stock solution of nickel was prepared. The required quantity of nickel solution was taken, mixed with the required quantity of the TEA, then mixed with the appropriate quantity of zinc solution and suitably diluted. The pH of the electrolyte was corrected to 13 with dilute sulphuric acid, measured with a pH meter (Systronix, Model 361).

Pure zinc anodes of 99.99% purity (Aldrich) were used for deposition. The solution was stirred using a magnetic

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stirrer and the electrolyte temperature was maintained using a constant temperature thermostat. The experiments were carried out for 15 min using 72 coulombs.

Cold rolled low carbon steel cathodes of dimensions 5×2.5 cm were mechanically polished in a buffing machine to a bright finish using successive grades of emery wheels, degreased with trichloroethylene, masked suitably to expose an area of 6.25 cm^2 , then electro-cleaned in a solution containing sodium hydroxide (35 g L^{-1}) and sodium carbonate (25 g L^{-1}) at 353 K for 3 min cathodically and 1 min anodically. The plates were then washed in running water followed by a dip in 5 vol.-% H_2SO_4 solution, washed, rinsed and introduced into the plating electrolyte. Experiments were conducted by varying nickel, TEA, PVA and PIP concentrations.

Hull cell studies were made using a 267 mL cell at current of 1 A, supplied by regulated power supply (Aplab, Model L3210), for 10 min. The operating current density range, composition of the alloy, brightness of the deposits, etc. were taken as the main criteria for optimising the conditions.

Composition analysis of the alloy deposits was made using X-ray fluorescence spectroscopy (XRF, CMI, XRX series, USA).

The cathode current efficiency (CCE) of the alloy deposition, was calculated using the formula

$$\text{Cathode efficiency} = \frac{P_1 W}{Q_1 It} + \frac{P_2 W}{Q_2 It}$$

where P_1 and P_2 are the percentage metal content of zinc and nickel respectively in the deposit, W is the weight of alloy deposited, Q_1 and Q_2 are the electrochemical equivalents of zinc and nickel respectively.³³ ' It ' is the total coulombs passed for depositing the alloy.

Throwing power of the solution was estimated using a Haring–Blum cell with a current distribution ratio of 5 using Field's formula⁴⁴

$$\% \text{ throwing power} = \frac{5 - MDR}{5 + MDR - 2} \times 100$$

where MDR is the ratio of the metal deposited in the near cathode to that in the far cathode.

The effect of addition of TEA, PVA and PIP on the cathode polarisation was evaluated galvanostatically using a steel cathode, platinum anode and a saturated calomel reference electrode (SCE) in a three necked H type cell. Constant current was applied in small increments using a constant current regulator unit (fabricated in the authors' laboratory) and corresponding potentials were recorded after giving sufficient time to reach the steady state.

Structural examination of the deposits was made using SEM (Model S3000H, Hitachi, Japan) and X-ray diffractometry (Panalitical, X'Pertpro, Netherland). The grain size was calculated from the XRD patterns using Scherrer's formula

$$D = \frac{0.99\lambda}{\beta \cos\theta}$$

where D is the grain size, β the broadening of the diffraction line measured at half of its maximum intensity in radians, θ the diffraction angle and λ the X-ray wavelength (1.5406 \AA) used.

Corrosion resistance of the deposits was assessed by potentiodynamic polarisation technique and impedance spectroscopy using an electrochem analyser (Model

IM6, Bioanalytical Systems, USA). A three necked cell of 250 mL capacity was used. The working electrode was electrodeposited zinc on steel with exposed area of 1 cm^2 with a platinum counter electrode and an SCE. A solution of 5% NaCl was used as the electrolyte. Corrosion tests were conducted at room temperature.

Potentiodynamic anodic polarisation tests were carried out at a scan rate of 1 mV s^{-1} . Potentials were scanned 200 mV from the open circuit potential (OCP) on both directions and the Tafel intercept was used to assess E_{Corr} and I_{Corr} values. Alternating current impedance measurements were made at the frequency range of 0.1 Hz to 20 kHz with 10 mV peak amplitude about the corrosion potential.

Results and discussion

The alkaline non-cyanide zinc bath reported earlier⁴¹ was found to yield alloy deposits with the required nickel content with the optimum addition of nickel ions. Being an alkaline bath, a suitable complexing agent becomes essential in order to maintain nickel in solution. Triethanolamine has been reported to be the best complexing agent for zinc–cobalt alloy deposition.^{8,37,41,42} However, in order to achieve maximum corrosion resistance, the nickel content of the deposit needs to be more than an order of magnitude higher (10–12%) than the cobalt content of the zinc–cobalt deposit (<1%). Hence, the nickel content in the solution and the complexant to keep it in solution must be correspondingly higher. The operating conditions of this bath need optimisation to produce the alloy of desired composition along with bright appearance.

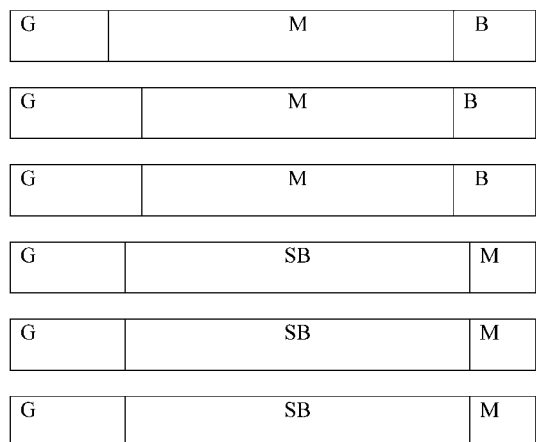
Deposition from an alkaline non-cyanide bath can yield only mossy non-coherent deposits due to the fast reaction kinetics.⁴¹ Addition of PVA is widely used as a primary additive to overcome this problem. Owing to the polarity of the carbon–oxygen bond, PVA forms a weak physical barrier at the cathode film that hinders zinc deposition. Also, the PVA chains can retain zinc hydroxyl anions and control the speed of the rate determining step. Addition of PVA enables grain refinement of the deposits but, at the same time, produces a yellow surface film. To obtain bright zinc deposits, additional organic brighteners are needed in addition to PVA. These organic brighteners are smaller molecules having unsaturated and polar characteristics by which they are attracted to the cathode by specific adsorption and influence deposition.

Piperonal has been identified as a suitable brightening additive in the authors' early reports.^{41,42} However, concentrations of the primary and the secondary additives need to be optimised in order to get bright alloy deposit containing 10–12% nickel.

Figure 1 shows the Hull cell patterns of the alloy deposited from solutions containing 7.2 g L^{-1} Zn, 75 g L^{-1} sodium hydroxide, 85 mL L^{-1} TEA and 2.6 g L^{-1} of PVA with varying nickel contents. The deposits obtained were matt grey in appearance with up to 4.0 g L^{-1} nickel in solution and with above 5.0 g L^{-1} they were semibright, probably indicating alloy formation. The operating current density range was identified as $0.5\text{--}4 \text{ A dm}^{-2}$.

As shown in Fig. 2, TEA addition has noticeable influence on the Hull cell patterns. Solutions with lower amounts of TEA (50 mL L^{-1}) were turbid initially and nickel started precipitating either during deposition or on

HULL CELL PATTERNS



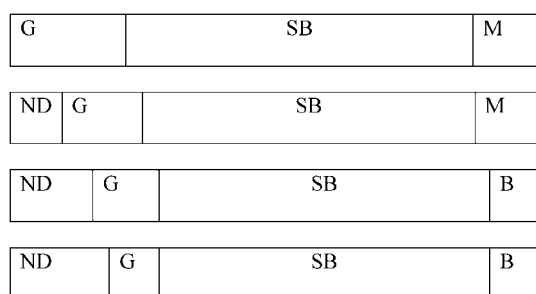
0.37 1.02 1.94 3.52 A dm⁻²
 a 2.0 g L⁻¹; b 3.0 g L⁻¹; c 4.0 g L⁻¹; d 5.0 g L⁻¹; e 7.0 g L⁻¹; f 10.0 g L⁻¹
1 Hull cell patterns showing effect of nickel concentration (solution contains 7.2 g L⁻¹ zinc, 75 g L⁻¹ NaOH (BE) and 85 mL L⁻¹ TEA): M – matte; B – black; G – grey; SB – semibright

storage indicating that its concentration is insufficient. Concentration in excess of 120 mL L⁻¹ reduced the operating current density and there was no deposition at the low current density range. The most suitable TEA/metal ratio is found to be 11.3–12.5.

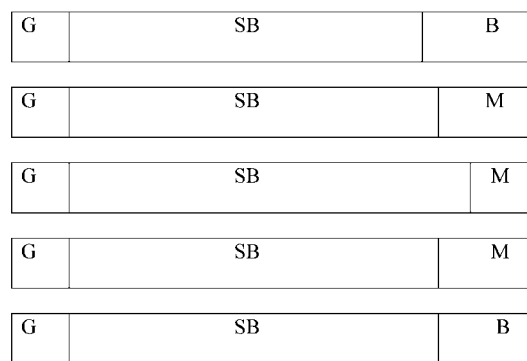
Figure 3 shows the effect of PVA concentration on the nature of deposits maintaining 7.2 g L⁻¹ Zn, 75 g L⁻¹ sodium hydroxide, 7.5 g L⁻¹ nickel and 85 mL L⁻¹ TEA in the solution. As the concentration of PVA increased from 2 to 2.4 g L⁻¹, the operating current density extended from 3.5 to 4.2 A dm⁻² while further increase in its concentration decreased the range.

Piperonal works synergistically in the presence of 2.4 g L⁻¹ PVA to produce bright deposits (Fig. 4). The semibrightness turned to mirror brightness when the concentration of PIP was increased from 0.4 to 1 g L⁻¹ associated with broadening of the operating current density. However, further increase caused reduction in the current density range as well as the finish.

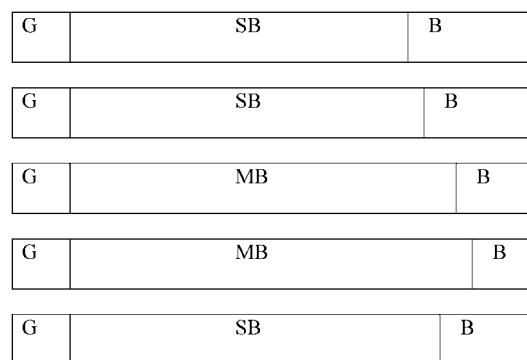
Figure 5 shows that the nickel content increased linearly with increase in its concentration in the solution.



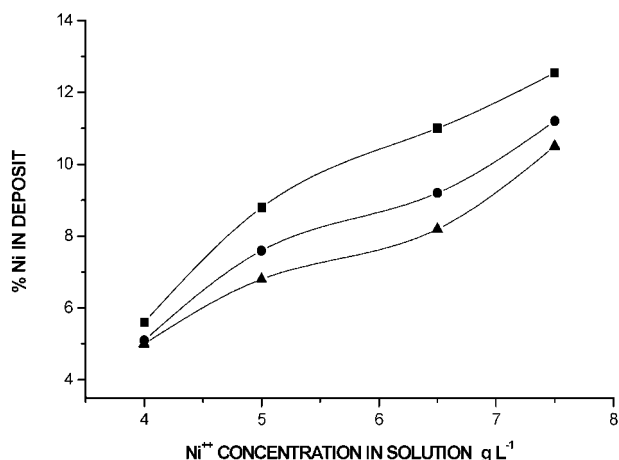
0.37 1.02 1.94 3.52 A dm⁻²
 a 85 mL L⁻¹; b 100 mL L⁻¹; c 120 mL L⁻¹; d 150 mL L⁻¹
2 Hull cell patterns showing effect of TEA concentration (solution contains BE and 7.5 g L⁻¹ Ni): M – matte; B – black; G – grey; SB – semibright; ND – no deposit



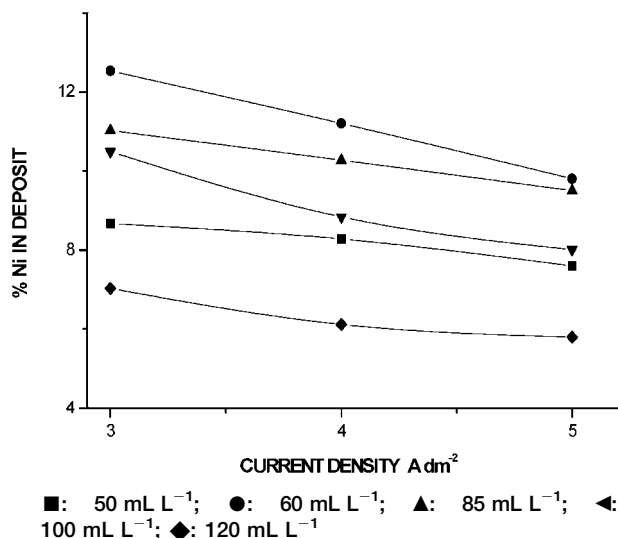
0.37 1.02 1.94 3.52 A dm⁻²
 a 2.0 g L⁻¹; b 2.2 g L⁻¹; c 2.4 g L⁻¹; d 2.6 g L⁻¹; e 2.8 g L⁻¹
3 Hull cell patterns showing effect of PVA concentration (solution contains BE, 85 mL L⁻¹ TEA and 7.5 g L⁻¹ Ni): M – matte; B – black; G – grey; SB – semibright



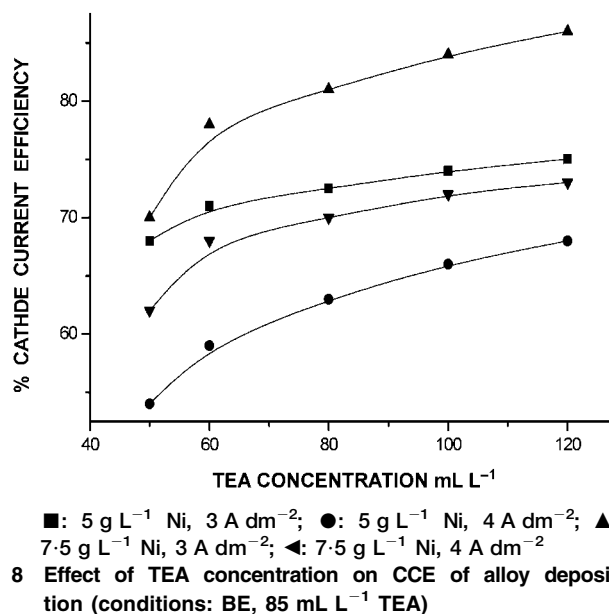
0.37 1.02 1.94 3.52 A dm⁻²
 a 0.4 g L⁻¹; b 0.6 g L⁻¹; c 0.8 g L⁻¹; d 1.0 g L⁻¹; e 1.2 g L⁻¹
4 Hull cell patterns showing effect of PIP concentration (solution contains BE, 85 mL L⁻¹ TEA, 7.5 g L⁻¹ Ni and 2.4 g L⁻¹ PVA): M – matte; B – black; G – grey; SB – semibright; MB – mirror bright



■: 3 A dm⁻²; ●: 4.0 A dm⁻²; ▲: 5 A dm⁻²
5 Effect of nickel concentration and current density on nickel percentage in deposit (solution contains BE and 85 mL L⁻¹ TEA)



6 Effect of current density on nickel percentage in deposit at different TEA concentration (solution contains BE and 7.5 g L⁻¹ Ni)



8 Effect of TEA concentration on CCE of alloy deposition (conditions: BE, 85 mL L⁻¹ TEA)

However, the nickel percent in the deposit is considerably less compared to its metal ratio in the solution confirming that the system follows the anomalous type of co-deposition. The figure also shows that the nickel content of the alloy is not significantly affected by increase in current density at all concentrations i.e. less composition dispersion.³³ This enables a uniform alloy composition even on a complex surface on which the current densities at different zones differ considerably. This feature provides a potential industrial application of the alkaline Zn-Ni electroplating. This cannot be expected from an acid solution where the variation of nickel content with current density is very high.⁴⁰

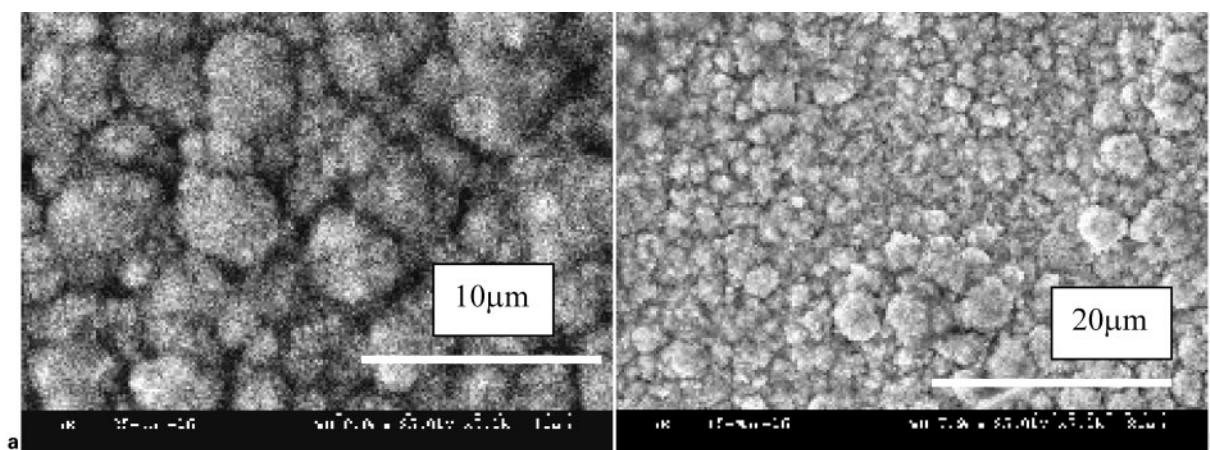
Similar behaviour is also observed in Fig. 6 where the effect of TEA concentration on the alloy composition is shown at different current densities. With 7.5 g L⁻¹ of nickel in solution, 50 mL L⁻¹ of TEA is insufficient to complex the metal completely. This results in slow precipitation of nickel resulting in less incorporation in the deposit. Increasing TEA content to 85 mL L⁻¹ forms a stable complex and so the nickel content in the deposit increases but, with excess addition, nickel ions are tightly bound to the complex making reduction of metal difficult.

Scanning electron microscopy images of the alloy deposits at different TEA concentrations, as shown in Fig. 7, indicate a coarse grained structure in the presence of insufficient TEA, and a relatively finer structure at optimum concentration.

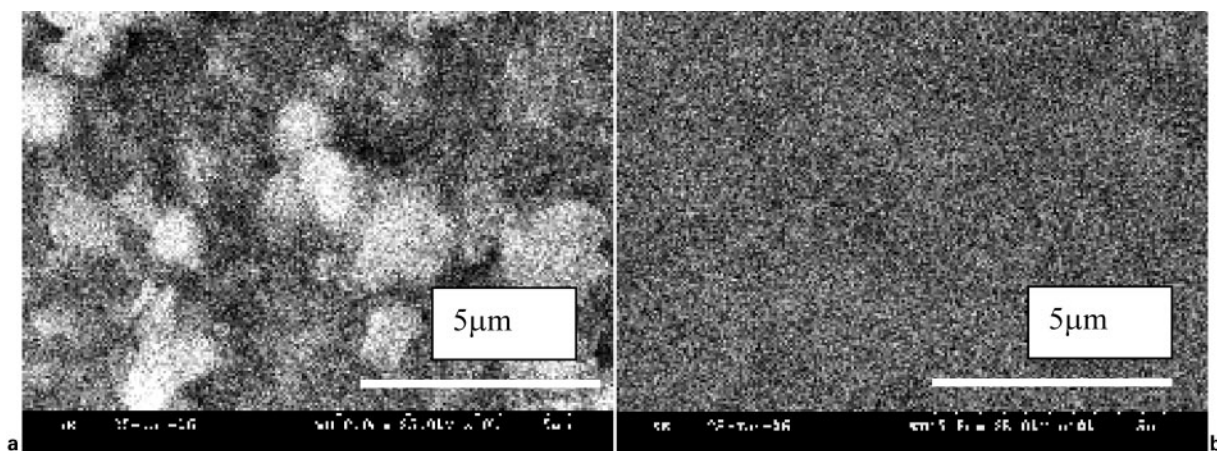
Figure 8 shows the CCE of alloy deposition at varying TEA concentrations. Cathode current efficiency of alloy deposition is less than individual zinc deposition from the zincate bath. Cathode current efficiency is higher in a solution containing 7.5 g L⁻¹ nickel than in a 5 g L⁻¹ solution. This could be due to the different Ni/TEA ratio in the solution. Cathode current efficiency is high at 4 A dm⁻² in both cases. Increasing TEA results in higher CCE. It could be inferred therefore that decrease in nickel content of the alloy results in enhanced CCE.

The presence of PIP decreases the nickel content and CCE but the change is not significant. Table 1 shows the effect of increasing the bath operating temperature and solution stirring on the nickel content of the alloy deposit.

Table 2 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.



7 Images (SEM) showing effect of TEA (conditions: BE, 7.5 g L⁻¹ Ni, current density 4 A dm⁻²)



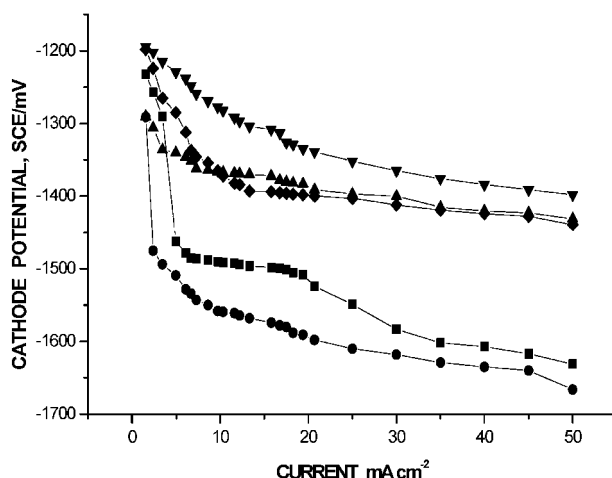
a 2.4 g L⁻¹ PVA; b 2.4 g L⁻¹ PVA+1 g L⁻¹ PIP

9 Images (SEM) showing effect of additives (condition: BE, 7.5 g L⁻¹ nickel, 85 mL L⁻¹ TEA, 4 A dm⁻²)

Figure 9 shows the SEM images of the deposits obtained in presence of PVA and PVA+PIP. Polyvinyl alcohol alone causes partial grain refinement compared to Fig. 7b. However, the presence of PIP gives rise to submicron sized (about 0.5–1.5 μm) grain structure.

From the cathode polarisation curves shown in Fig. 10, it is observed that the deposition of Zn starts at about -1.4 V versus SCE and the presence of PVA increases it to -1.45 V due to complexation, which helps in reducing the fast reaction kinetics.⁴¹ Increasing addition of nickel ions in the form of its complex to the zinc bath shifts the polarisation curve towards less negative potentials indicating the formation of a solid solution.³³ Addition of PIP enhances polarisation due to specific adsorption which influences the appearance and grain structure as indicated in SEM examination.

Figure 11 shows the effect of increasing the TEA concentration on the polarisation behaviour of the alloy deposition. With increasing TEA concentration, the curves shift towards negative potentials enabling efficient complexation of nickel ions and their compatibility to codeposit with zinc.



■: BE; ●: BE+PVA; ▲: BE+PVA+5 g L⁻¹ Ni+85 mL L⁻¹ TEA; ◀: BE+PVA+7.5 g L⁻¹ Ni+85 mL L⁻¹ TEA; ◆: BE+PVA+7.5 g L⁻¹ Ni+85 mL L⁻¹ TEA+PIP

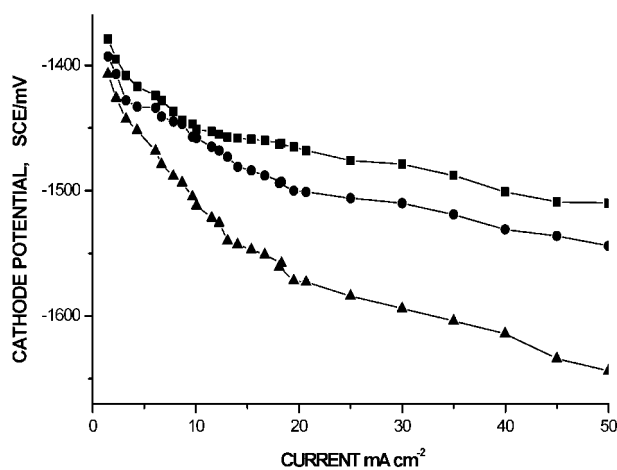
10 Polarisation curves for zinc and Zn-Ni alloy deposition

Table 1 Effect of bath operating temperature and stirring on nickel content of deposit

Ni content in the bath, g L ⁻¹	Current density, A dm ⁻²	Ni in deposit, %		
		Without stirring		With stirring
		30°C	60°C	30°C
5.0	3.0	8.6	9.1	9.8
5.0	4.0	7.5	8.5	10.0
7.5	3.0	12.0	17.9	13.6
7.5	4.0	10.8	15.2	12.2

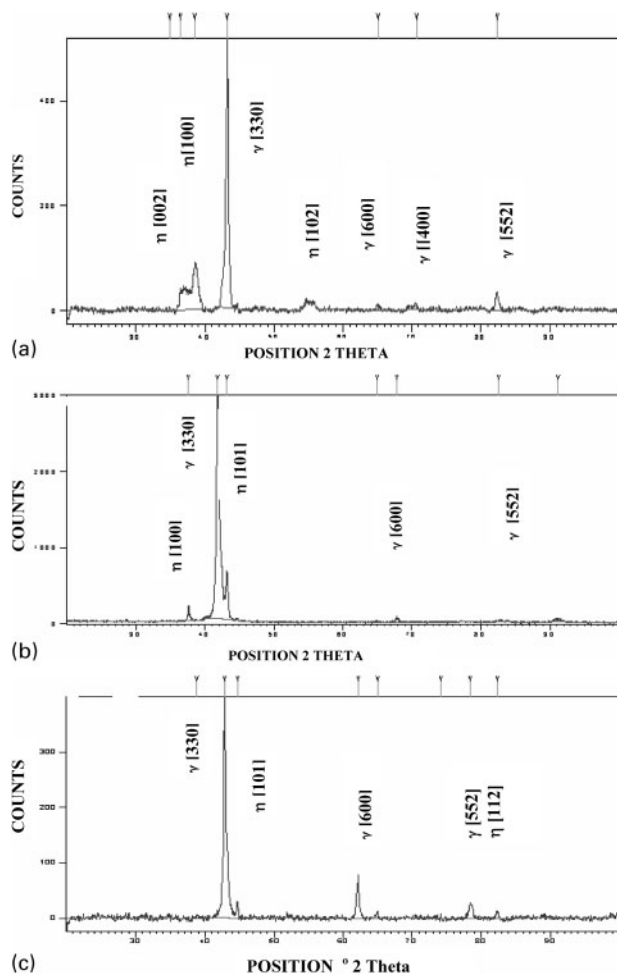
Table 2 Throwing power of alloy plating

Ni content in the bath, g L ⁻¹	Throwing power, %		
	3 A dm ⁻²	4 A dm ⁻²	5 A dm ⁻²
5.0	60.4	51.5	43.5
7.5	63.9	57.9	46.9



■: 50 mL L⁻¹; ●: 85 mL L⁻¹; ▲: 120 mL L⁻¹

11 Effect of TEA concentration on polarisation behaviour of alloy deposition (BE+PVA+7.5 g L⁻¹ Ni+TEA)



a BE+7.5 g L⁻¹ Ni+85 mL L⁻¹ TEA+2.4 g L⁻¹ PVA; b BE+7.5 g L⁻¹ Ni+85 mL L⁻¹ TEA+2.4 g L⁻¹ PVA+1 g L⁻¹ PIP; c BE+5 g L⁻¹ Ni+85 mL L⁻¹ TEA+2.4 g L⁻¹ PVA+1 g L⁻¹ PIP

12 X-ray diffraction patterns of Zn–Ni alloy deposits

The identification of the phases of the deposits was obtained from the X-ray diffractograms, as shown in Fig. 12, using the value of the angles corresponding to the peaks found, the indices of the crystallographic planes of the phases being identified.^{39,45,46} Electro-deposited Zn–Ni alloys exhibit three main phases:

- the α phase, which is a solid solution of zinc in nickel with an equilibrium solubility of $\sim 30\%$ Zn
- the γ phase, an intermediate phase with a composition Ni₅Zn₂₁
- the η phase, which is a solid solution of nickel in zinc with a very low amount of nickel.³⁹

Figure 12a shows the X-ray diffractogram of a deposit obtained from a solution containing 7.5 g L⁻¹ of nickel and TEA with PVA alone. The figure shows the presence of the γ phase along with many peaks, which do not

correspond to zinc, or to other phases of Zn–Ni alloys. According to Muller *et al.*,³⁹ the texture of the η phase is similar to that of zinc and the maximum amount of Ni in the η phase is 6%. The main difference between acid and alkaline Zn–Ni formulation, observed by Muller *et al.*,³⁹ is that the first layer of the deposit has nickel content lower than the remainder of the coating, as against the nickel rich α phase in the initial layers in acid baths. This can also be the reason for the observed zinc rich phases.

Figure 12b and c presents the diffractograms of the alloy deposits obtained with 5 and 7.5 g L⁻¹ nickel with the addition of PVA and PIP. The presence of the η phase in these figures is considerably reduced. As understood from the polarisation studies in Fig. 9, increase in the cathode potential caused by the addition of PIP might have suppressed the formation of η phase.

The figures show that the cell parameter ' a_0 ' varies from 8.88–8.94 which is in agreement with the reported literature for the presence of γ phase.^{39,45}

Table 3 presents the corrosion resistance of the alloy deposits obtained from the alkaline bath and compares it with that of zinc deposits obtained from a similar bath. It could be seen that the matt alloy deposit shows considerable enhancement in corrosion current compared with the bright coatings. The R_{Ct} values also support this result.

Conclusions

An alkaline non-cyanide zincate electrolyte with 7.5 g L⁻¹ nickel, 85 mL L⁻¹ TEA, 2.4 g L⁻¹ PVA and 1 g L⁻¹ PIP at 4 A dm⁻² yielded bright Zn–Ni alloy deposits containing $\sim 10\%$ nickel. Sufficient TEA concentration is essential to get a stable electrolyte. Polyvinyl alcohol yields compact deposits and causes partial grain refinement, but the deposits were only semibright. However, the presence of PIP gives rise to submicron sized (around 0.5–1.5 μ m) grain structure and enables bright deposition in the presence of PVA.

The nickel content of the alloy is not significantly affected with increase in current density at all concentrations. This enables a uniform alloy composition even on a complex surface on which the current densities at different zones differ considerably.

The new bath also has the additional advantage of being ecofriendly in that it uses only easily disposable organics.

Acknowledgements

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Table 3 Corrosion data with potentiodynamic polarisation and impedance

Deposit details	OCP, V	E_{Corr} , mV	I_{Corr} , μ A cm ⁻²	R_{Ct} , Ω cm
Zn+PVA	1.055	1020	101.0	26
Zn+PVA+PIP	1.022	1000	26.8	180
Zn–Ni+PVA	0.97	970	5.5	320
Zn–Ni+PVA+PIP	0.96	950	4.7	380

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