

Bright zinc–cobalt alloy deposits from an alkaline non-cyanide bath

S. Sigamani and M. Pushpavanam*

Cobalt ions were added to a non-cyanide alkaline zinc bath to produce an alloy of zinc containing 0.6–0.8%Co. Bright deposits were produced using organic additives. The effect of different parameters such as cobalt concentration, current density, complexant concentration, additive concentration, temperature, agitation, etc. on the composition of the alloy and current efficiency was studied. Structural characterisation using scanning electron microscopy showed that the deposits are nanocrystalline.

Keywords: Alloy deposition, Composition and current efficiency, Hull cell studies, Scanning electron microscopy, Structure

Introduction

Electrodeposited zinc alloyed with cobalt, iron or nickel is used for protective and decorative applications.^{1,2} These alloys are harder, stronger, fine grained and more corrosion resistant than pure zinc deposit.^{3,4} The desired cobalt content in the alloy to achieve the above advantages is only 0.6–0.8% compared with Zn–Ni alloy requiring ~12% nickel.⁵ Moreover, switching over from the existing neutral zinc plating line to the zinc–cobalt alloy plating line is very simple unlike the zinc–nickel system.⁶

Codeposition of zinc with iron group metals follows anomalous type of deposition in which the less noble metal deposits preferentially under certain conditions. The alloy can be deposited from both acid^{7–11} and alkaline electrolytes.^{12–14} Since in acid electrolytes the metals are present as simple ions, the operating current density and rate of deposition are considerably high but they suffer from the disadvantage of poor throwing power and varied composition dispersion since the cobalt content in the alloy varies almost linearly with current density. The anomaly in codeposition is reported to be less in an alkaline bath,³ since both metals are present as complex and deposition of cobalt from alkaline solutions is rather difficult. Hence, deposition from complex solutions is preferred where improved throwing power and low composition dispersion, which decide the corrosion properties of the coating, are mandatory.

As a continuation of the authors' earlier report on bright zinc deposition from an alkaline non-cyanide bath, work on the production of zinc alloys was initiated from the same bath. The present paper deals with bright zinc–cobalt alloy deposition from the same bath using selected organic addition agents. The dependence of alloy composition and cathode efficiency on the metal ions concentration, their ratio, complexant

concentration, current density, and bath temperature and addition agents has been reported.

Experimental

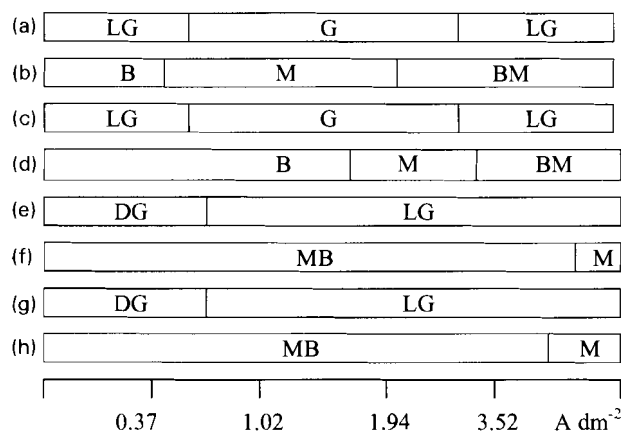
Zinc–cobalt alloy plating bath used for the study comprised ZnO, NaOH, cobaltous sulphate and a chelating agent (BE). The bath composition is shown in Table I. A stock solution of zinc was prepared with due purification treatments.¹⁵ Cobaltous sulphate $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was mixed with the complexant (triethanolamine, TEA) and made as a homogenous solution in order to avoid precipitation in the alkaline medium. Required amount of cobalt solution was added to the electrolyte before deposition.

Polished, degreased, alkaline cleaned, acid dipped and washed mild steel panels were used as cathodes and plating grade zinc as anodes. Panels of 8×2.5 cm with an effective area of 2.5×2.5 cm and 10×7 cm size were used for the efficiency and composition estimation and for Hull cell experiments respectively. A 267 mL Hull cell was used for the study. Experiments were conducted at varying cobalt concentrations, complexant concentrations, additives' concentrations, operating temperature, hydrodynamic condition and so on. The deposits were stripped in a suitable medium and cobalt content was estimated using atomic absorption spectrophotometry (AAS). The thickness of the deposits was measured using X-ray fluorescence spectroscopy.

The current efficiency of alloy deposition was estimated since the composition of the alloy deposits and its mass were known. The effect of cobalt addition in zinc deposition and of additives on the cathode polarisation were evaluated using a steel cathode, platinum anode and a saturated calomel reference electrode in a three necked cell. Structural examination of the deposits was made using scanning electron microscopy (SEM).

Results and discussion

Since cobalt salt is insoluble in alkaline conditions, it has to be solubilised with the help of the complexing agent.



a Hull cell pattern using 10 mL L⁻¹ complexant, BE; b Hull cell pattern using 10 mL L⁻¹ complexant, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP; c Hull cell pattern using 15 mL L⁻¹ complexant, BE; d Hull cell pattern using 15 mL L⁻¹ complexant, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP; e Hull cell pattern using 20 mL L⁻¹ complexant, BE; f Hull cell pattern using 20 mL L⁻¹ complexant, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP; g Hull cell pattern using 25 mL L⁻¹ complexant, BE; h Hull cell pattern using 25 mL L⁻¹ complexant, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP

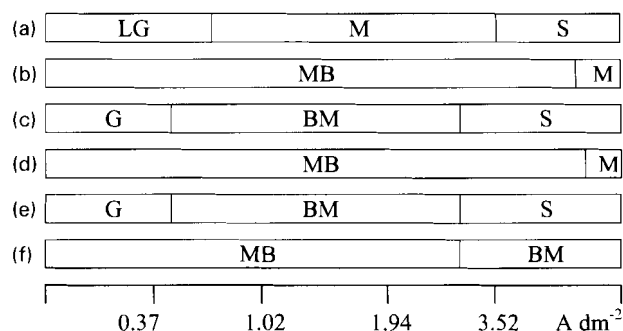
1 Effect of complexant concentration at 0.5 g L⁻¹ cobalt in solution: light grey (LG), grey (G), bright (B), black matte (BM), matte (M), mirror bright (MB), dark grey (DG)

Figures 1 and 2 show the effects of complexing agent concentration in alkaline zinc solutions containing 0.5 and 0.75 g L⁻¹ cobalt on the Hull cell patterns of zinc-cobalt alloy deposits. In absence of any additive, the alloy deposits appeared grey in colour differing only in their hues. Increase in the complexant concentration produced only a marginal improvement. Increase in the metal ion concentration along with the required amount of complexant could modify the deposit nature from grey to matte (Fig. 3). However, to achieve maximum corrosion resistance, the desirable reported limit for cobalt content in the alloy is only 0.6–0.8%. This restricts the use of higher cobalt concentration in the solution. As discussed in the earlier communication,¹⁶ the formation of grey deposits is due to the fast reaction kinetics and to produce bright, useful deposits, the rate of reaction must be reduced which is possible only with the help of additives.

The effects of varying concentrations of the carrier additive and the brightener additive on the Hull cell patterns are depicted in Figs. 4 and 5. Based on the earlier studies,¹⁶ Polyvinyl alcohol (PVA) was chosen as the carrier additive and piperonal (PIP) as the brightener

Table 1 Bath composition used

Bath	Concentration, g L ⁻¹
Zinc oxide	9–12
Sodium hydroxide	90–120
Cobalt as CoSO ₄ .7H ₂ O	0.5–1.2
Triethanolamine, mL L ⁻¹	15–30
Polyvinyl alcohol (PVA)	0.5–2.0
Piperonal	0.6–1.5
Temperature, °C	25–60
Chemical grade	Laboratory grade reagents

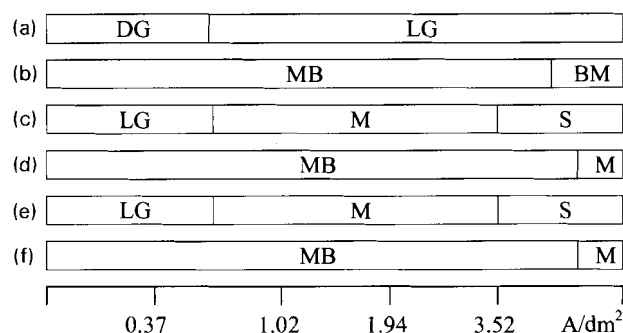


a Hull cell pattern using 20 mL L⁻¹ complexant, BE; b Hull cell pattern using 20 mL L⁻¹ complexant, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP; c Hull cell pattern using 25 mL L⁻¹ complexant, BE; d Hull cell pattern using 25 mL L⁻¹ complexant, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP; e Hull cell pattern using 30 mL L⁻¹ complexant, BE; f Hull cell pattern using 30 mL L⁻¹ complexant, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP

2 Effect of complexant concentration at 0.75 g L⁻¹ cobalt in solution: light grey (LG), grey (G), bright (B), black matte (BM), matte (M), streaky (S), mirror bright (MB)

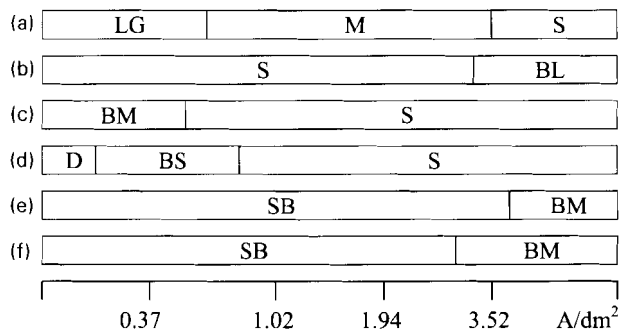
additive. The tremendous improvement produced by PVA addition is obvious from Fig. 4, which shows that with increasing concentration, the deposits change in appearance from grey/matte to semibright. As reported earlier,¹⁶ this could be attributed to the polarity of the carbon-oxygen bond, which made it to be present in significant amounts in the cathode film, forming a weak physical barrier to hinder deposition. It could also be possible that PVA replaces the H₂O present in the complex and the PVA chains can retain zinc hydroxyl anions and control the speed of the reaction kinetics.¹⁷

Figure 5 shows the effect of piperonal on the Hull cell patterns of alloy deposition. It is obvious that this addition causes a dramatic influence on the deposit nature in that they change from semibright to mirror bright appearance. Based on the above results, it could be concluded that addition of 0.8 g L⁻¹ PVA along with 0.2 g L⁻¹ piperonal is the best combination to produce mirror bright deposits from an alkaline non-cyanide zinc bath.



a Hull cell pattern at 0.5 g L⁻¹ cobalt, BE; b Hull cell pattern at 0.5 g L⁻¹ cobalt, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP; c Hull cell pattern at 0.75 g L⁻¹ cobalt, BE; d Hull cell pattern at 0.75 g L⁻¹ cobalt, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP; e Hull cell pattern at 1 g L⁻¹ cobalt, BE; f Hull cell pattern at 1 g L⁻¹ cobalt, BE+0.8 g L⁻¹ PVA+0.2 g L⁻¹ PIP

3 Effect of metal ion concentration using 20 mL L⁻¹ complexant: light grey (LG), black matte (BM), matte (M), streaky (S), mirror bright (MB), dark grey (DG)



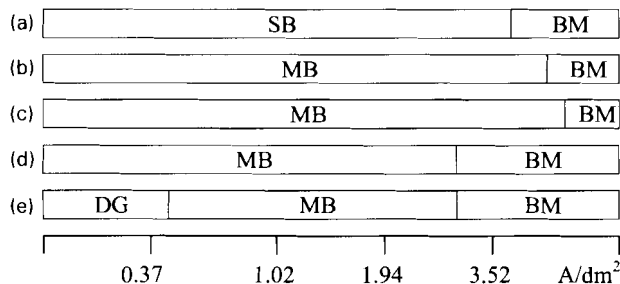
a BE, BE+PVA; b 0.2 g L⁻¹; c 0.4 g L⁻¹; d 0.6 g L⁻¹; e 0.8 g L⁻¹; f 1 g L⁻¹

4 Effect of primary additive concentration with 0.75 g L⁻¹ cobalt and 20 mL L⁻¹ complexant (BE): light grey (LG), grey (G), bright+streaky (BS), black matte (BM), matte (M), streaky (S), semibright (SB), dark grey (DG), black (BL)

Figures 1–3 also depict the effects of varying complexant concentration and cobalt concentration in presence of the above optimised additive. It is clear that bright deposits could be obtained when the complexant concentration is in the range 20–25 mL L⁻¹ when cobalt ion in the solution is 0.5–1.0 g L⁻¹.

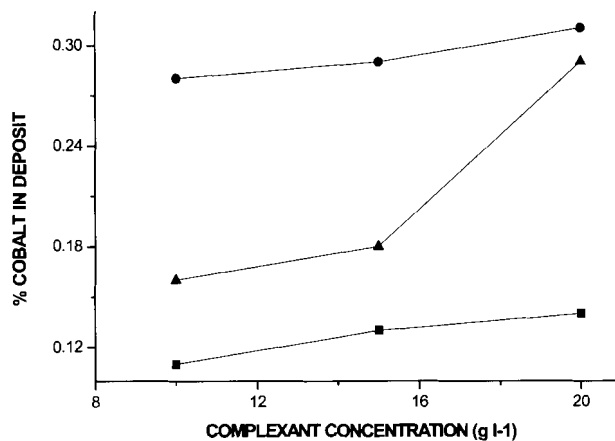
Figures 6 and 7 depict the effect of increasing the complexant concentration on the alloy composition. TEA in the bath has an important role in the dissolution of cobalt salt in the alkaline solution. When the amount of TEA in the bath was insufficient to stabilise the metal species, during preparation the precipitation of cobalt salt was observed on mixing the two solutions. No significant effect of TEA was observed above 15 mL L⁻¹ in the case of 0.5 g L⁻¹ cobalt and above 25 mL L⁻¹ in the case of 0.75 g L⁻¹ cobalt. This was the lowest concentration found to obtain a precipitate free solution. During deposition, owing to the same reason, increase in complexing agent concentration up to 25 mL L⁻¹ causes a gradual increase in cobalt content of the alloy but still higher concentration causes a reduction. Free TEA present in the solution should have inhibited cobalt codeposition.⁸

Figure 8 indicates the variation of cobalt content in the alloy with increasing cobalt content in the solution. It is clear that the system belongs to the anomalous type wherein the less noble metal zinc is depositing in preference to cobalt as indicated by the position of the cobalt line falling below the composition reference line

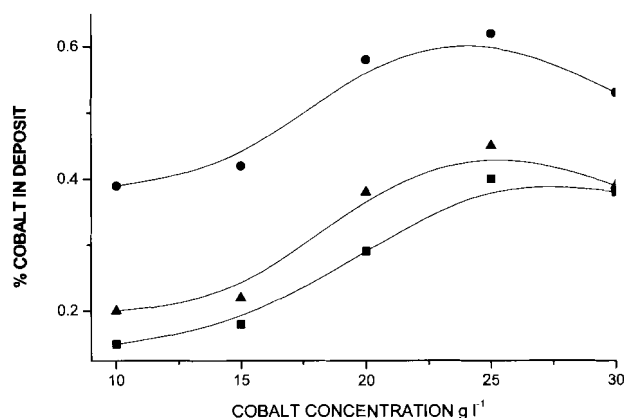


a BE+PVA, 0.8 g L⁻¹; BE+PVA, 0.8 g L⁻¹+PIP; b 0.1 g L⁻¹; c 0.2 g L⁻¹; d 0.3 g L⁻¹; e 0.4 g L⁻¹

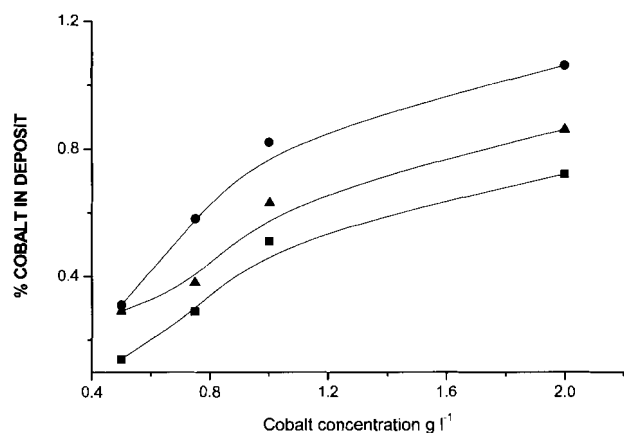
5 Effect of secondary additive concentration with 0.75 g L⁻¹ cobalt and 20 mL L⁻¹ complexant: bright+streaky (BS), black matte (BM), mirror bright (MB), dark grey (DG), semibright (SB)



■ 1 A dm⁻²; ● 2 A dm⁻²; ▲ 3 A dm⁻²
6 Cobalt per cent in deposit obtained with 0.5 g L⁻¹ cobalt and 10, 20, 25 mL L⁻¹ complexant at different current densities

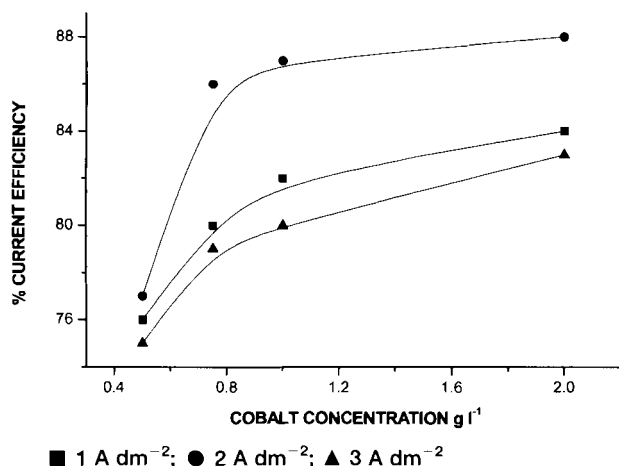


■ 1 A dm²; ● 2 A dm²; ▲ 3 A dm²
7 Cobalt per cent in deposit obtained with 0.75 g L⁻¹ cobalt and 10, 20, 25, 30 mL L⁻¹ complexant at different current densities



■ 1 A dm⁻²; ● 2 A dm⁻²; ▲ 3 A dm⁻²
8 Cobalt per cent in deposit with 0.5, 0.75, 1 and 2 g L⁻¹ cobalt and 20 mL L⁻¹ complexant at different current densities

(CRL).³ This contrasts with the observation of Muller *et al.* who state that in alkaline solutions zinc–nickel codeposition is of normal type.¹⁸ Cobalt content increases with increase in cobalt concentration in the electrolyte. Figure 8 also depicts the effect of current



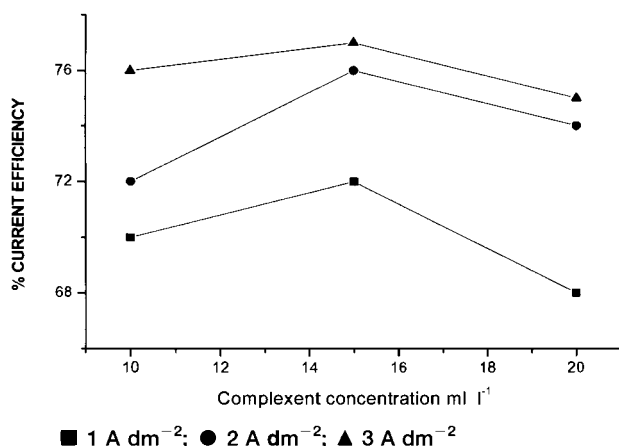
9 Current efficiencies for different concentrations of cobalt using 20 mL L⁻¹ complexant at different current densities

density on the cobalt content of the alloy. The curves show a maximum at 2 A dm⁻² and then decline. This could be attributed to the low metal content of the solution along with the complexing agent. It was also found that cathode current efficiency (CCE) increases with increase in the cobalt ion concentration in solution and that the maximum is achieved at 2 A dm⁻² (Fig. 9).

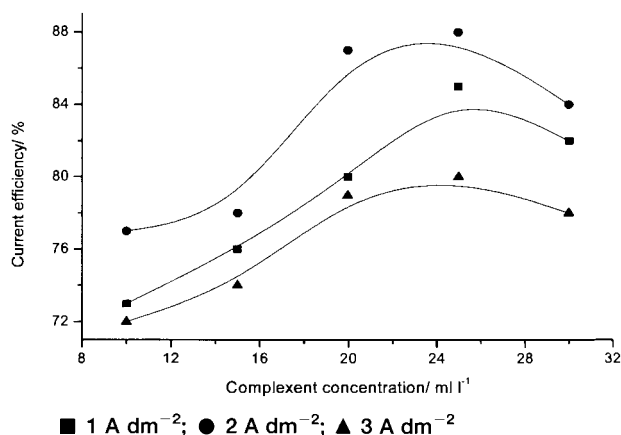
It could be noticed that the amount of cobalt codeposited is considerably lower in alkaline baths¹⁹ compared with the acid baths since it is tightly bound by the complexant. For the given cobalt concentration, the variation of cobalt content is marginal unlike the acid baths.²⁰ Moreover, with increasing current density, the cobalt content remains almost constant and the CCE shows a decrease. This accounts for the uniform composition of the alloy (composition dispersion) and for better throwing power of the electrolyte compared with the acid baths.

Figures 10 and 11 show the variation of CCE of alloy deposition with the complexing agent concentration. With 0.5 g L⁻¹ cobalt in solution, the CCE diminishes above 15 mL L⁻¹ complexant whereas with 0.75 g L⁻¹ cobalt, it occurs above 25 mL L⁻¹.

It was noticed that electrolyte stirring and increase in operating bath temperature increased the cobalt content as well as the CCE, indicating that cobalt deposition is diffusion controlled.



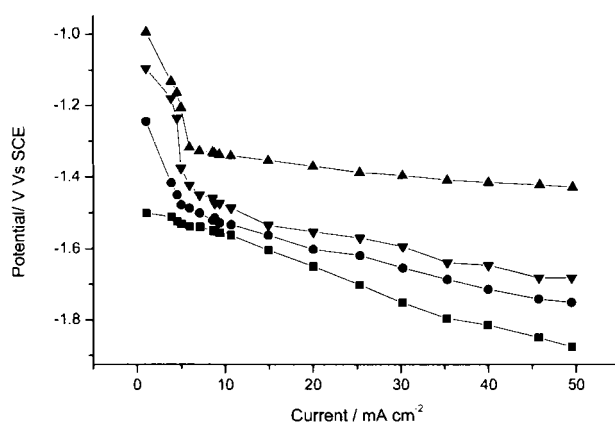
10 Current efficiencies for different concentrations of complexant with 0.5 g L⁻¹ cobalt at different current densities



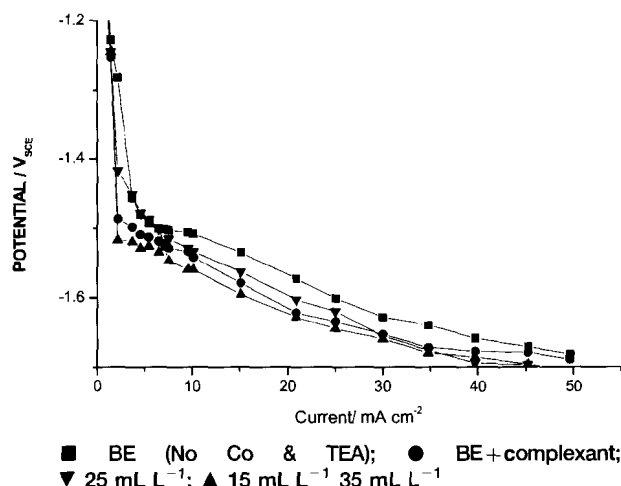
11 Current efficiencies for different concentrations of complexant with 0.75 g L⁻¹ cobalt at different current densities

The galvanostatic polarisation curves, given in Fig. 12, indicate that with increasing cobalt addition, the curves got shifted to positive potentials indicating the formation of a solid solution. The curves originated at more positive values, attained a plateau and then showed steady polarisation.

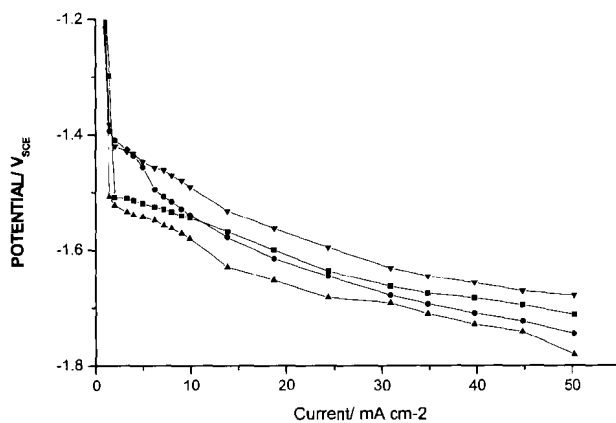
It has been documented that during zinc-nickel deposition, the initially formed layer is a nickel rich alloy and with the increase in current density, it gets transformed into zinc rich alloy. The formation of this plateau has been reported by many authors and has been attributed to the transformation of phase structure. The hydroxide suppression mechanism is a widely accepted one, according to which zinc gets adsorbed on the electrode surface more strongly than nickel and inhibits nickel deposition leading to anomalous type codeposition.^{21,22} According to Higashi *et al.*,²¹ the alloy deposition proceeds with preceding zinc hydroxide formation on the cathode, which results in a rise in pH in the vicinity of the cathode favouring zinc deposition. On the other hand, since the critical pH for Co(OH)₂ precipitation is not attained in the cathode layer, cobalt deposition occurs by direct discharge of Co²⁺ ions through the Zn(OH)₂ film which makes cobalt deposition difficult. The same mechanism proposed for acid solution holds good for alkaline solutions also since both metals are present as complexes. The formation of



12 Polarisation curves for zinc-cobalt deposition at different cobalt concentrations: 20 mL L⁻¹ complexant



13 Polarisation curves for zinc-cobalt deposition at different complexant concentrations: $0.75 \text{ g L}^{-1} \text{ Co}$



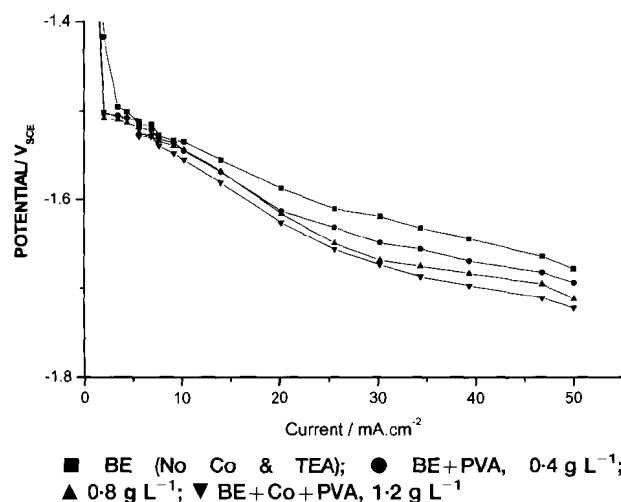
15 Polarisation curves for zinc-cobalt deposition with different secondary additive concentrations: $0.75 \text{ g L}^{-1} \text{ Co} + 20 \text{ mL L}^{-1} \text{ complexant} + 0.8 \text{ g L}^{-1} \text{ PVA}$

adsorbed zinc hydroxide layer from the zincate complex should have been easier than the formation of adsorbed cobalt hydroxide species from TEA complex.

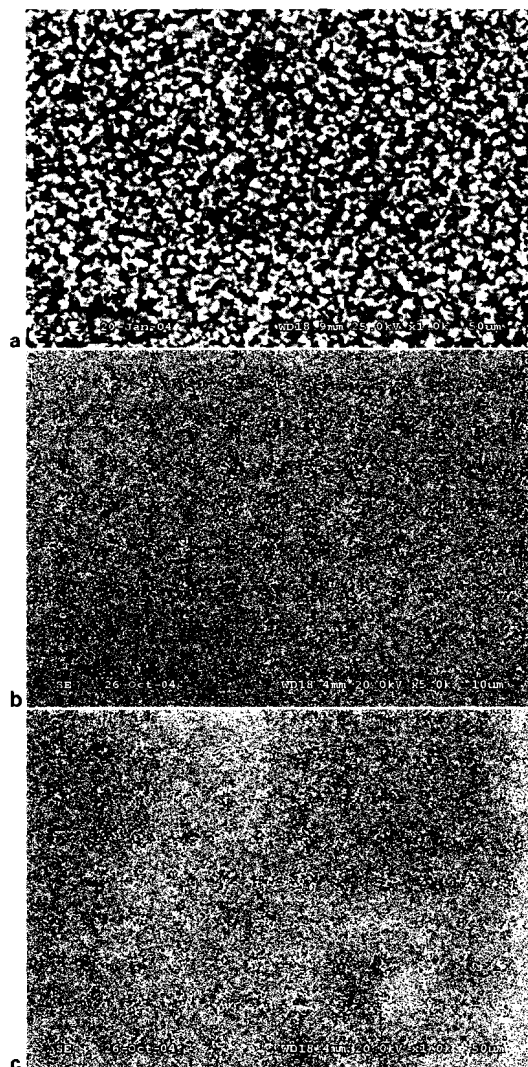
Figure 13 depicts the effect of TEA on the polarisation behaviour of the alloy deposition. Addition of TEA increases polarisation the curves show polarisation. PVA²³ addition further increased the polarisation (Fig. 14). This is due to the specific adsorption of the additive on the electrode surface, which resulted in producing bright deposits since normally deposits obtained at high overpotentials are fine grained in nature.²⁴ Also, this resulted in reduction in cobalt content in the alloy since polarisation curves shift closer to that of zinc. Piperonal further causes shift towards more negative potentials up to 0.2 g L^{-1} but still higher concentrations cause depolarisation that might increase the cobalt content of the alloy (Fig. 15).

Images (SEM) shown in Fig. 16 are in support of the above findings. The microstructure of the alloy deposit without any additive as depicted in Fig. 16 shows finer grains compared with bright zinc deposits from the same electrolyte.¹⁶ The above structure is further refined in presence of PVA and PIP and the final structure shows grain homogenisation.^{25,26} Unlike in zinc deposits there

was no film formation on the alloy deposit with the addition of PVA, which could be attributed to the presence of cobalt ions.



14 Polarisation curves for zinc and cobalt deposition at different primary additive concentrations: $0.75 \text{ g L}^{-1} \text{ Co} + 20 \text{ mL L}^{-1} \text{ complexant}$



16 Images (SEM) obtained using $0.75 \text{ g L}^{-1} \text{ cobalt}$, $20 \text{ mL L}^{-1} \text{ complexant}$: $0.8 \text{ g L}^{-1} \text{ PVA}$ and $0.2 \text{ g L}^{-1} \text{ PIP}$ at 2 A dm^{-2}

Conclusion

Bright zinc–cobalt alloy deposits could be obtained from an alkaline non-cyanide electrolyte containing TEA with the addition of PVA and PIP.

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References

1. E. O. S. Carpenter and J. P. G. Farr: *Trans. IMF*, 1998, **76**, 135–143.
2. T. Tsuru, S. Kobayashi, T. Akiyama, H. Fukushima, S. K. Gogia and R. Kammel: *J. Appl. Electrochem.*, 1997, **27**, 209–214.
3. A. Brenner: 'Electrodeposition of alloys: principles and practice', Vol. I; 1963, New York, Academic Press.
4. N. R. Short, J. K. Dennis and S. Zhou: *Surf. Coat. Technol.*, 1996, **79**, 218.
5. M. A. Pech-Canul, R. Ramanauskas and L. Maldonado: *Electrochim. Acta*, 1997, **42**, 255–260.
6. Z. M. Tu, J. S. Zhang, W. L. Li, Z. L. Yang and M. Z. An: *Trans. IMF*, 1995, **73**, 48–49.
7. R. Fratesi, G. Roventi, G. Giuliani and C. R. Tomachuk: *J. Appl. Electrochem.*, 1997, **27**, 1088–1094.
8. S. Rajendran, S. Bharathi, C. Krishna and T. Vasudevan: *Plat. Surf. Finish.*, 1997, **84**, 53–56.
9. W. M. J. C. Verbeke: *Trans. IMF*, 1986, **64**, 30.
10. D. E. O. S. Carpenter and J. P. G. Farr: Proc. 9th Int. Symp. on 'Advanced materials', Lahore, Pakistan, September 2005, Kahuta Research Laboratory, Abstracts 101.
11. H. Yan, J. Downes, P. J. Boden and S. J. Harris: *J. Electrochem. Soc.*, 1996, **143**, 1577.
12. D. E. O. S. Carpenter, S. D. Carpenter and J. P. G. Farr: *Trans. IMF*, 2000, **78**, 152.
13. G. D. Wilcox and P. J. Mitchell: *Trans. IMF*, 1987, **65**, 75.
14. O. Gircine, P. Ramanauskas, P. Castro and P. Bertolo-Perez: *Trans. IMF*, 2001, **79**, 199.
15. H. Geduld: 'Zinc plating', 90; 1988, Metals Park, OH, ASM International.
16. S. Sigamani and M. Pushpavanam: *J. Appl. Electrochem.*, 2006, **36**, 315.
17. R. Ramanuskas, P. Quintana, L. Maldonado, R. Pomes and M. A. Pechcanul: *Surf. Coat. Technol.*, 1997, **92**, 16–21.
18. C. Muller, M. Sarret and M. Benballa: *J. Electroanal. Chem.*, 2002, **519**, 85–92.
19. L. Y. Hwa and K. G. Sung: *Surf. Coat. Technol.*, 2000, **135**, 69–74.
20. M. Michael: PhD thesis, Protection of Metals: Role of Electro deposited alloys Madurai Kamaraj University, Tamil Nadu, India, 1996.
21. K. Higashi, H. Fukushima and T. Urakawa: *J. Electrochem. Soc.*, 1981, **128**, 2081–2085.
22. H. Dahms and J. Croll: *J. Electrochem. Soc.*, 1965, **112**, 771–775.
23. M. Schlesinger and M. Paunovic: 'Modern electroplating', 4th edn, 555; 2000, New York, John Wiley & Sons.
24. L. Oniciu and L. Muresan: *J. Appl. Electrochem.*, 1991, **21**, 565–574.
25. A. J. Rethinam, G. N. K. R. Bapu and V. S. Muralidharan: *Indian J. Chem. Technol.*, 2004, **11**, 207–212.
26. G. Y. Li, J. S. Lian, L. Y. Niu and Z. H. Jiang: *Surf. Coat. Technol.*, 2005, **191**, 59–67.