J Appl Electrochem (2009) 39:1313-1321
DOI 10.1007/s10800-009-9801-x

ORIGINAL PAPER

ZnNi alloy electrodeposition from acid baths containing sorbitol or glycerol and characterization of ZnNi deposits

E. M. de Oliveira · W. Rubin · I. A. Carlos

Received: 3 July 2008 / Accepted: 14 January 2009 / Published online: 5 February 2009

Abstract The influence of sorbitol or glycerol on the electrodeposition of ZnNi alloys and on the morphology, composition and structure of the ZnNi deposits was investigated. The highest current efficiency (CE), around 90%, was obtained in the presence of glycerol in the potential range from approximately −1.30 V to −1.40 V, while in the presence of sorbitol or absence of either polyalcohol the CE was 82–85%, for the same potential range. Scanning electron microscopy (SEM) analysis showed that ZnNi deposition at −1.26 V or −1.40 V from a bath with sorbitol led to the formation of more compact deposits than with glycerol. Energy dispersive X-ray spectroscopy (EDS) analysis showed that the Ni content in the deposit obtained in the presence of sorbitol remained in the range of 7–9.5 wt% Ni, over a large range of deposition conditions. On the other hand, ZnNi deposits with variable Ni content (5.5–19.5 wt% Ni) were obtained from baths with glycerol or without either polyalcohol, by shifting the deposition potential. All ZnNi deposits showed uniform distribution of the elements Zn and Ni. X-ray analysis of ZnNi deposits obtained from plating baths with and without polyalcohol's at −1.26 and −1.40 V presented the γ, γ^1 and Pt_3–Zn phases.

Keywords Electrodeposited ZnNi alloys · Sorbitol-boric complex · Glycerol · Potentiodynamic · Scanning electronic microscopy · X-ray diffraction

---

E. M. de Oliveira · W. Rubin · I. A. Carlos (✉)
Departamento de Química, Universidade Federal de São Carlos, CP 676, 13565-905 Sao Carlos, SP, Brazil
e-mail: diac@ufscar.br

1 Introduction

ZnNi alloys are used mainly as a surface layer to protect steel against corrosion. This alloy has replaced Zn, Cd, or Cr deposits used for this purpose [1]. The Zn deposit has the disadvantage of rapid dissolution [2, 3], while Cd and Cr are highly toxic [3–5]. The ZnNi alloys provide good sacrificial protection when the Ni content in the deposit is in the range 10–15 wt% [6] or 15–18 wt% [3].

Zn and Ni co-deposition is of the anomalous type. Moreover, the electrodeposited ZnNi alloys show three main phases, η ($Zn_{89}Ni_1$), γ ($Zn_{21}Ni_5$) and α (Zn_2Ni_5) [7]. According to some authors [8] the δ ($Zn_{22}Ni_3$) and β (ZnNi) phases are only observed when obtained by a metallurgical method. However, some research has demonstrated that δ and β phases can be observed in electrodeposited ZnNi alloy [9, 10].

ZnNi alloys have been obtained from alkaline or acid plating baths. In both cases it is possible to deposit ZnNi alloy with the required percentage of Ni, but acid plating is utilized more often, owing to its high deposition rate and cathodic efficiency. Moreover, this bath does not require Ni complexing agents, leading to a less expensive deposition process than alkaline plating. On the other hand, it is reported that the alkaline bath produces a better distribution of Ni in the alloy electrodeposited [11].

The acid plating baths are based on solutions of chloride [2, 5, 8, 10, 12–24] or sulfate salts [3, 9, 25–28], or both [29, 30]. These baths may contain electrolytes such as ammonium chloride or sulfate [8, 12, 16, 24, 27, 28], boric acid [2, 3, 9, 10, 14, 15, 17, 19, 21, 23, 30, 31], sodium [9, 17] or potassium chloride [10, 13, 15, 23, 24], sodium acetate [10, 28], sodium citrate [3, 9, 27], etc.

There is a strong trend to replace the ammonium chloride by another electrolyte. Although the plating bath containing ammonium chloride is widely used, the removal of nickel from the waste electrolyte is difficult and this has limited its use [11]. Hence, boric acid has been used as a substitute for ammonium chloride with good results. In addition, the ZnNi plating bath contains other additives, usually aromatic or sulfur compounds, for example: aromatic sulfonimides, chlorohydrated imines [16], phenolic derivatives, unsaturated aromatic, aromatic carboxylates [17], *p*-toluenesulfonic acid [19], benzoic acid salts, benzylidene acetone, Na-decylsulfate [29].

Studies on the influence of the polyalcohols sorbitol or glycerol on the electrodeposition of other metals or alloys [32, 33] have shown excellent results, with the formation of smooth deposits that do not burn, even in the region of high hydrogen evolution. Crucially, these organic additives are not toxic.

In this article the effect of adding sorbitol or glycerol to a ZnNi alloy plating bath containing boric acid is described. The electrodeposition process was studied potentiodynamically and the morphology, composition and structure of the ZnNi deposits were determined by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD), respectively.

2 Experimental details

All experiments were carried out at room temperature (25 °C), in a glass single-compartment cell of 50 mL capacity. A platinum disc (0.16 cm^2), a platinum plate (~2 cm^2) and a calomel electrode (1 M KCl) were employed as working, auxiliary, and reference electrodes, respectively. Immediately before each experiment, the Pt working electrode was ground with 0.3 μm alumina, immersed in concentrated sulfuric–nitric acid solution and then rinsed with deionized water. The ZnNi alloy electrodeposits were obtained in the baths described in Table 1. The ZnNi electrodeposition baths were a compound of Watts bath traditional (0.22 M $NiSO_4$ + 0.33 M $NiCl_2$ + 0.13 M H_3BO_3), used in Ni electrodeposition, +0.55 $ZnSO_4$. For formation of complex boric–sorbitol in the proportion 1:2, 0.52 M sorbitol was added to the bath. This bath, named ZnNi2, contained 0.26 M H_3BO_3. The pH of the freshly prepared plating baths, with or without glycerol ($C_3H_8O_3$), were ~4.0 and ~3.9. However, it was found that after some deposition voltammetric cycles the pH of the baths decreased to ~pH 3.0. Therefore, the pH of ZnNi baths, with or without glycerol, as prepared, were adjusted to ~3.0 with H_2SO_4. The plating baths containing sorbitol ($C_6H_{14}O_6$) had a pH of 2.80 (0.26 M sorbitol); 2.60 (0.39 M sorbitol) and 2.50 (0.52 M sorbitol). pH was measured with a Micronal B474 pH meter. Potentiodynamic curves were recorded using a PARC electrochemical system consisting of a model 173 potentiostatic/galvanostat. SEM and EDS measurements were made with a Philips FEG XL 30 microscope. XRD patterns of the ZnNi deposit surface were produced with Cu Kα radiation (1.5406 Å), using an X-ray Rigaku Rotaflex RU200B goniometer, in 2θ scanning mode (fixed *ω* = 2°).

Table 1 Composition of baths

Baths
1. ZnNi1
2. ZnNi1 + 0.26 M sorbitol
3. ZnNi1 + 0.39 M sorbitol
4. ZnNi2 + 0.52 M sorbitol
5. ZnNi1 + 0.26 M glycerol
6. ZnNi1 + 0.39 M glycerol
7. ZnNi2 + 0.52 M glycerol

ZnNi1 = 0.55 M $ZnSO_4$ + 0.22 M $NiSO_4$ + 0.33 M $NiCl_2$ + 0.13 M H_3BO_3

ZnNi2 = 0.55 M $ZnSO_4$ + 0.22 M $NiSO_4$ + 0.33 M $NiCl_2$ + 0.26 M H_3BO_3

3 Results and discussion

3.1 Electrochemical studies in the absence of polyalcohol

Figure 1 shows the deposition voltammetric curves of pure metals Zn, Ni, and alloys ZnNi on the Pt electrode. The initial deposition potential ($E_{d,i}$) of the ZnNi alloy (−1.15 V) does not coincide with those of Zn (−1.18 V) and

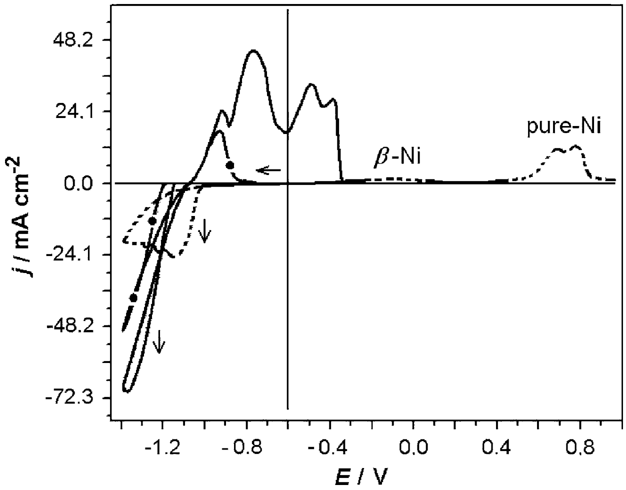

Fig. 1 Voltammetric curves for Pt substrate in 0.55 M $ZnSO_4$ + 0.13 M H_3BO_3 (− • −), 0.22 M $NiSO_4$ + 0.33 M $NiCl_2$ + 0.13 M H_3BO_3 (− −) and ZnNi1 bath (—), Table 1; *υ* = 10 mV s^{-1}

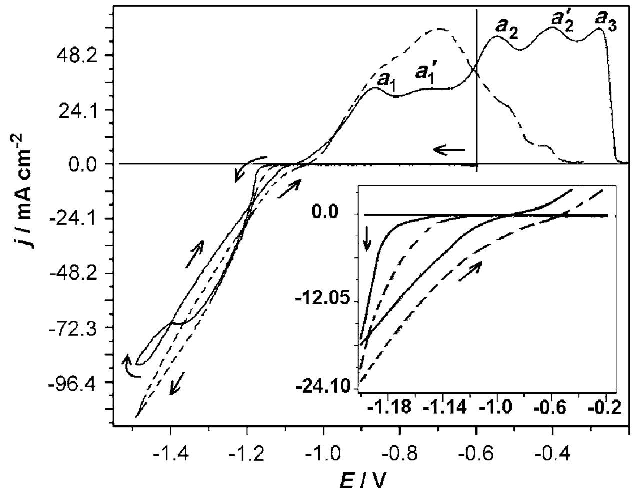

Fig. 2 Voltammetric curves for Pt substrate in solution 0.55 M $ZnSO_4$ + 0.22 M $NiSO_4$ + 0.33 M $NiCl_2$ (– –) and ZnNi1(—), Table 1; υ = 10 mV s^{-1}

Ni (−1.0 V) as pure metals. However, it is closer to the deposition potential of Zn than of Ni. These results indicate that ZnNi alloy was probably formed. Moreover, the dissolution potential (E_{diss}) range of the ZnNi deposit (−1.08 V to −0.33 V) is between those of the pure metals, i.e., −1.08 V to −0.70 V for Zn and −0.50 V to +0.95 V for Ni. This suggests that possibly the ZnNi deposit contains a high percentage of Zn, since its range of E_{diss} is close the to Zn dissolution potential. Also, the formation of several peaks in the anodic scan indicates that various ZnNi phases are present in the deposit.

The effect of H_3BO_3 during deposition of ZnNi was investigated further by cyclic voltammetry (Fig. 2). Figure 2 inset shows that in the presence of H_3BO_3 (—) the $E_{d,i}$ of ZnNi alloy, −1.15 V, was 30 mV more negative than that in its absence (- -), −1.12 V. Also, the deposition current density (j_d) decreased significantly, suggesting that H_3BO_3 inhibits ZnNi alloy deposition. At −1.4 V, the j_d decreased from ~90 mA cm^{-2} (absence) to ~70 mA cm^{-2} (presence). This behavior can be attributed to adsorption of H_3BO_3 on the cathodic surface, in preference to H^+ and Zn^{2+} [31]. Pushpavanam and Balakrishnan [31] reported that the adsorption of H_3BO_3 inhibits Zn deposition, resulting directly in a drop in the alloy j_d. Also, it is known [31] that both Ni and Zn deposit from their hydroxides and that the boric acid has buffering action at the electrode-solution interface [34]. Thus, the boric acid inhibited the formation of $(ZnOH)^+$, $(NiOH)^+$, due to its buffering action and also HER inhibition. Hence, ZnNi alloy deposition was inhibited.

In the anodic scan (Fig. 2), in the presence of H_3BO_3 (—), the charge densities of peaks a_2 a_2' and a_3 are bigger than those of a_1 and a_1' showing that Zn deposition was inhibited. However, in the absence of H_3BO_3 (– –), the peaks a_2 a_2' and a_3 were suppressed. These results corroborate those reported in the literature [31], i.e., in the presence of H_3BO_3 the Ni deposition in the ZnNi alloy is probably favored, owing to preferential adsorption of H_3BO_3, relative to H^+ or Zn^{2+} ions, inhibiting both Zn and β-Ni (phase rich in hydrogen) deposition.

Figure 3a, b shows voltammetric deposition curves of ZnNi from plating baths with various sorbitol or glycerol contents, respectively. Figure 3a shows that j_d decreases with rising sorbitol concentration. Comparing j_d at approximately −1.30 V in the absence (~56 mA cm^{-2}) and presence (~29 mA cm^{-2}) of 0.52 M sorbitol, it can be seen that in the latter case it was reduced by ~48%. In contrast, in the presence of glycerol (Fig. 3b), there were no significant changes in j_d with different concentrations of the additive. For 0.52 M glycerol (~40 mA cm^{-2}), at −1.30 V, the decrease in the j_d was ~28%. The lower values of j_d in baths containing sorbitol (Fig. 3a) was due to the formation of a boric–sorbitol complex ($2C_6H_{14}O_6$–H_3BO_3) [32, 33,

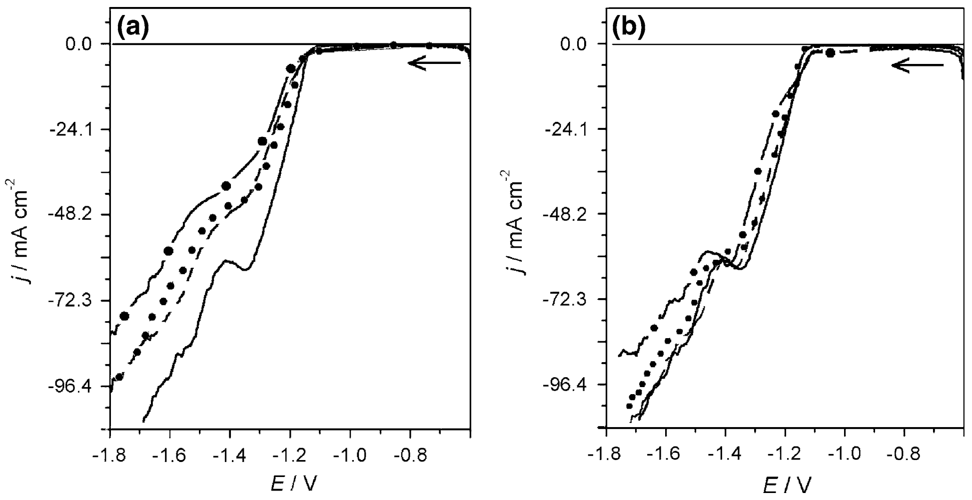

Fig. 3 ZnNi alloy deposition voltammetric curves from electrolytic solutions: **a** ZnNi1 (—); ZnNi1 + 0.26 M sorbitol (• • •); ZnNi1 + 0.39 M sorbitol (– –) and ZnNi2 + 0.52 M sorbitol (– • –); **b** ZnNi1 (—); ZnNi1 + 0.26 M glycerol (• • •); ZnNi1 + 0.39 M glycerol (– –) and ZnNi2 + 0.52 M glycerol (– • –); υ = 10 mV s^{-1}

35, 36] which effectively blocks the cathode surface [32, 33]. As reported above (Sect. 2) the pH values of the plating baths with or without glycerol ($C_3H_8O_3$), as prepared, were ~4.0 and ~3.9, indicating that there was effectively no formation of boric–glycerol complex. Thus, it must be expected that when the pH of the plating bath was adjusted to ~pH 3.0, the boric acid would be protonated at this acidity and, consequently, the formation of boric–glycerol complex can be disregarded. However, it must be stressed that we were unable to find the pK_a values of either the boric–sorbitol complex or the boric–glycerol complex.

Also, Fig. 3a, b shows that $E_{d,i}$ did not change, in any of the baths studied, implying that there was no complex formation between zinc or nickel ions and the boric–sorbitol anion or glycerol.

3.2 Analysis of the ZnNi alloy composition and current efficiency of the cathodic process

EDS analysis of ZnNi deposits was performed to verify the influence of the polyalcohol concentration and E_d on the percentage of Ni in the deposits. Figure 4a, b shows the content of Ni wt% in the ZnNi deposits versus different E_d and plating bath compositions. It can be seen in Fig. 4a that ZnNi deposits obtained from solutions without (1) or with 0.52 M glycerol (7) show an increase of ~5.5 wt% Ni to ~19.5 wt% Ni in the deposits, as E_d becomes more negative, from −1.26 V to −1.55 V. These results corroborate the voltammetric deposition curves, (Fig. 3b), i.e., these curves were similar and those obtained by Petraukas et al. [10] and Pushpavanam and Balakrisnan [31], who report that the content of Ni in the ZnNi deposits obtained from ZnNi solutions with H_3BO_3 increases with increasing polarization. Also, it was reported that ZnNi baths: without H_3BO_3 [25]; with H_3BO_3-citrate [9] or ammoniacal solutions with and without H_3BO_3 [2] showed the opposite behavior, i.e., Ni wt% in the ZnNi alloy decreased as the E_d became more negative. In our work, this behavior was not observed for ZnNi deposits.

However, the proportion of Ni in the ZnNi deposits obtained from baths containing 0.52 M sorbitol remains in the range of 7.0–9.5 wt% Ni as E_d shifts to more negative potentials, i.e., from −1.26 V to −1.55 V (Fig. 4a). These results imply that the sorbitol–boric complex in the plating bath did not inhibit zinc or nickel deposition, when the deposition potential became more negative.

The results of Fig. 4a showed that all ZnNi alloys, obtained with baths without or with sorbitol or glycerol, will have sacrificial protection in the potential range studied. Also, the alloys obtained from baths without polyalcohol or with glycerol must be obtained in the potential range −1.40 V to −1.55 V to show better sacrificial protection of the steel substrate. On the other hand, though ZnNi alloys obtained from baths containing sorbitol show a Ni percentage below 10 wt% Ni, in this case the change in Ni percentage in the alloy for various deposition potentials was smaller. Thus, for ZnNi alloys electrodeposition on to irregular substrates, from baths with low throwing power [37], the use of sorbitol is indicated with the aim of obtaining a uniform distribution of Ni in the layer. It can be observed in Fig. 4b that there was no significant change in wt% Ni in the deposits for changing concentrations of the same polyalcohol, at the same deposition potential, except for 0.52 M glycerol, at −1.26 V, which showed ~5.0 wt% Ni, while the Ni content obtained in the presence of 0.26 M or 0.39 M glycerol was between 12.5 and 11.0 wt% Ni, respectively.

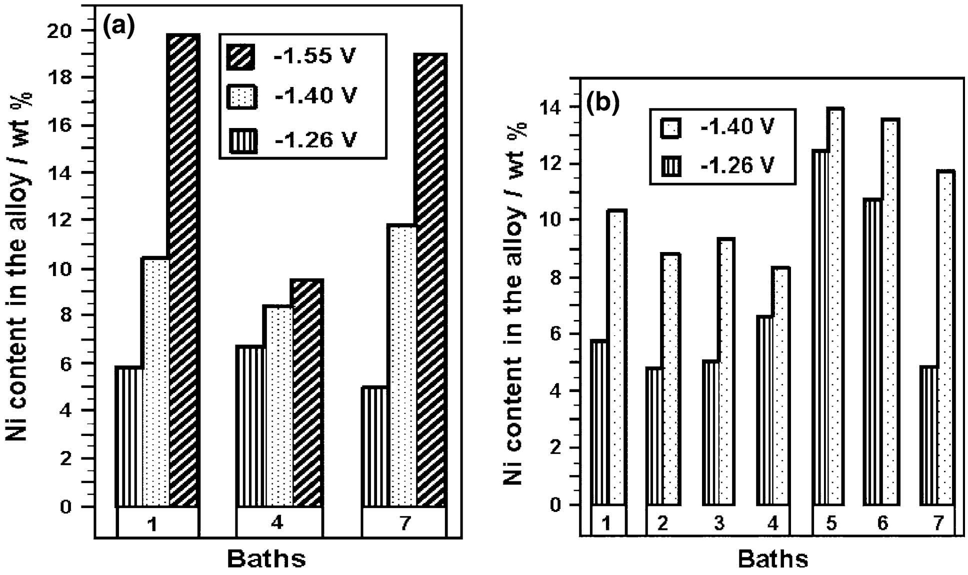

Fig. 4 Ni element content (wt%) in the alloy ZnNi obtained chronoamperometrically from −0.20 V to: **a** −1.26 V, −1.40 V and −1.55 V; **b** −1.26 V and −1.40 V from baths ZnNi1 (1); ZnNi1 + 0.26 M sorbitol (2); ZnNi1 + 0.39 M sorbitol (3) and ZnNi2 + 0.52 M sorbitol (4); ZnNi1 + 0.26 M glycerol (5); Zn1 + 0.39 M glycerol (6) and Zn2 + 0.52 M glycerol (7)

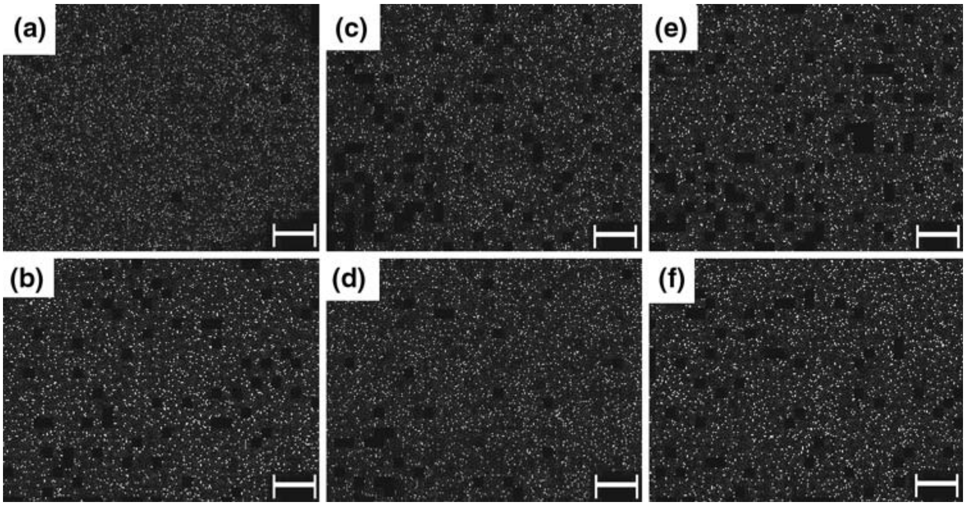

Fig. 5 X- ray dot maps of ZnNi films obtained chronoamperometrically from −0.20 V: to −1.26 V (**a**, **c**, and **e**) and to −1.40 V (**b**, **d**, and **f**). Plating baths: ZnNi1 **a** and **b**; ZnNi2 + 0.52 M sorbitol **c** and **d** and ZnNi2 + 0.52 M glycerol **e** and **f**; q = 4 C cm $^{-2}$. ├──┤ (200 μm)

Finally, these results suggest that codeposition of Zn and Ni in the absence and presence of polyalcohols is of anomalous type [7].

X-ray dot maps and contrast backscattered electron images (BSE) were used to intensify the contrast between regions containing Zn and Ni (Fig. 5a–f). These figures showed that the distribution of these elements, in all deposits studied, was uniform. Thus, the main problem (bad distribution of elements) that can occur in the ZnNi alloy electrodeposition from acid baths was not observed in this study.

The deposition current efficiency (CE) was calculated from the stripping/deposition charge ratio. In these experiments, the ZnNi deposits were laid down for a deposition time of 40 s. Previous studies were necessary to choose the best conditions for dissolution of the electrodeposits. 1 M NH_4Cl solution was used at various pH, 1.0, 1.5 and 2.0 and different sweep rates, 10, 20 and 30 mV s^{-1} to dissolve the electrodeposits. Thus, in 1 M NH_4Cl pH 1.0 the formation of bubbles during dissolution of the electrodeposits was observed at all sweep rates, due to chemical dissolution; in 1 M NH_4Cl pH 2.0 the electrodeposits did not dissolve completely; in 1 M NH_4Cl pH 1.5 and a scan rate of 10 mV s^{-1}, chemical dissolution was also observed, but for scan sweep of 20 and 30 mV s^{-1} the electrodeposits dissolved completely with no formation of bubbles. A larger CE was also obtained. Thus, the conditions of 1 M NH_4Cl pH 1.5 and sweep rate of 30 mV s^{-1} were chosen for ZnNi electrodeposit dissolution. The experimental error was 2%.

Figure 6a, b shows the current efficiency (CE) of ZnNi deposition from plating baths without and with various sorbitol (Fig. 6a) or glycerol (Fig. 6b) concentrations. Values of CE lower than 100% can be attributed to HER taking place simultaneously with the deposition process. At E_d − 1.15 V the CE values were appreciably lower than those obtained at more negative deposition potentials. These results imply that in the initial moments of the ZnNi reduction process (E_d − 1.15 V), on to Pt, the HER is more significant than ZnNi deposition, particularly in the presence of sorbitol. For the E_d range from −1.30 V to −1.40 V, the CE in the presence of glycerol was ~90% and, with sorbitol or without polyalcohols, between 82 and 85%. Comparing the CE values obtained in this potential range and those at −1.15 V, it can be suggested that the increase in the CE, in the first case, is due to the increase in the j_d of ZnNi deposits (Fig. 3a, b). When the deposition potential was more negative than −1.50 V, the CE fell, since the contribution of HER at these potentials becomes significant, compared to the formation of ZnNi deposit, and burn-out deposits were obtained. It can be inferred from these results that the presence of glycerol in the plating bath inhibits the HER.

3.3 Morphological analysis of ZnNi deposits

Figure 7a–g shows micrographs of the ZnNi deposits obtained at −1.26 V. The ZnNi deposit obtained without polyalcohols (Fig. 7a) was compact and formed of irregular grains. The addition of various sorbitol concentrations (Fig. 7b–d) did not lead to significant changes in the deposit morphology compared to that without polyalcohol. Actually, there was only a small refinement of grains at 0.26 M and 0.39 M sorbitol, while for 0.52 M sorbitol, the deposit was more compact than the others and formed of spherical grains. The presence of glycerol in the bath (Fig. 7e–g) led to significant changes in morphology of; as the glycerol concentration increased, the grains were refined. For the bath containing 0.26 M glycerol, grains larger that ~5 μm were formed and the deposit was not compact. However, for 0.52 M glycerol the hexagonal grain size was smaller that ~2 μm and the deposit was compact.

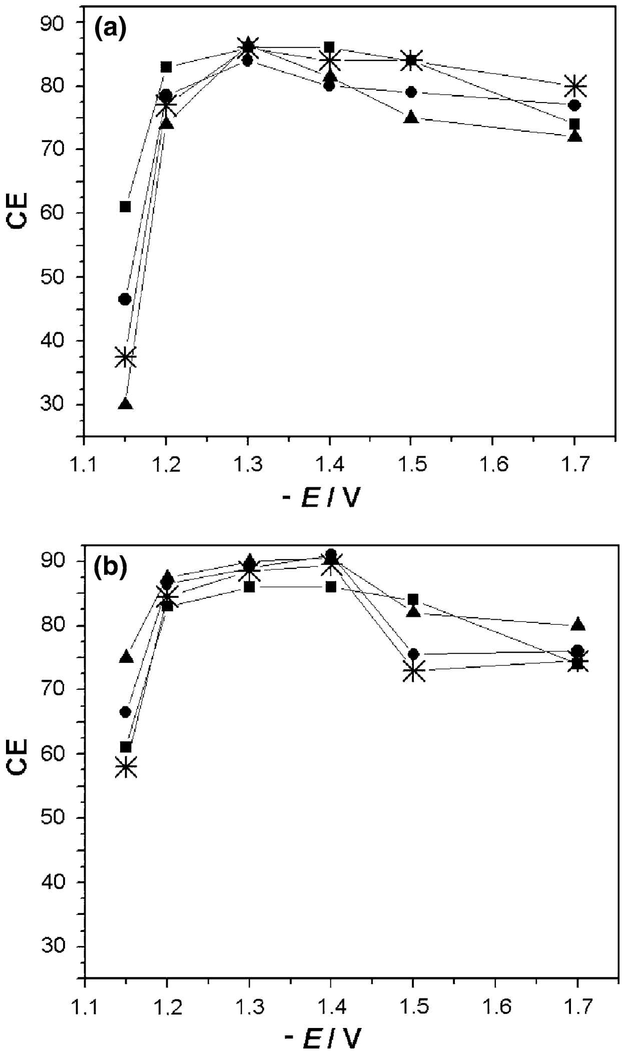

Fig. 6 ZnNi deposition current efficiency (CE) at several deposition potentials and a deposition time of 40 s. Plating baths: **a** ZnNi1 (■); ZnNi1 + 0.26 M sorbitol (●); ZnNi1 + 0.39 M sorbitol (▲) and ZnNi2 + 0.52 M sorbitol (*); **b** ZnNi1 (■); ZnNi1 + 0.26 M glycerol (●); Zn1 + 0.39 M glycerol (▲) and Zn2 + 0.52 M glycerol (*)

Figure 8a–g shows micrographs of the ZnNi deposits obtained at −1.40 V. The ZnNi deposit obtained from baths without polyalcohols (Fig. 8a) now has a non-compact structure with grains of size ~5 µm. The ZnNi deposits obtained from baths containing sorbitol (Fig. 9b–d) were compact and formed, in general, by coalesced globular crystallites, with a grain size smaller than ~1 µm. The most compact deposit was obtained with 0.26 M sorbitol. The presence of glycerol in the bath (Fig. 9e–g) also led to the formation of globular grains more refined than in the absence of either additive, but there was no systematic trend in terms of the concentration. The deposit obtained from the bath containing 0.52 M glycerol was more compact than those at other glycerol concentrations.

EDS analysis of ZnNi deposits obtained at −1.26 V without and with polyalcohols at various concentrations (Fig. 4b) and morphological studies of deposits (Fig. 7a–d, g) showed correlation between deposit morphologies and Ni contents, i.e., as the Ni content in the deposits was ~6 wt% the grains were more refined than for deposits containing ~12 wt% Ni (Fig. 7e–f). However, for ZnNi deposits obtained at −1.40 V (Fig. 8) was not possible to make a direct correlation between deposit morphologies and Ni contents (Fig. 4b).

Deposits obtained from the baths with sorbitol showed more refined grains than those obtained without polyalcohol or with glycerol for both potentials, −1.26 V and −1.40 V. These results corroborate the voltammetric studies (Fig. 3a), which indicate that the adsorption of boric–sorbitol complex on the Pt cathode during deposition will lead to formation of ZnNi deposits with more refined grains. Also, these results corroborate those for nickel or zinc electrodeposition, in the presence and absence of polyalcohols, reported in the literature [32, 33].

3.4 X-ray analysis of ZnNi deposit

Figures 9a–c and 10a–c show typical X-ray diffraction patterns of ZnNi deposits obtained at −1.26 V and at −1.40 V, respectively, from solutions of Zn and Ni salts without and with 0.52 M sorbitol or 0.52 M glycerol. It must be stressed that for the ZnNi2 + 0.52 M glycerol bath an effect of the glycerol and of the boric acid on the electrodeposition process is observed, since in this bath the boric acid was added in double in the solution and did not react completely with glycerol. In contrast, for the ZnNi2 + 0.52 M sorbitol bath the effect the boric–sorbitol complex is observed, since boric acid totally reacted with sorbitol.

The X-ray diffractograms of the ZnNi deposits indicated the presence of γ, γ^1 (Zn_3Ni) and Pt_3Zn phases. Moreover, the diffractograms also suggested the occurrence of the δ-phase. Although, the formation of the δ-phases with Ni content of 0–25 at. % by electrodeposition has been reported [38] its formation is controversial [2, 38].

Finally, these results are also consistent with the EDS (Fig. 4) finding that Zn was present in larger amounts than Ni and also with the ZnNi potentiodynamic deposition studies (Fig. 1), which suggested that ZnNi deposits could have high Zn content and be formed of several ZnNi phases.

4 Conclusions

ZnNi electrodeposit was successfully obtained from solutions of Zn and Ni salts and boric acid, with and without the polyalcohols glycerol or sorbitol.

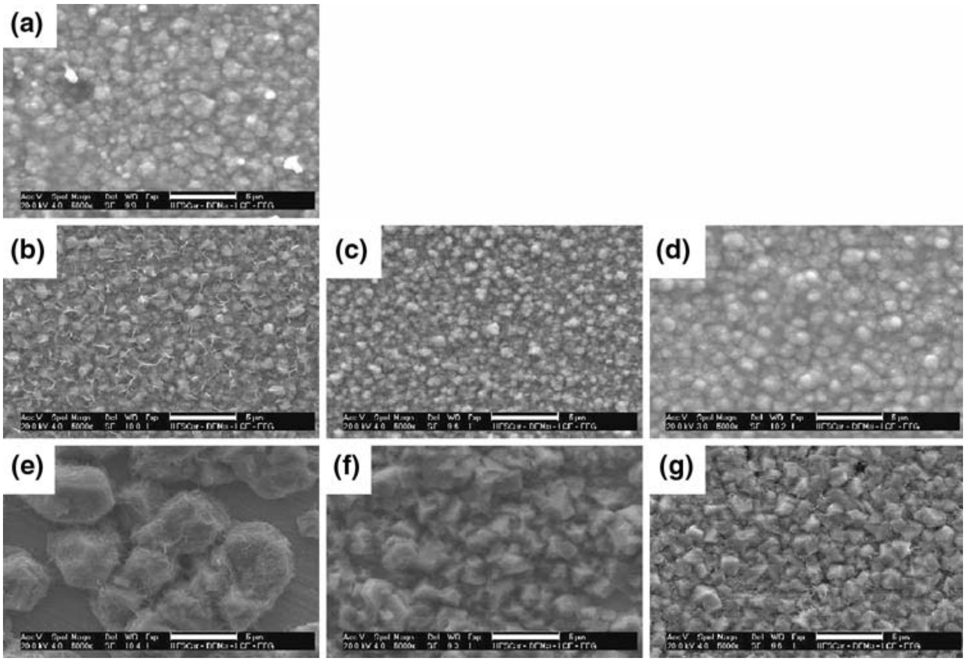

Fig. 7 SEM micrographs of ZnNi films obtained chronoamperometrically from −0.20 V to −1.26 V with 4.0 C cm^{-2}. Plating baths: **a** ZnNi1; **b** ZnNi1 + 0.26 M sorbitol; **c** ZnNi1 + 0.39 M sorbitol; **d** ZnNi2 + 0.52 M sorbitol; **e** ZnNi1 + 0.26 M glycerol; **f** ZnNi1 + 0.39 M glycerol, and **g** ZnNi2 + 0.52 M glycerol; ├──┤ (5 μm)

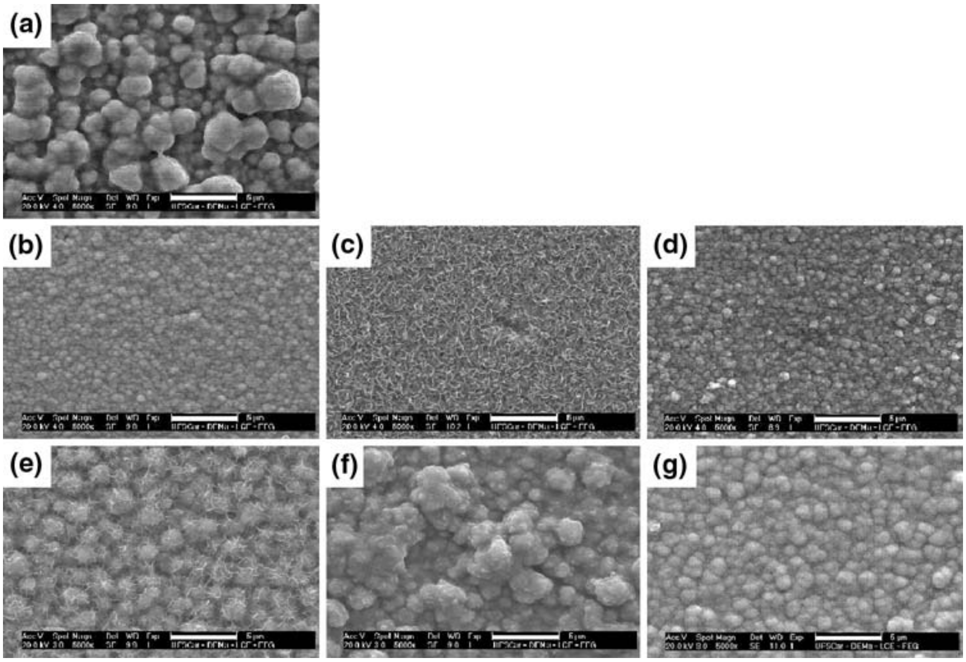

Fig. 8 SEM micrographs of ZnNi films obtained chronoamperometrically from −0.20 V to −1.40 V with 4.0 C cm^{-2}. Electrolytic solutions: **a** ZnNi1; **b** ZnNi1 + 0.26 M sorbitol; **c** ZnNi1 + 0.39 M sorbitol; **d** ZnNi2 + 0.52 M sorbitol; **e** ZnNi1 + 0.26 M glycerol; **f** ZnNi1 + 0.39 M glycerol, and **g** ZnNi2 + 0.52 M glycerol; ├──┤ (5 μm)

The presence of glycerol in the baths did not result in significant changes in the voltammetric curves, whereas in the presence of sorbitol there was a decrease in the j_d as the sorbitol concentration increased. The j_d values at approximately −1.30 V in absence and for 0.52 M sorbitol were ~56 and ~29 mA cm^{-2}, respectively. This fall in j_d was ~48%, due to the adsorption of boric–sorbitol complex on the electrode.

The highest CE values (~90%) were obtained in the presence of glycerol in the E_d range from approximately −1.30 V to −1.40 V, while in the presence of sorbitol or absence of either polyalcohol, the CE values were 82–85%, for the same potential range. Thus, it can be concluded that the presence of glycerol in the plating bath inhibits the HER.

EDS analysis showed that the Ni content in the ZnNi deposits obtained in the absence of polyalcohols or presence of glycerol increased from ~5.5 wt% Ni to ~19.5 wt% Ni, in the E_d range of −1.26 V down to −1.55 V. It can be concluded from the results that this occurred because of the

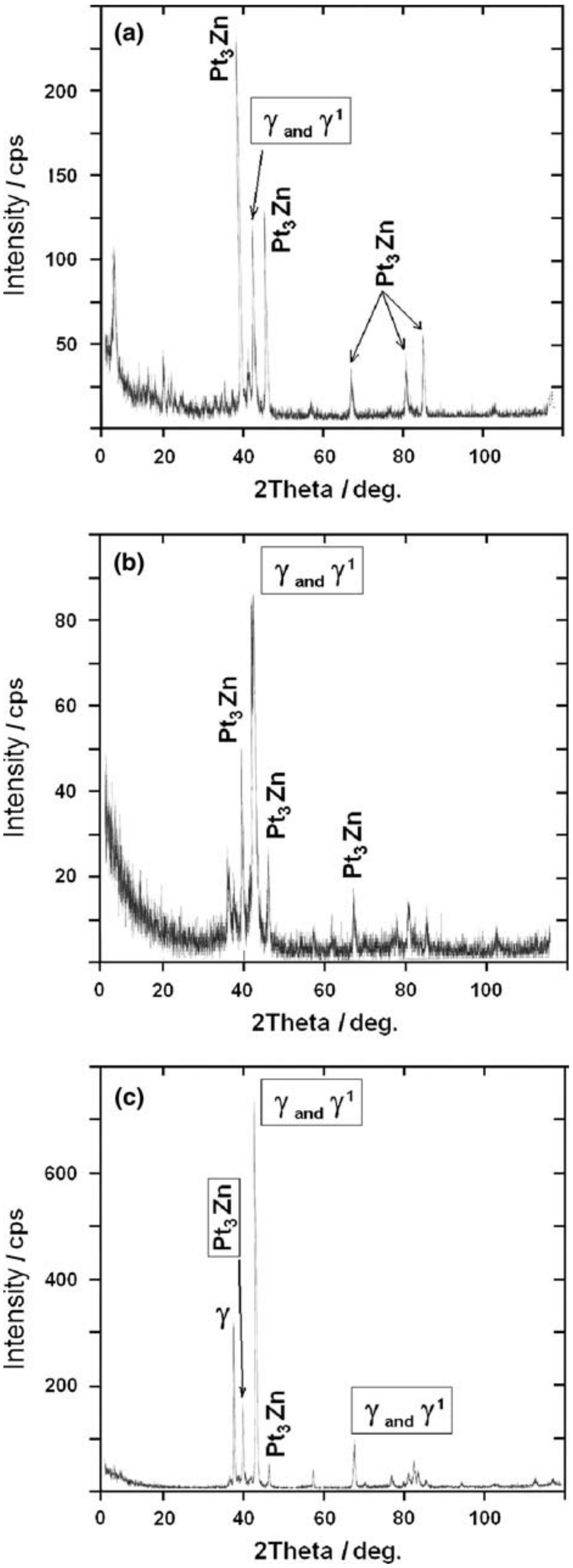

Fig. 9 X-ray diffraction patterns of ZnNi alloy obtained chronoamperometrically from −0.20 V to −1.26 V with 4.0 C cm^{-2}, from baths: **a** ZnNi1; **b** ZnNi2 + 0.52 M sorbitol, and **c** ZnNi2 + 0.52 M glycerol

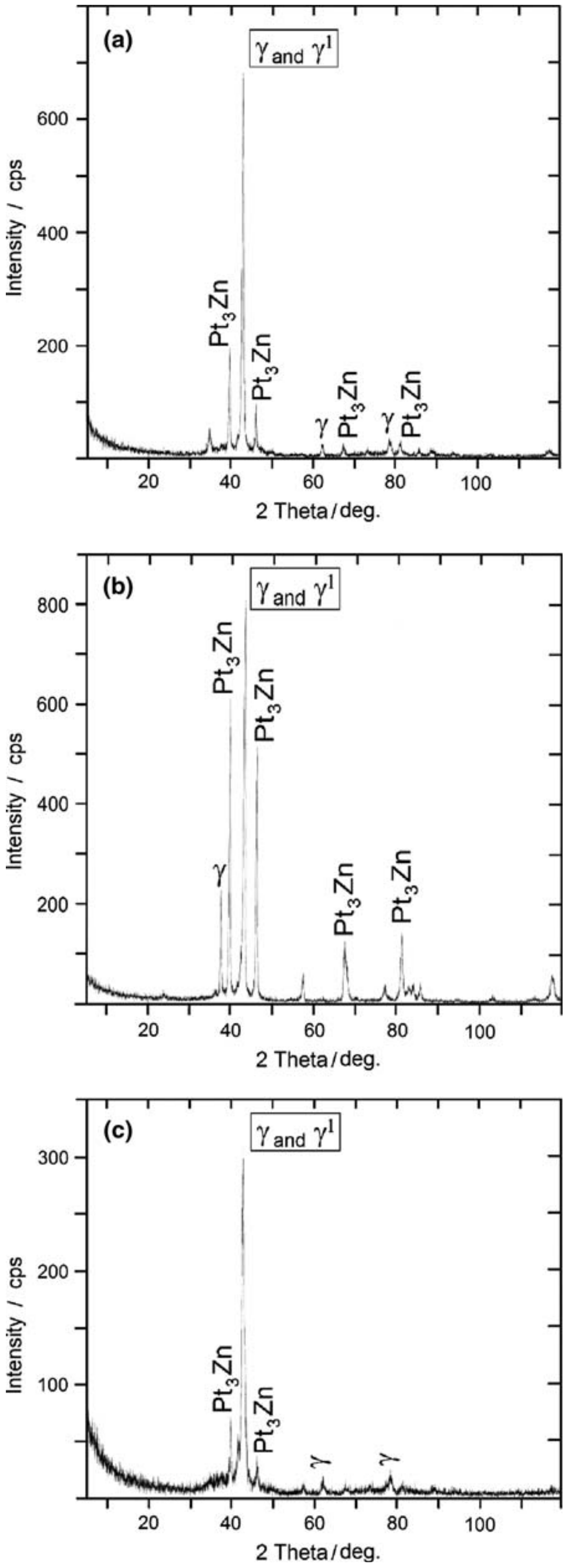

Fig. 10 X-ray diffraction patterns of ZnNi alloy obtained chronoamperometrically from −0.20 V to −1.40 V with 4.0 C cm^{-2}, from baths: **a** ZnNi1; **b** ZnNi2 + 0.52 M sorbitol, and **c** ZnNi2 + 0.52 M glycerol

presence of boric acid in the plating bath. However, in the presence of sorbitol, the Ni content remained in the range of 7.0–9.5 wt% Ni, for the same E_d range, owing to the formation of a sorbitol–boric complex, which did not inhibit the zinc or nickel deposition as the E_d became more negative. These results suggest that the ZnNi deposits obtained from these baths containing Ni wt% lower than 19 wt% probably offers sacrificial protection to the substrate. Moreover, relative distribution analysis of Zn and Ni in the deposits by dot mapping showed that the distribution of the elements, in all deposits studied, was uniform.

SEM examination revealed that the best morphology of all the ZnNi deposits was obtained at −1.40 V from baths containing sorbitol, since these deposits were compact and formed of spherical grains smaller than 1 μm. Thus, it can be concluded that sorbitol works as a brightener of ZnNi deposits.

X-ray analysis of the ZnNi deposits obtained at −1.26 V and at −1.40 V, in all baths, indicated the presence of γ, γ^1 and Pt_3Zn phases.

Acknowledgments CNPq (Financial support from the Brazilian agencies CNPq is gratefully acknowledged) and FAPESP.

References

1. Pushpavanam M (2000) Bull Electrochem 16:559
2. Rodriguez-Torres I, Valentin G, Lapicque F (1999) J Appl Electrochem 29:1035
3. Pushpavanam M, Natarajan SR, Balakrishnan K, Sharma LR (1991) J Appl Electrochem 21:642
4. Coleman DH, Popov BN, White RE (1998) J Appl Electrochem 28:889
5. Fratesi R, Roventi G (1992) J Appl Electrochem 22:657
6. Hall DE (1983) Plat Surf Finish 70:59
7. Brenner A (1963) Eletrodeposition of alloys, vol 2. Academic Press, New York
8. Elkhatabi F, Sarret M, Muller C (1996) J Electroanal Chem 404:45
9. Stevanovic J, Gojkovic S, Despic A, Obradovic M, Nakic V (1998) Electrochim Acta 43:705
10. Petrauskas A, Grincevicience L, Cesuniene A, Matulionis E (2005) Surf Coat Technol 192:299
11. Mertens MLAD (2007) Tratam Superf 142:42
12. Muller C, Sarret M, Bendalla M (2001) Electrochim Acta 46:2811
13. Chassaing E, Wiart R (1992) Electrochim Acta 37:545
14. Sheela G, Pushpavanam M, Pushpavanam S (2002) Int J Hydrogen Energy 27:627
15. Roventi G, Fratesi R, Guardia RAD, Barucca G (2000) J Appl Electrochem 30:173
16. Barcelo G, Garcia J, Sarret M, Muller C (1994) J Appl Electrochem 24:1249
17. Albalat R, Gomez E, Muller C, Pregonas J, Sarret M, Valles E (1991) J Appl Electrochem 21:44
18. Lin YP, Selman JR (1993) J Electrochem Soc 140:1299
19. Chen L, Lasia A (1991) J Electrochem Soc 138:3321
20. Brooks I, Erb U (2001) Scripta Mater 44:853
21. Ashassi-Sorkhabi H, Hagrah A, Parvini-Ahmadi N, Manzoori J (2001) Surf Coat Technol 140:278
22. Pagotto SO Jr, Freire CMA, Ballester M (1999) Surf Coat Technol 122:10
23. Wu Z, Fedrizzi L, Bonora PL (1996) Surf Coat Technol 85:170
24. Short NR, Zhou S, Dennis JK (1996) Surf Coat Technol 79:218
25. Miranda FJF, Barcia OE, Diaz SL, Mattos OR, Wiart R (1996) Electrochim Acta 41:1041
26. Miranda FJF, Barcia OE, Mattos OR, Wiart R (1997) J Electrochem Soc 144:3441
27. Beltowska-Lehman E, Ozga P, Swiatek Z (2002) Cryst Eng 5:335
28. Beltowska-Lehman E, Ozga P, Swiatek Z, Lupi C (2002) Surf Coat Technol 151:444
29. Ivanov I, Kirilova I (2003) J Appl Electrochem 33:239
30. Bobrikova IG, Kukoz FI, Selivanov VN, Kopin AV (2002) Russian J Electrochem 38:1269
31. Pushpavanam M, Balakrishnan K (1996) J Appl Electrochem 26:283
32. Oliveira EM, Carlos IA (2008) J Appl Electrochem 38:1203
33. Oliveira EM, Finazzi GA, Carlos IA (2006) Surf Coat Technol 200:5978
34. Hoare JP (1986) J Electrochem Soc 133:2491
35. Kolthoff IM, Saldell EM, Meehan EJ, Bruckenstein S (1969) Quantitative chemical analysis, vol 1, 4th edn. The Macmillan Company, New York
36. Bassett J, Denney RC, Jeffery GH, Mendham J (1978) Vogel's textbook of inorganic quantitative analysis, 4th edn. Longman, New York
37. Paunovic M, Schlesinger M (1998) Fundamentals of electrochemical deposition. Wiley, New York
38. Cavallotti PL, Nobili L, Vicenzo A (2005) Electrochim Acta 50:4557