
Potentiodynamic study of anodic dissolution of Zn–Ni alloy

A. Petrauskas,
A. Češūnienė,
L. Grincevičienė and
E. Matulionis

*Institute Of Chemistry,
A. Goštauto 9,
LT-2600 Vilnius, Lithuania*

Anodic behaviour of electrolytic Zn–Ni alloy platings obtained from acetate-chloride electrolyte has been investigated under potentiodynamic conditions as a function of the Zn/Ni ratio. The Zn/Ni ratio in the alloy has been determined to be responsible for its phase composition. The data obtained show that in the potentiodynamic curves, in the region of potentials $-0.35 \div -0.45$ V Zn dissolves from phase γ , in the region of potentials $-0.25 \div -0.35$ V from phase β , while the peak of Ni dissolution is located in the region of positive potentials $0.6 \div 0.8$ V. Dissolution of phase η of Zn–Ni alloy occurs in a chromating solution, while phases γ and β become passivated in it.

Key words: electroplated Zn–Ni alloy, cyclic voltammetry, anodic dissolution, acetate-chloride electrolytes

INTRODUCTION

Coatings of pure Ni, due to their allergic action, nowadays lose their demand in domestic equipment. Decorative Zn coatings corrode rapidly in the atmosphere, and among the methods protecting them from corrosion chromating is popular. However, today chromated films also become rejected more and more often due to the same reason, *i. e.* they fail to comply with ecological requirements. This problem can be solved by using Zn–Ni alloys containing less Ni. In this case a harmful chromated film is absent, but corrosion resistance of the coatings is higher.

It has been determined that by changing the Zn^{2+}/Ni^{2+} ratio in the electrolyte one can obtain coatings containing different amounts of Ni. According to [1, 2], the highest corrosion resistance is characteristic of the coatings of alloys containing $10 \div 20\%$ Ni. They are distinguished not only by slower corrosion as compared with Zn coatings, but also by anodic protection in respect of steel products. Despite the fact that the first investigations dealing with the deposition mechanism of Zn–Ni, Zn–Co, Zn–Fe alloys were started as early as the middle of the last century, works in this field are still carried out [3–16]. At present, the main attention is paid to the phase composition of the alloys. The Zn–Ni alloy has been found to contain η , α , β and γ phases, their quantities depending on the ra-

tio Ni/Zn in the alloy. Existence of the phases has been confirmed by voltammetric studies [17–21]. When increasing the Zn–Ni alloy potential (E_a), in potentiodynamic curves (PDCs) the peaks of anodic currents (i_a) corresponding to the processes of anodic dissolution of separate Zn–Ni alloy phases have been recorded. According to [18, 19], Zn–Ni alloy exhibits the following four phases: η – 1% Ni solid solution in Zn, α – 30% Zn solution in Ni, β – ZnNi and γ – Ni_5Zn_{21} . The authors of [19] suggest that the formation of β phase occurs in the course of anodic oxidation of γ phase. It is difficult to obtain a Zn–Ni alloy whose PDC of anodic dissolution would exhibit all the four peaks corresponding to the dissolution of the above-mentioned phases of Zn–Ni alloy, as many conditions influence the formation of these phases. Therefore the anodic dissolution PDCs recorded by most authors show only two or three peaks.

In the literature, various opinions can be found on the nature of increased corrosion resistance of Zn–Ni alloys. Some authors suggest that this increase is caused by spontaneous formation of a passivating film on the surface. Such an effect is known to take place during chromating galvanic Zn and Cd coatings. In an opinion of many authors, the increased corrosion resistance of Zn–Ni alloy is determined by its structural peculiarities. The highest corrosion resistance is suggested to be characteristic of Zn–Ni alloy γ phase [17, 18] whose anodic dissolution occurs in the region of the most positive potentials.

** Corresponding author: apetra@ktl.mii.lt

In [25, 26] it is shown that the potential of anodic dissolution of Ni coatings, as a function of the quantity of inclusions in it and of their nature, reflects corrosion resistance of bright Ni platings. When summarizing the presented data, one can maintain that the process of anodic dissolution of electrolytic coatings reflects their corrosion resistance.

In literature [16–21], the mechanism of Zn–Ni alloy electrodeposition, alloy structure and anodic processes are studied best in sulphide and chloride electrolytes containing up to 200 g/l NH_4Cl . However, ammonium ions make the treatment of sewage water in industrial processes very difficult, this being the main reason for a poor perspective of these electrolytes. Therefore, in literature there have appeared works dealing with Zn–Ni alloy electrodeposition from acetate electrolytes containing no ammonium ions [13, 27, 28].

The peaks in the curves of potentiodynamic dissolution of Zn–Ni alloy are marked often in the literature as A, B, C and D peaks [17, 18, 30]. The first peak, observed in the region of the most negative potentials, is attributed to Zn dissolution from phase η , peaks B and C – to Zn dissolution from phases β and α , respectively, and peak D is the peak of Ni oxidation. From the data obtained earlier [28] one cannot say exactly whether Ni oxidation in the potential region of peak D is possible. Therefore the aim of the present work was to study more exactly the processes occurring in different PDC peaks of Zn–Ni alloy.

EXPERIMENTAL

Potentiodynamic studies were performed with a potentiostat PI 50–1 in an ISE-2 thermostated electrochemical cell on a Pt electrode 1 cm^2 in area. Pure Ni was used as an anode. The Ni anode was separated from the cathode by a membrane partition. For preparation of the solutions there were used the following salts: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$, KCl, CH_3COOH , H_3BO_3 . All the reagents used were of no lower qualification than *analytically pure*. All the experiments were performed in electrolytes of the following composition (g/l): I – acetate chloride electrolyte: $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ – 140; KCl – 10, H_3BO_3 – 30; $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ – 0–60; II – sulphate-chloride electrolyte: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ – 150, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – 40, H_3BO_3 – 300; III – sulphate electrolyte: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ – 150, H_3BO_3 – 30. All the data of the potentiodynamic study are referred to the saturated silver chloride electrode.

The Fe electrode as a substrate for Zn–Ni alloy coating was rejected, as under conditions of the stu-

dy it influenced the magnitude of i_a peaks in PDCs because of its anodic dissolution. Authors of the work [18] which deals with a Zn–Ni alloy obtained on Fe substrate and the alloy's anodic dissolution in a chloride electrolyte containing 250 g/l NH_4Cl also reported the influence of Fe on the process.

The quantity of Ni in the alloy 8 μm thick was determined with a JXA–50A microanalyzer. To determine the phase composition of Zn–Ni alloy the XRD method was used.

RESULTS AND DISCUSSION

In Figure 1, PDCs obtained on electrolytic Ni, Zn and Zn–Ni alloy coatings are presented. Anodic dissolution of pure zinc occurs at potentials by 0.08V more negative as compared with the η phase of Zn–Ni alloy (Fig. 1, curves 1 and 5). The coatings deposited from electrolyte I containing 1g/l ZnCl_2 consist of 28.1% Zn and 71.9% Ni (Fig. 1, curve 3). The PDCs of the coatings exhibit only peak D and peak Ni i_a at 0.65V. After increasing the ZnCl_2 concentration in the electrolyte of plating up to 2 g/l the coating was found to contain 63.2% of Zn and 36.8% of Ni, and PDC with it did not show any peak of Ni anodic oxidation (Fig. I, curve 4). This is indicative of all Ni presence in the alloy. As is seen from comparison of Curves 2 and 3 in Fig. 1, anodic dissolution of pure Ni occurs at the potentials by 0.1V more positive as compared with Ni dissolution from Zn–Ni alloys. This shows that under these conditions Ni is not pure and behaves similarly as bright electrolytic Ni platings [25, 26].

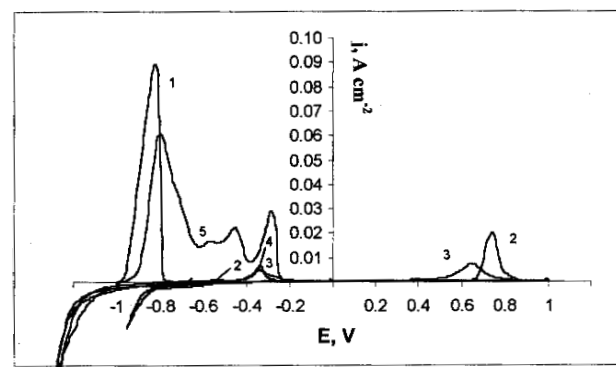


Fig. 1. Potentiodynamic curves (PDC) obtained in coating deposition electrolytes: 1 – for pure Zn; 2 – for pure Ni; 3, 4, 5 – for Zn–Ni from electrolyte I; 3 – with 1 g/l ZnCl_2 (28.1% Zn and 71.9% Ni); 4 – with 2 g/l ZnCl_2 (63.2% Zn and 36.8% Ni); 5 – with 20 g/l ZnCl_2 (86.5% Zn and 13.5% Ni). Coating deposition $i_c = 10 \text{ mA/cm}^2$, $t = 6 \text{ min}$, $T = 20 \text{ }^\circ\text{C}$, E sweeping rate (v) 5mV/s. pH, T and v is the same in all Figures

Anodic investigations were performed *in situ*, while Zn and Ni analysis on a JXA-50A microanalyzer and phase composition by XRD were performed *ex situ* in the course of 24 hours. Therefore Zn-Ni alloy stability in time has been investigated.

The Zn-Ni alloy coating deposited under galvanostatic conditions was kept in the air for 14 and 48 hours. Then the coating was dissolved anodically in the electrolyte of plating under potentiodynamic conditions. As is seen from the data of Fig. 2, PDCs of Zn-Ni alloy anodic dissolution obtained immediately after its deposition and those obtained after 14 and 48 hours coincide in the limits of error. This enables us to state that Zn-Ni alloy does not undergo phasic changes at room temperature during the first 48 hours after electrodeposition.

With increasing Zn^{++} concentration in the electrolyte [29], the quantity of zinc in the alloy obtained from acetate-chloride electrolyte augments. An increase in Zn quantity leads to a decrease in phase η quantity (peak A) and correspondingly to a decrease in the quantities of other phases in the alloy. As has been determined by XRD method, in the coating obtained from acetate-chloride electrolyte with Zn portion $\geq 90\%$ the η phase and with $Zn \leq 80\%$ the γ phase prevails*. The other phases are of negligible quantities. According to Swathirajam [17], in peak A dissolution of Zn from η and β phases occurs, but this opinion was rejected by the authors of [18] who have showed that dissolution of Zn occurs only from η phase. Peak D is attributed to Ni oxidation.

To obtain a coating with a single phase that would dissolve in peak D, an electrolysis was performed

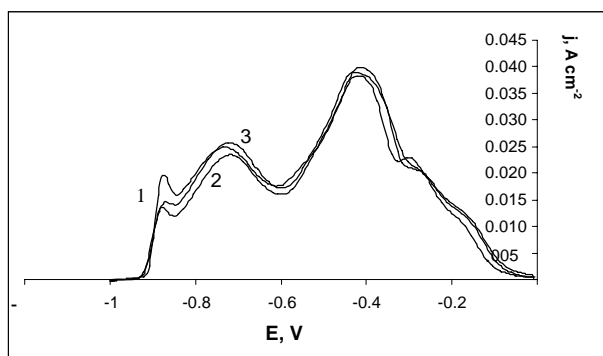


Fig. 2. PDC of the coatings obtained from electrolyte I with 10 g/l $ZnCl_2$ (78.8% Zn and 21.2% Ni). $i_c = 2.5 \text{ mA/cm}^2$, $t = 30 \text{ min}$. 1 – just after deposition; 2 – after 14 hours; 3 – after 48 h of keeping in the air

* The studies and data analysis have been performed by Dr R. Juškėnas.

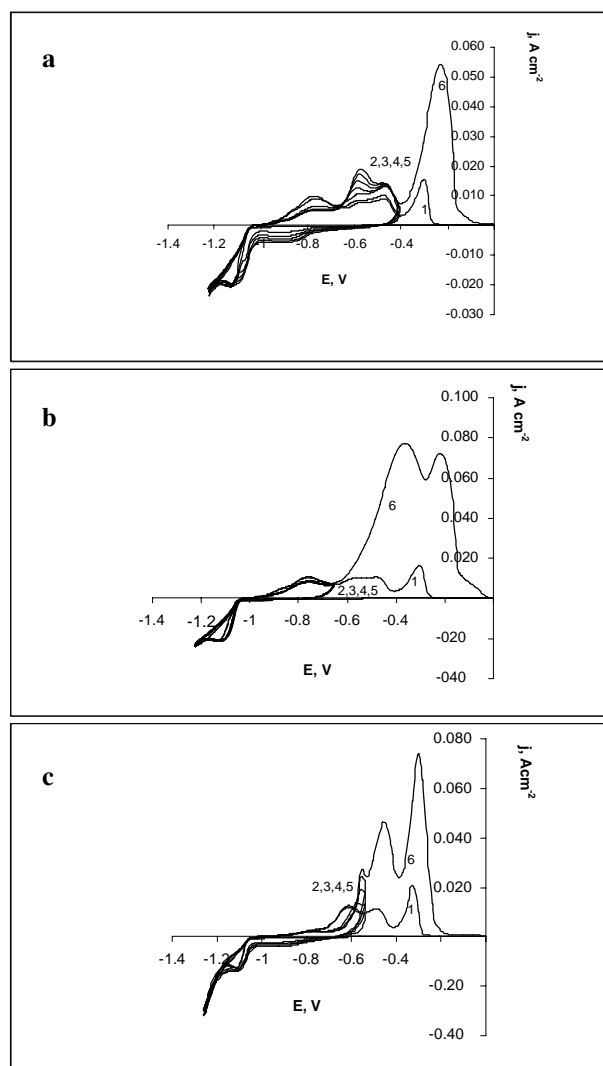


Fig. 3. Cyclic PDC of coatings obtained from electrolyte I with 20 g/l $ZnCl_2$: a) the 1st cycle from Pt 0.3 V ÷ -1.23 V ÷ 0.0 V; 2) 6 cycles from 0.0 V ÷ -1.23 V ÷ -0.4 V ÷ -1.23 V; the 7th cycle from -1.23 V ÷ 0.0 V; b) the 1st cycle from Pt 0.3 V ÷ -1.23 V ÷ 0.0 V; 2-6 cycles from 0.0 V ÷ -1.23 V ÷ -0.65 V ÷ -1.23 V; the 7th cycle from -1.23 V ÷ 0.0 V; c) the 1st cycle from Pt 0.3 V ÷ -1.23 V ÷ 0.0 V; 2-6 cycles from 0.0 V ÷ -1.23 V ÷ 0.53 V ÷ -1.23 V; the 7th cycle from ÷ -1.23 V ÷ 0.0 V

potentiodynamically (Fig. 3, a) by dissolving the other phases anodically during each cycle. For this purpose, E was swept to anodic side up to the beginning of peak D, *i. e.* up to -0.45V. After five such cycles, when sweeping E up to 0.0V a large peak D was obtained. According to the data of literature [17], this is a peak of Ni anodic dissolution. Analysis of such a coating obtained after 25 cycles showed 43.5% of Ni and 56.5% of Zn, *i. e.* Zn:Ni ~ 1:1. This ratio lets us to suggest that the coating obtained is ZnNi β phase.

For a coating deposited in the same way, but with anodic dissolution performed up to -0.65V, *i.*

e. up to the beginning of occurrence of peak C, after five cycles the E sweep up to 0V gives rise to large peaks C and D (Fig. 3, b).

For a coating deposited analogously, but with E sweep up to -0.53 V, peak C is smaller as compared with peak D (Fig. 3, c). In the first case only η phase was dissolved, whereas in the second case partial removal of the phase that can be dissolved in the potential region of phase C occurred.

The prevalence of phases η and γ in the coatings obtained from acetate-chloride electrolyte with 20g/l ZnCl_2 allows to suggest that in the potential region of peak C the dissolution of Zn from phase γ occurs. After removing in the course of anodic dissolution the portion of Zn from phase γ , the β phase is obtained, which can be dissolved anodically at more positive potentials in the region of peak D.

When the coating was deposited by 25 cycles of potentiodynamical sweep of E from -1.230 to -0.4 V and then E was swept up to 1.23 V, a large peak D at -0.3 V and a small peak at 0.7 – 0.8 V were obtained. The latter peak can be attributed to anodic dissolution of Ni. (Fig. 4). During Zn dissolution from the alloy, the portion of Ni is most probably removed from the electrode in a non-electrochemical dissolution way.

The Ni dissolution peak for Zn–Ni alloy coatings can be obtained only in the presence of a large quantity of Ni (79.8%) in it. In this case the portion of Ni that is not bonded with Zn remains on the substrate being plated (Fig. 1). Even as large a portion of Ni as 36.8% in the coating does not cause a Ni i_a peak in PDC.

When polarizing pure Ni anodically in a sulphate electrolyte (III) without Cl^- ions, the PDC does not exhibit a Ni i_a peak. Under these conditions passivation of Ni occurs and with increasing the po-

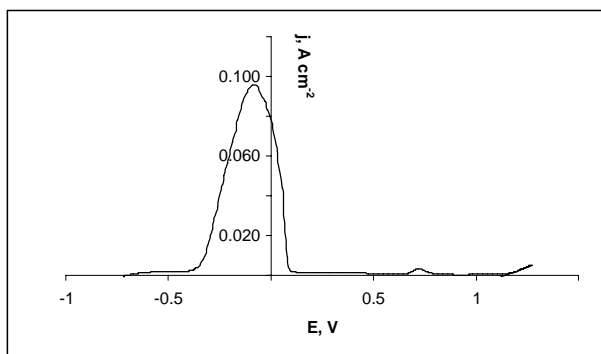


Fig. 4. PDC of Zn–Ni alloy deposited by 25-fold cyclical potential sweep in an interval from $0.4 \div -1.23\text{V} \div -0.4\text{V}$ (as in Fig. 3, a)

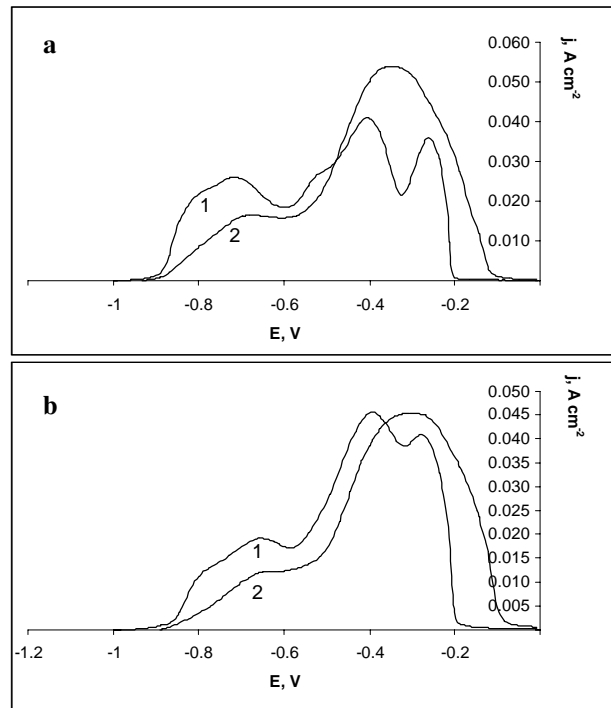


Fig. 5. PDC on Zn–Ni alloy deposited $i_c = 20 \text{ mA/cm}^2$, $t = 3 \text{ min}$: a) 1, 2 – in electrolyte I with 30 g/l ZnCl_2 (84.3% Zn and 15.7% Ni). E was swept: 1 – in the deposition electrolyte; 2 – in electrolyte III; b) 1, 2 – in electrolyte II with 30 g/l ZnCl_2 (82.3% Zn and 17.7% Ni). E was swept: 1 – in the deposition electrolyte; 2 – in electrolyte III

tential up to 1.16 V the evolution of O_2 begins. Therefore anodic dissolution of Zn–Ni alloy was performed in a sulphate electrolyte with and without Cl^- ions. For the study, coatings were deposited from electrolytes I and II. When sweeping E (Fig. 5) in both cases, *i. e.* with and without Cl^- ions, anodical dissolution of Zn–Ni alloy occurs. In the event of E sweeping in sulphate electrolyte without Cl^- ions, the peaks in PDC are shifted to the direction of more positive potentials. This allows to suggest that it is not Ni oxidation that occurs in i_a peak D.

In order to increase the corrosion resistance of electrolytic Zn coatings they are chromated. During the formation of a chromate film a portion of Zn becomes dissolved [30]. The data obtained show that at the presence of small quantities (7.4–8.3%) of Ni in the alloy the PDCs exhibit a large i_a peak A (Fig. 6, a and b) corresponding to Zn dissolution from phase η . In the coatings with 15.7% of Ni the γ phase prevails and PDC show large peaks A and D.

When keeping a Zn–Ni alloy with a portion of Zn $>90\%$ in the chromating solution of (Likonda 2 AT), chemical dissolution of the η phase occurs, proved by an E sweep resulting in a PDC with a

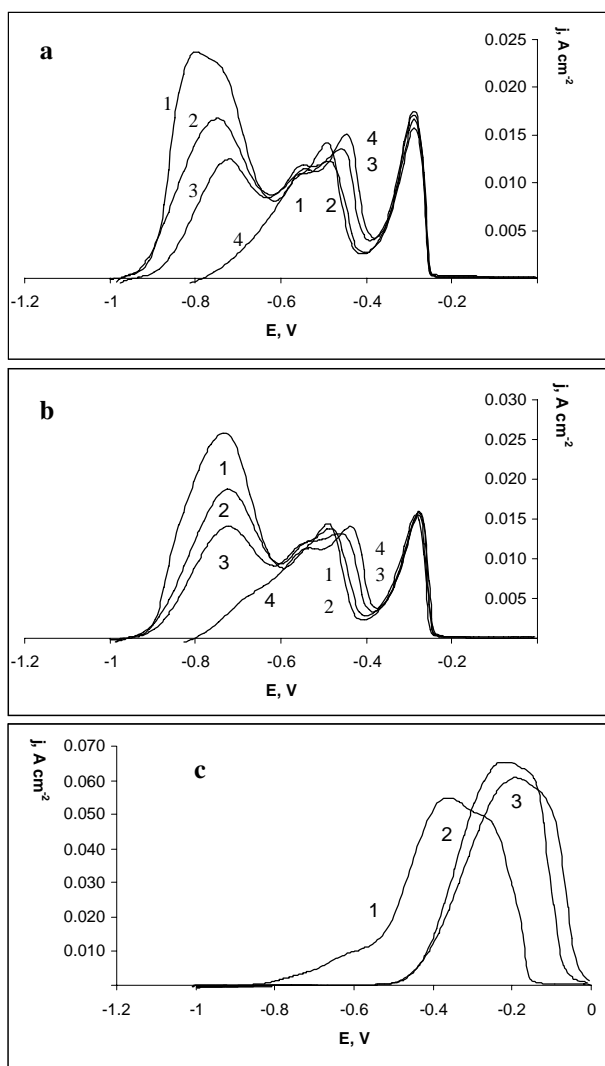


Fig. 6. PDC on Zn–Ni alloy deposited from electrolyte I (a and c – with 30 g/l; b – with 60 g/l ZnCl₂) as a function of the duration of keeping in chromatizing solution (Likonda 2AT): 1 – 0.0; 2 – 3; 3 – 6; 4 – 12 min. a – $i_c = 10$ mA/cm², $t = 6$ min (91.7% Zn and 8.3% Ni). b – $i_c = 10$ mA/cm², $t = 6$ min (92.6% Zn and 7.4% Ni). c – $i_c = 20$ mA/cm², $t = 3$ min (84.3% Zn and 15.7% Ni)

distinct decrease in the quantity of this phase. The coatings containing large quantities of phase γ (Fig. 6, c) under these conditions are not dissolved chemically. In the chromatizing solution the γ phase undergoes passivation, and therefore a double peak (C+D) of anodical dissolution does not decrease and only shifts to the direction of more positive potentials.

CONCLUSIONS

1. For anodical dissolution of Zn–Ni alloy under potentiodynamic conditions, the peak of Ni dissolution is absent in PDC up to 0.7 V.

2. In the potential region from –0.35 to –0.45 V (peak C) Zn dissolves from γ phase and in the region from –0.25 to –0.35 V from β phase.

3. In the chromatizing solution Likonda 2AT Zn has been found to dissolve from phase η whereas phase γ undergoes passivation.

Received 8 May 2002
Accepted 29 July 2002

References

1. D. E. Hall, *Plating and Surface Finish*, **70** (11), (1983).
2. J. Barcelo Garcia, M. Sarret, C. Müller and J. Pregonas, *J. Appl. Electrochem.*, **24**, 1249 (1994).
3. Brenner A., *Electrodeposition of Alloys*, Academic Press, Vol. 1, P. 77, New York and London (1963).
4. Б. П. Юрьев и Л. В. Волков, *Журнал прикладной химии*, **38** (1), 66 (1965).
5. Л. В. Волков, *Тр. Ленинград. политехн. ин-та*, **304**, 90 (1970).
6. Б. Г. Карбасов и Н. Н. Исаев, *Электрохимия*, **22** (3), 427 (1986).
7. Н. С. Григорян, В. Н. Кудрявцев and П. А. Ждан и др., *Защита металлов*, **25**, 289 (1989).
8. Ж. П. Шальтене and А. В. Петраuskas, *Защита металлов*, **30**, 315 (1994).
9. St. Rashkov, M. Petrova and Chr. Bozhkov, *J. Appl. Electrochem.*, **20** (1), 11 (1990).
10. Chr. Bozhkov, M. Petrova and St. Rashkov, *J. Appl. Electrochem.*, **20** (1), 17 (1990).
11. J. Balej, J. Divisek, H. Schmitz and J. Mergel., *J. Appl. Electrochem.*, **22** (8), 705 (1992).
12. F. J. Fabri Miranda, O. E. Barcia, S. L. Diaz, O. R. Mattos and R. Wiart, *Electrochem. Acta*, **41** (7–8), 1041 (1996).
13. S. S. Abd El Rehim, E. E. Foad, S. M. Abd El Wahab and H. Hamdy Hassan, *Electrochem. Acta*, **41** (9), 1413 (1996).
14. F. J. Fabri Miranda, O. E. Barcia, O. R. Mattos and R. Wiart, *J. Electrochem. Soc.*, **144** (10), 3441 (1997).
15. R. Fratesi, G. Roventi, G. Giuliani and C. R. Tomachuk, *J. Appl. Electrochem.*, **27** (9), 1088 (1997).
16. T. Ohtsuka and A. Komori, *Electrochem. Acta*, **43** (21–22), 3269 (1998).
17. S. Swathijaran, *J. Electrochem. Soc.*, **133** (4), 671 (1986).
18. F. Elkhabati, M. Sarret and C. Müller., *J. Electroanal. Chem.*, **404** (1), 45 (1996).
19. F. Elkhabati, M. Benballa, M. Sarret and C. Müller, *Electrochem. Acta*, **44** (10), 1645 (1999).
20. A. V. Velichenko, J. Portillo, M. Sarret and C. Müller, *Electrochem. Acta*, **44** (19), 3377 (1999).
21. C. Müller, M. Sarret and M. Benballa, *Electrochem. Acta*, **46** (18), 2811 (2001).
22. L. Felloni, R. Fratesi, E. Quadrini and G. Roventi, *J. Appl. Electrochem.*, **17** (3), 574 (1987).
23. В. П. Артамонов, *Защита металлов*, **25**, 873 (1989).

24. R. Ramanauskas, *Appl. Surf. Sci.*, **153**, 53 (1999).
25. A. Петраускас и Р. Гальдикене, *Chemija*, **3**, 57 (1994).
26. A. Петраускас и Р. Гальдикене, *Chemija*, **2**, 43 (1996).
27. A. Петраускас и Л. Гринцявичене, *Заццта*, **37** (6), 641 (2001).
28. A. Petrauskas, L. Grincevičienė, A. Češūnienė and E. Matulionis, *Cheminė technologija*, 2002 (in press).
29. L. Grincevičienė, S. Jakobsonas ir J. Matulis, *Lietuvos TSR Mokslų akademijos darbai*, B serija, **4** (95), 65–76 (1976).
30. R. Šarmaitis, V. Rezaitė, V. Dikinis ir L. Demčenko, *Cheminė technologija*, **1** (14), 48 (2000).

**A. Petrauskas, A. Češūnienė, L. Grincevičienė,
E. Matulionis**

**Zn–Ni LYDINIO ANODINIO TIRPIMO POTENCIODI-
NAMINĖMIS SĄLYGOMIS TYRIMAI**

S a n t r a u k a

Potenciodinaminėmis sąlygomis ištirta anodinė elgsena elektrolitinių Zn–Ni lydinio dangų, gautų iš acetatinio-chloridinio elektrolito priklausomai nuo Zn ir Ni santykio jose. Nustatyta, kad Zn ir Ni santykis lydinyje sąlygoja jo fazinę sudėtį. Gauti duomenys rodo, kad potenciodinaminių kreivių i_a smailės C srityje Zn tirpsta iš γ fazės, D smailėje iš β fazės, o Ni tirpimo i_a smailė yra teigiamų potencialų 0,6–0,8 V srityje. Zn–Ni lydinio η fazė tirpsta chromatavimo tirpale, o γ ir β fazės jame pasyvuojasi.