

Electrodeposition of Zn–Ni–Fe alloy in acidic chloride bath with separated anodes

M. M. YOUNAN, T. OKI

Department of Materials Science and Engineering, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Received 4 July 1995; revised 28 November 1995

The electrodeposition of ternary Zn–Ni–Fe alloy films was investigated in acidic chloride electrolyte. Electrodeposition was performed onto mild steel plates at pH 3 and 43 °C. The influence of the chloride concentration (ZnCl₂, NiCl₂ and FeCl₂) on the surface appearance and deposit composition, as well as cathodic current efficiency, were investigated. Bright Zn–Ni–Fe alloy deposits were obtained in the electrolyte containing 0.4 M of each of ZnCl₂ and NiCl₂ with 0.02 to 0.08 M FeCl₂. The influence of current density, pH and temperature were also examined.

1. Introduction

Electrodeposition of Zn–Ni alloy has been investigated since 1980 in order to improve its chemical and physical properties [1–3]. Dini and Johnson [4] concluded that a brightener system has to be developed to obtain bright Zn–Ni electrodeposits. Suitable organic brighteners were developed to obtain bright Zn–Ni alloy coatings from sulfate [2,3] and chloride baths [5].

Singh *et al.* [6] developed an acetate bath (pH 5.3) containing boric acid and high Ni²⁺/Zn²⁺ molar ratio (>15). Deposits were fine-grained, dense and bright at current densities of 10 to 20 mA cm⁻². Current efficiencies were generally low, usually below 55%. Increasing the zinc content in the bath resulted in dull grey and mossy deposits.

The purpose of the present work is to obtain smooth and bright ternary Zn–Ni–Fe electroplates from acidic chloride bath without organic brighteners. The effects of different parameters influencing the deposits (e.g., metal ions concentration, current density, temperature and pH) are also studied.

2. Experimental procedure

Electrolytes were freshly prepared from distilled water and analytical grade reagents. Zn–Ni–Fe alloy electrodeposits were usually prepared at 43 ± 2 °C, 30 mA cm⁻² and pH 3. The basic bath composition for Zn–Ni–Fe alloy electrodeposition is given in Table 1.

Zn–Ni alloy was also electrodeposited, as reference, from the above electrolyte without ferrous chloride under the same electrolysis conditions.

A rectangular glass cell containing 200 cm³ of the electrolyte solution was used with a suitable electric circuit, as shown in Fig. 1. Electrodeposits were obtained on one side surface of mild steel substrate (exposed area: 9 cm²). Before electrodeposition, steel

substrates were pretreated as follows: degreasing by organic solvent (acetone), water rinsing, alkaline soaking in 6% NaOH, water rinsing, neutralization and activation in 10% HCl solution and finally rinsing with distilled water.

As for Zn–Ni–Fe alloy deposition, pure anodes of zinc (7.2 cm²), nickel (1.2 cm²) and iron (0.6 cm²) sheets were used separately. Anodic dissolution was regulated by three separate circuits fed by two d.c. power sources, where 86% of the total current was supplied through the zinc anode, 13% through the nickel anode and 1% through the iron, in order to compensate the cathodic consumption of each metal. Also for Zn–Ni alloy deposition, zinc and nickel anodes were used separately in a similar way.

A pure copper substrate was used in the experiment for determination of deposit composition, where the deposits were stripped in 10% HCl solution and analysed by means of atomic absorption spectrophotometry.

A Hull cell test of 276 cm³ capacity was performed to assess the influence of Fe codeposition on the surface brightness of the deposits. A zinc anode (5 mm thickness) was used as a positive electrode, while the total current (1 A) was applied for 5 min.

3. Results and discussion

3.1. Effect of metal ions concentration

The influence of the concentration of Zn²⁺ and Ni²⁺ on the Zn–Ni deposit composition was determined, as shown in Figs 2 and 3. These figures show that zinc is the most readily deposited metal, under these electrolysis conditions, and that the deposition is of the anomalous type [1,7], as the content of zinc (the less noble metal) in the deposit is always higher than its metal ratio in the solution. The nickel content in the deposits was linearly correlated to the concentration ratio of Ni²⁺.

Table 1. The basic bath composition for electrodeposition of ternary Zn-Ni-Fe alloy

Bath ingredient	Concentration/M
Zinc chloride (ZnCl_2)	0.40
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	0.40
Ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)	0.06
Sodium chloride (NaCl)	2.50
Sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$)	0.30
Boric acid (H_3BO_3)	0.50
Dodecyl sodium sulfate (wetting agent)	0.50*

* This concentration was in g L^{-1}

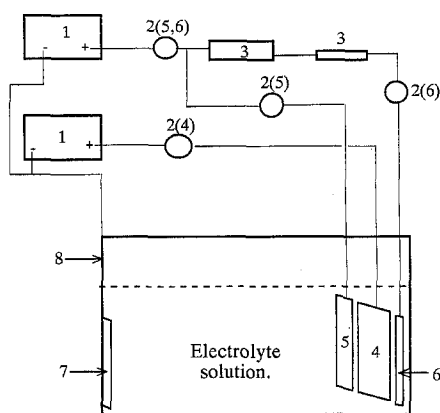


Fig. 1. Schematic diagram for experimental setup of Zn-Ni-Fe alloy deposition using pure Zn, Ni and Fe anodes. Key: (1) regulated d.c. power supply, (2) ammeter, (3) resistance, (4) pure Zn anode, (5) pure Ni anode, (6) pure Fe anode, (7) mild steel sample, and (8) rectangular glass cell.

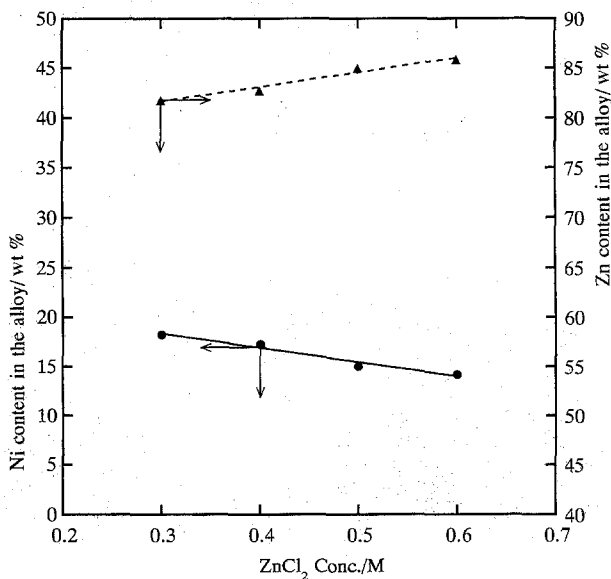


Fig. 2. Effect of zinc chloride concentration in the bath on electro-deposited Zn-Ni alloy composition. Bath composition: basic (except ZnCl_2 and FeCl_2); parameters: c.d. 30 mA cm^{-2} ; temp. 43°C ; pH 3; time 10 min. Key: (-----) Zn(%); (—) Ni(%).

The influence of Fe^{2+} in the electrodeposits was examined at different concentration levels of ferrous chloride in the range from 0.02 to 0.08 M, under constant electrolysis conditions. Figures 4 and 5 show that the nickel content in deposits is not affected

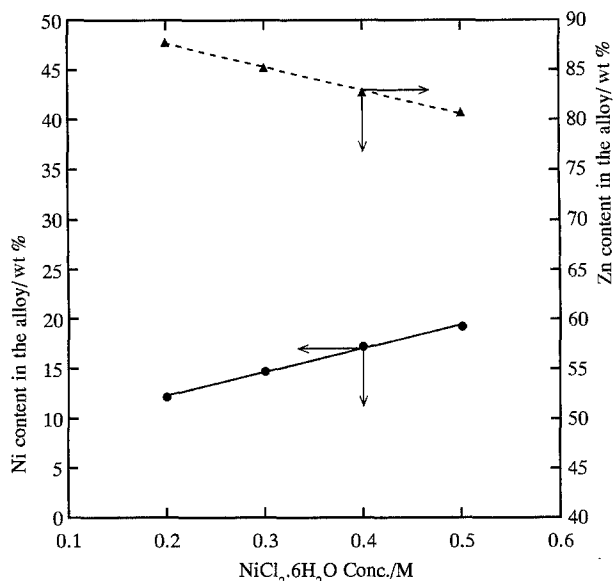


Fig. 3. Effect of nickel chloride concentration in the bath on electro-deposited Zn-Ni alloy composition. Bath composition: basic (except NiCl_2 and FeCl_2); parameters: c.d. 30 mA cm^{-2} , temp. 43°C , pH 3, time 10 min. Key: (-----) Zn(%), (—) Ni(%).

significantly in both the presence and absence of ferrous chloride. However, the iron content in the deposits increases linearly with increasing Fe^{2+} concentration.

Figures 4 and 5 show also that the iron content in the deposits not only increases with increasing Fe^{2+} concentration but also an increasing $\text{Ni}^{2+}/\text{Zn}^{2+}$ molar ratio in the bath. For example, the iron content in the deposits was changed to 1.50%, 3.95% and 5.80%, respectively with different molar ratios of 0.4/0.6, 0.4/0.4 and 0.5/0.4 of $\text{Ni}^{2+}/\text{Zn}^{2+}$ in the electrolyte with 0.06 M Fe^{2+} . The increase in deposit iron content corresponds to the increasing $\text{Ni}^{2+}/\text{Zn}^{2+}$ molar ratio.

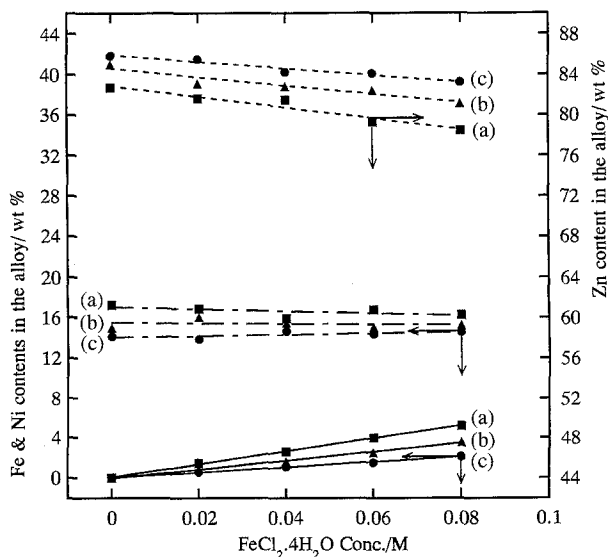


Fig. 4. Effect of ferrous chloride concentration in the bath on electro-deposited Zn-Ni-Fe alloy composition, from baths containing: (a) 0.4, (b) 0.5 and (c) 0.6 M ZnCl_2 . Bath composition: basic (except the variables, ZnCl_2 and FeCl_2); parameters: c.d. 30 mA cm^{-2} , temp. 43°C , pH 3, time 10 min. Key: (-----) Zn(%), (—) Ni(%), (—) Fe(%).

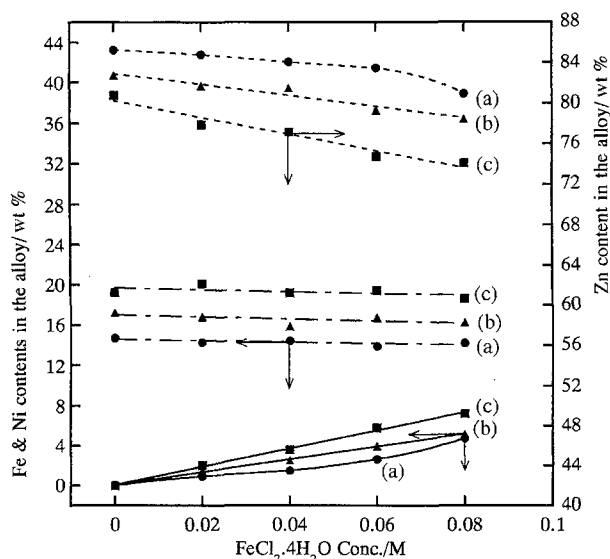


Fig. 5. Effect of ferrous chloride concentration in the bath on electrodeposited Zn-Ni-Fe alloy composition, from baths containing: (a) 0.3, (b) 0.4 and (c) 0.5 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. Bath composition: basic (except the variables, NiCl_2 and FeCl_2); parameters: c.d. 30 mA cm^{-2} , temp. 43°C , pH 3, time 10 min. Key: (-----) Zn(%), (— · —) Ni(%), (—) Fe(%).

This may be attributed to the decrease in the overpotential of iron deposition due to the increasing $\text{Ni}^{2+}/\text{Zn}^{2+}$ molar ratio in the bath.

Under the same electrolysis conditions, the surface appearance of Zn-Ni-Fe alloy deposits was brighter and more uniform in comparison with only Zn-Ni

Table 2. The effect of metal ions concentration on cathodic current efficiency

Run	Metal ions concentration*			Cathodic current efficiency/%
	Zn^{2+}/M	Ni^{2+}/M	Fe^{2+}/M	
1(i)	0.6	0.4	0.00	92.9
(ii)	0.6	0.4	0.02	92.2
(iii)	0.6	0.4	0.04	92.5
(iv)	0.6	0.4	0.06	92.9
(v)	0.6	0.4	0.08	91.7
2(i)	0.5	0.4	0.00	91.5
(ii)	0.5	0.4	0.02	92.6
(iii)	0.5	0.4	0.04	90.1
(iv)	0.5	0.4	0.06	90.2
(v)	0.5	0.4	0.08	89.3
3(i)	0.4	0.4	0.00	88.2
(ii)	0.4	0.4	0.02	88.5
(iii)	0.4	0.4	0.04	86.8
(iv)	0.4	0.4	0.06	85.0
(v)	0.4	0.4	0.08	84.8
4(i)	0.4	0.3	0.00	92.9
(ii)	0.4	0.3	0.02	92.9
(iii)	0.4	0.3	0.04	92.5
(iv)	0.4	0.3	0.06	88.2
(v)	0.4	0.3	0.08	86.4
5(i)	0.4	0.5	0.00	84.3
(ii)	0.4	0.5	0.02	79.2
(iii)	0.4	0.5	0.04	78.2
(iv)	0.4	0.5	0.06	77.6
(v)	0.4	0.5	0.08	76.8

* The other plating parameters are constant, as shown in Figs 4 and 5.

deposits. Bright and smooth Zn-Ni-Fe alloy coatings were obtained from baths containing equal molar ratio of $\text{Ni}^{2+}/\text{Zn}^{2+}$ (0.4 M for each) with Fe^{2+} (0.02 to 0.08 M).

The cathodic current efficiency of both Zn-Ni and Zn-Ni-Fe alloys depends on the $\text{Zn}^{2+}/\text{Ni}^{2+}$ ratio. However, the cathodic current efficiency decreased slightly with increasing ferrous chloride content in the bath, as indicated in Table 2.

3.2. Effect of current density

The effect of current density on Zn-Ni-Fe deposits was examined in the range $10\text{--}50 \text{ mA cm}^{-2}$. Bright deposits were obtained at current density greater than 20 mA cm^{-2} .

Figure 6 illustrates the influence of current density in the composition of Zn-Ni-Fe deposits. The nickel content is generally not affected significantly over a wide range of the tested current densities (except at 10 mA cm^{-2}). A similar tendency has been reported by Fratesi and Roventi [8] and Fukushima *et al.* [9] in their investigations on Zn-Ni alloy deposition. However, the deposit iron content increases with increasing current density.

The cathodic current efficiency increased with increasing current density up to 30 mA cm^{-2} . However, the cathodic current efficiency decreased slightly with further increase in current density, as shown in Table 3. The low value of cathodic current efficiency, at 10 mA cm^{-2} , was due to the increased hydrogen reduction [8].

3.3. Effect of pH

A bright and uniform appearance of the Zn-Ni-Fe alloy coating was obtained in pH range of 1–3. Higher pH (>4) tended to give hazy and mossy deposits and

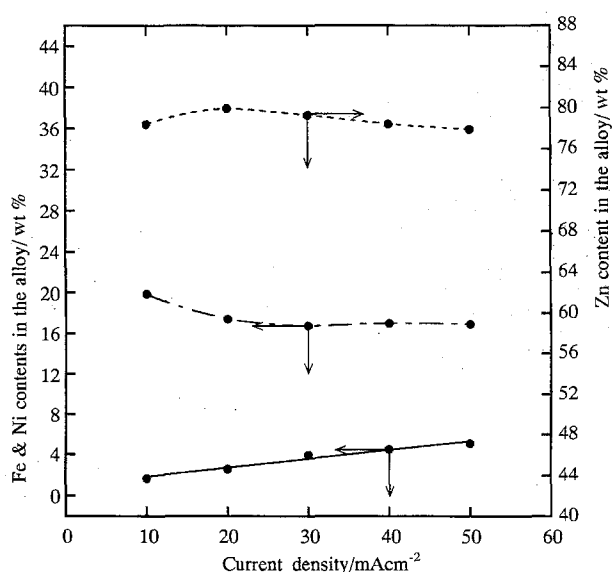


Fig. 6. Effect of current density on electrodeposited Zn-Ni-Fe alloy composition. Parameters: basic bath composition, temp. 43°C , pH 3, time 10 min. Key: (-----) Zn(%), (— · —) Ni(%), (—) Fe(%).

Table 3. The effect of current density* on cathodic current efficiency

Run	Current density /mA cm ⁻²	Cathodic current efficiency /%
1	10	76.5
2	20	84.2
3	30	85.0
4	40	82.3
5	50	81.2

* The other plating parameters are constant, as shown in Fig. 6.

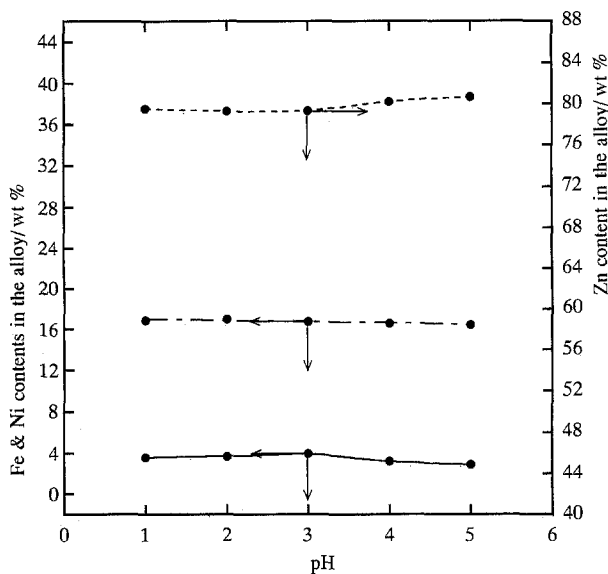


Fig. 7. Effect of pH on electrodeposited Zn-Ni-Fe alloy composition. Parameters: basic bath composition, c.d. 30 mA cm⁻², temp. 43 °C, time 10 min. Key: (-----) Zn(%), (-.-.-) Ni(%), (—) Fe(%).

indicated very poor stability of the bath. This implies decomposition of the electrolyte due to precipitation of ferrous and ferric hydroxides during the plating process.

pH had no effect on the deposit composition, as shown in Fig. 7. Decreasing the pH from 3 to 1 reduced the cathodic current efficiency considerably, as indicated in Table 4. This may be due to the increase in hydrogen reduction with decreasing pH.

Table 4. The effect of pH* on cathodic current efficiency

Run	pH	Cathodic current efficiency /%
1	5†	96.6
2	4†	90.1
3	3	85.0
4	2	78.7
5	1	75.4

* The other plating parameters are constant, as shown in Fig. 7.

† At these pH values, the bath stability is very poor.

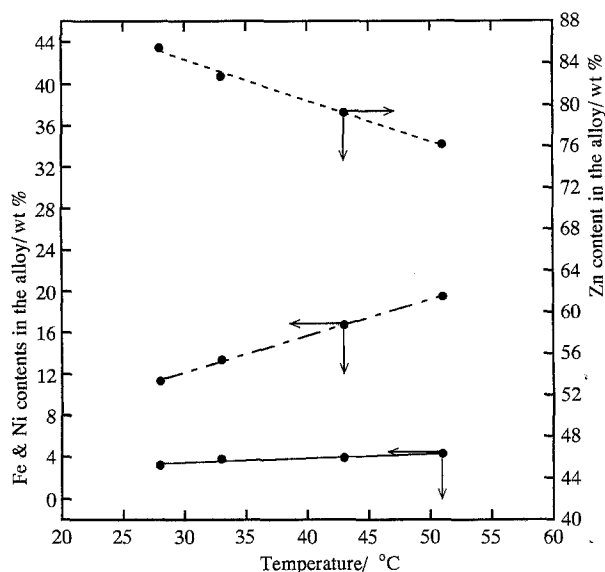


Fig. 8. Effect of temperature on electrodeposited Zn-Ni-Fe alloy composition. Parameters: basic bath composition, c.d. 30 mA cm⁻², pH 3, time 10 min. Key: (-----) Zn(%), (-.-.-) Ni(%), (—) Fe(%).

3.4. Effect of bath temperature

Bright, smooth and adherent Zn-Ni-Fe deposits were obtained at temperatures higher than 33 °C in the range 28–51 °C. The bath temperature also played an important role in the deposit composition of Zn-Ni alloys [3,8] and of Fe-Ni and Fe-Ni-Co alloys [10].

Figure 8 illustrates the influence of temperature in the composition of Zn-Ni-Fe deposits. The nickel content increases strongly with increase in temperature, but the iron content increases only slightly. Increase in alloy nickel content with increasing temperature may be attributed to a decrease in the overpotential for nickel deposition.

There is a gradual decrease in cathodic current efficiency with increasing temperature from 28 to 51 °C, as indicated in Table 5. This may be attributed to an increase in hydrogen reduction at higher temperatures.

3.5. Hull cell test

The surface brightness of electrodeposited Zn-Ni and Zn-Ni-Fe coatings on brass substrate was examined at 45 °C and 54 °C, as shown in Figs 9 and 10, respectively. The basic bath composition (Table 1) was used

Table 5. The effect of bath temperature* on cathodic current efficiency

Run	Temperature /°C	Cathodic current efficiency /%
1	28	90.1
2	33	86.1
3	43	85.0
4	51	78.0

* The other plating parameters are constant, as shown in Fig. 8.

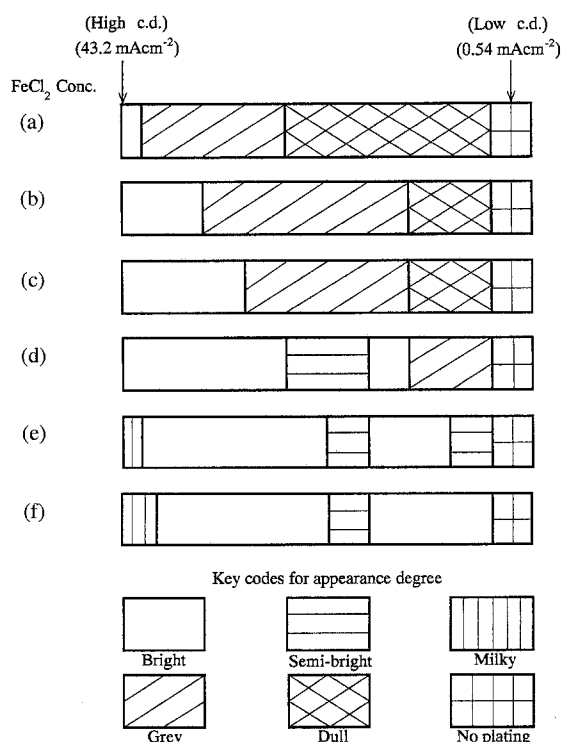


Fig. 9. Effect of ferrous chloride addition into the basic bath on the surface appearance brightness of electroplated Zn–Ni and Zn–Ni–Fe alloy coatings by using a Hull cell at 45 °C. FeCl₂ concentration: (a) 0.00, (b) 0.02, (c) 0.04, (d) 0.06, (e) 0.08 and (f) 0.10 M.

for the Hull cell test with and without ferrous chloride at pH 3.

Figures 9 and 10 show that the Zn–Ni deposits were dull or grey on all the plated area, except at the highest current density. The surface brightness area of Zn–Ni–Fe alloy deposits increased with increasing ferrous chloride concentration. Approximately all the surface area of the Zn–Ni–Fe deposit was bright when electroplating with 0.1 M FeCl₂ at 45 °C (Fig. 9) and 0.06 to 0.08 M FeCl₂ at 54 °C (Fig. 10).

4. Conclusion

The electrodeposition of Zn–Ni–Fe alloys from acidic chloride electrolyte exhibited the phenomenon of anomalous codeposition. The ternary Zn–Ni–Fe deposits had brighter surface appearance in

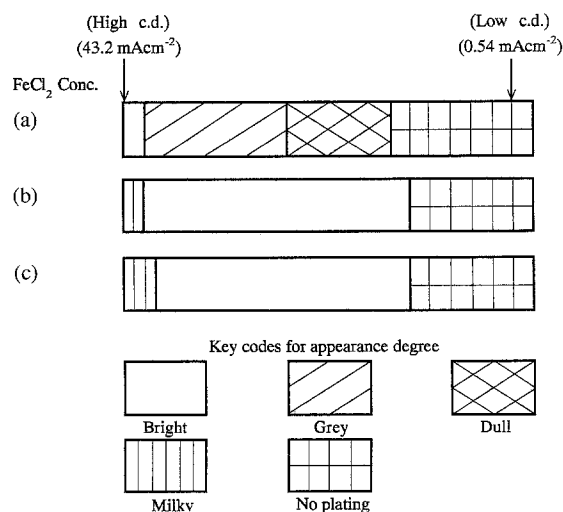


Fig. 10. Effect of ferrous chloride addition into the basic bath on the surface appearance brightness of electroplated Zn–Ni and Zn–Ni–Fe alloy coatings by using a Hull cell at 54 °C. FeCl₂ concentration: (a) 0.00, (b) 0.06 and (c) 0.08 M.

comparison with binary Zn–Ni deposits, without any organic brighteners. Bright Zn–Ni–Fe alloy coatings were obtained from baths containing an equimolar ratio of Ni²⁺/Zn²⁺ (each 0.4 M) with (0.02–0.08 M) Fe²⁺ and also at temperature above 33 °C, current density above 20 mA cm⁻² and pH below 3.

The iron content in the Zn–Ni–Fe deposits increased with increasing Ni²⁺/Zn²⁺ molar ratio with the same FeCl₂ concentration.

References

- [1] D. E. Hall, *Plat. Surf. Finish.* **71** (1983) 59.
- [2] G. F. Hsu, *ibid.* **72** (1984) 52.
- [3] V. Raman, M. Pushpavanam, S. Jayakrishnan and B. A. Sheno, *Met. Finish.* **81** (1983) 85.
- [4] J. A. Dini and H. R. Johnson, *ibid.* **77** (1979) 53.
- [5] R. Albalat, E. Gomez, C. Muller, M. Sarret, E. Valles and J. Pregonas, *J. Appl. Electrochem.* **20** (1990) 635.
- [6] V. B. Singh, P.K. Tikoo, V. N. Singh and M. M. Singh, *J. Electrochem. Soc., India* **25** (1976) 115.
- [7] A. Brenner, 'Electrodeposition of Alloys', vol. 1, Academic Press, New York and London (1963).
- [8] R. Fratesi and G. Roventi, *J. Appl. Electrochem.* **22** (1992) 657.
- [9] H. Fukushima, T. Akiyama, K. Higashi, R. Kammel and M. Karimkhani, *Metall.* **42** (1988) 242.
- [10] N. Phan, M. Schwartz and K. Nobe, *Plat. Surf. Finish.* **76** (1988) 46.