Electrochemical deposition and characterization of zinc-nickel alloys deposited by direct and pulse current

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Abstract: Chemical composition and phase structure of Zn-Ni alloys obtained by electrochemical deposition under various conditions were investigated. The alloys were deposited on a rotating disc electrode and steel panel from chloride solutions by direct and pulse current. The influence of the pulse plating variables (on-time, off-time, relation of off- and on-time) on the composition, phase structure and corrosion properties were investigated. The phase composition affects the anticorrosive properties of Zn-Ni alloys during exposure to a corrosive agent (3 % NaCl solution). It was shown that a Zn-Ni alloy electrodeposited by pulse current with a pulse time of 1 ms and an off- and on-time ratio of 1 exhibits the best corrosion properties.

Keywords: Zn-Ni alloy, electrodeposition, pulse current, ALSV, corrosion.

INTRODUCTION

It has been shown[1–3] that zinc alloys can provide improved corrosion resistance compared to pure zinc in the protection of ferrous-based metals. It is well known that the application of pulse plating leads to improvements in the quality of electrodeposits: smooth deposits are achieved, with decreased porosity, better ductility, hardness and control of the deposit composition are obtained.[4]

Zinc-nickel alloy exists in various phases and its structure and morphology also determine the corrosion resistance of a deposit.[5]

In this paper an attempt was made to find pulse plating parameters that would lead to Zn-Ni alloy with the best corrosion resistance being obtained. Three variables can be varied in pulse plating (PC) instead of just one (deposition current density) in direct current (DC) plating. The variables are: pulse current density (j_p), pulse time (T_{on}) and pause (relaxation) time (T_{off}). In an earlier work[6] the corrosion properties of Zn-Ni deposits obtained from chloride and sulphate plating solutions at various current densities were exam-

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ined, and the alloy obtained from a chloride bath using a current density of 20 mA cm^{-2} at 40 ºC showed the best corrosion properties. This current density was chosen as an average current density (j_{av}) for the pulse plating in this work. The influence of the other two variables (T_{on} and T_{off}) on the chemical composition, phase structure and corrosion properties of the obtained Zn-Ni alloys was investigated.

EXPERIMENTAL

Zn-Ni alloys were elctrodeposited onto a steel panel or onto a rotating disc electrode from a chloride bath[7]: 15 g dm^{-3} ZnO, 60 g dm^{-3} NiCl$_2$·6H$_2$O, 250 g dm^{-3} NH$_4$Cl and 20 g dm^{-3} H$_3$BO$_3$ at 40 ºC. The electrolytes used were prepared using p.a. chemicals and double distilled water.

Zn-Ni alloys were deposited galvanostatically by constant current, $j = 20$ mA cm^{-2}, and by pulse current, using cathodic square wave pulses, with average current density $j_{av} = 20$ mA cm^{-2}. The cathodic deposition times (on period) investigated in pulse plating were: 0.1 ms, 1ms, 10 ms, 100 ms and 1 s. The pause-to-pulse ratios were: 1:1, 1:2, 1:5 and 1:10. The cathodic time duration was the same for all investigated deposits. Working electrode was: a) Pt rotating disc electrode ($d = 8$ mm; at 2000 rpm), in the case of determining chemical content and phase structure of the alloy, as well as for polarisation measurements and b) steel panel (20 mm × 20 mm × 0.25 mm) for corrosion measurements. Prior to each electrodeposition Pt disc surface was mechanically polished cloth (Buehler Ltd.), impregnated with a water suspension of alumina powder (0.3 μm grade) and then rinsed with pure water in an ultrasonic cleaner. Test panels were pretreated by mechanical cleaning (polishing) and then degreased in a saturated solution of sodium hydroxide in ethyl alcohol, pickled with hydrochloric acid solution at 1:1 dilution for 30 s and rinsed with distilled water. Counter electrodes were either a Ni spiral wire, placed parallel to the RDE at a distance of 1.5 cm, or platinum anodes, placed parallel to the steel panel electrode at a distance of 1.5 cm.

For alloy phase structure determination alloys were dissolved anodically at room temperature (23 ± 1 ºC) using a slow sweep voltametry technique (sweep rate 1 mV s^{-1} and rotation of 2000 rpm) in N$_2$ saturated 0.5 mol dm^{-3} Na$_2$SO$_4$ + 0.05 mol dm^{-3} EDTA solution. The counter electrode used in these experiments was a Pt-spiral wire and the reference electrode was a saturated calomel electrode (SCE). All potentials are referred to the SCE.

The chemical composition of the Zn-Ni alloys were determined by atomic absorption spectroscopy in a Perkin Elmer spectrophotometer (AAS-1100).

The current efficiency was calculated on the basis of the chemical composition and Faraday's law.

All experiments were carried out using a EG & G Princeton Applied Research potentiostat-galvanostat Model 273A and Model 175 connected to a PC and a Pine Instrument Company rotator, model AFASR.

RESULTS AND DISCUSSION

Chemical composition

Zn-Ni alloys were electrodeposited at constant current density (DC) and by pulse current (PC) with different values of the cathodic deposition time (on-time) and different pause-to- pulse ratios ($T_{off}/T_{on} = p$). The effects of the cathodic deposition time and the pause-to- pulse ratio on the Ni content of the deposit, as well as the composition of alloy obtained at constant current density, are shown in Figs. 1 and 2. Figure 1 shows that Ni content is relatively constant in the investigated T_{on} range. Alfantazi and coworkers[8] investigated the influence of the cathodic deposition time on the chemical composition of Zn-Ni alloys in the range of 0.2 – 2.5 ms, and they also found that T_{on} has very little effect on the alloy composition. Increasing the pause-to-pulse ratio, p, on the other hand, results in a decrease of the Ni content in the alloy (Fig. 2), but all the Zn-Ni alloys had a Ni content necessary for good corrosion protection (10–15 wt. %).
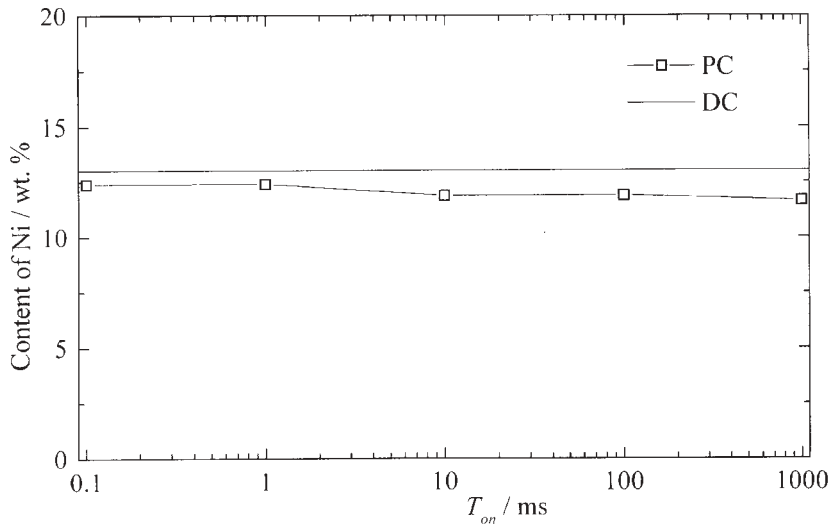
Fig. 1. The Ni content of the alloy formed by direct current plating and by pulse plating with different cathodic times (T_{on}).
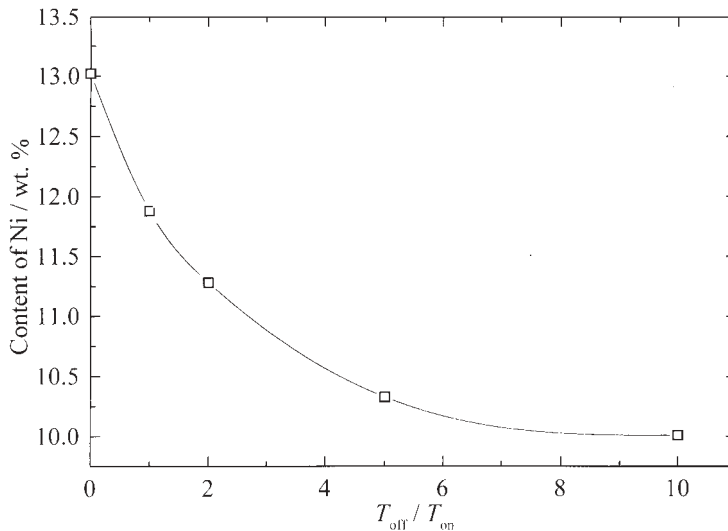

Fig. 2. The dependence of the Ni content of the alloy on the pause-to-pulse ratio.

Alloy phase structure

The phase structure of the alloys was investigated by anodic linear sweep voltammetry (ALSV) in a solution containing complex forming agents. ALSV has been shown to be a convenient electrochemical method for the characterization of the phase structure of an alloy.[9–11] This results from the main characteristics of ALSV, *i.e.*, its possibility of revealing the phase structure of metal deposits. In particular, ALSV gives rise to various current peaks and the peak structure is characteristic of the components of an alloy and the phase structure of the
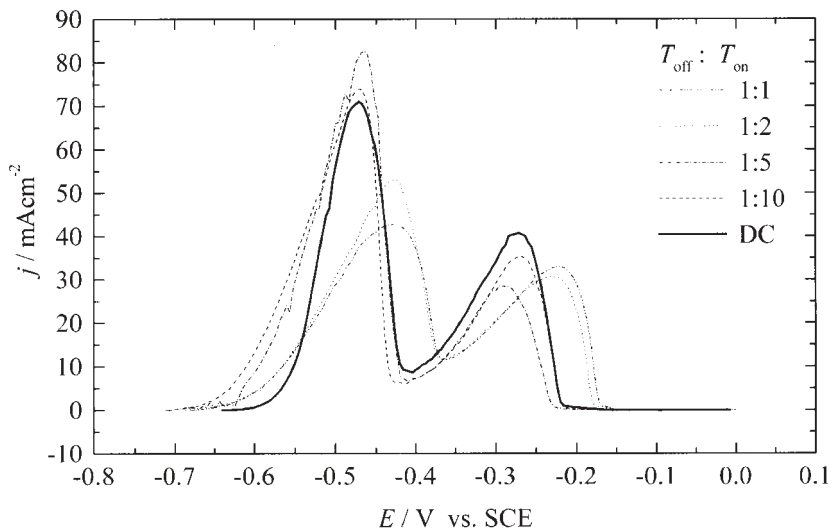
Fig. 3. ALSVs in Na_2SO_4 + EDTA solution of the dissolution of Zn-Ni alloys deposited by DC and PC with T_{on} = 100 ms and different ratio of T_{off} : T_{on}.

Fig. 4. ALSVs in Na_2SO_4 + EDTA solution of the dissolution of Zn-Ni alloys deposited by DC and PC with T_{on} = 10 ms and different ratio of T_{off} : T_{on}.

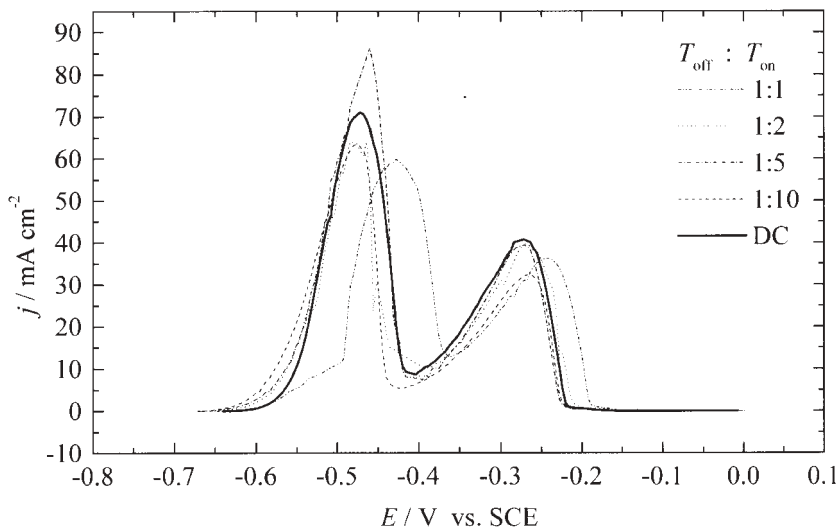deposit. The voltammetric peak structure is, therefore, a convenient spectra-like diagram depicting the various phases present in an electrodeposited film.

For phase structure determination, the Zn-Ni alloys were electrodeposited at constant current density (20 mA cm^{-2}) and by pulse current with j_{av} = 20 mA cm^{-2} with different cathodic times and pause-to-pulse ratios. Four series of pulse plating experiments were done with cathodic times of 100, 10, 1 and 0.1 ms. The pause-to-pulse ratios (T_{off}/T_{on})
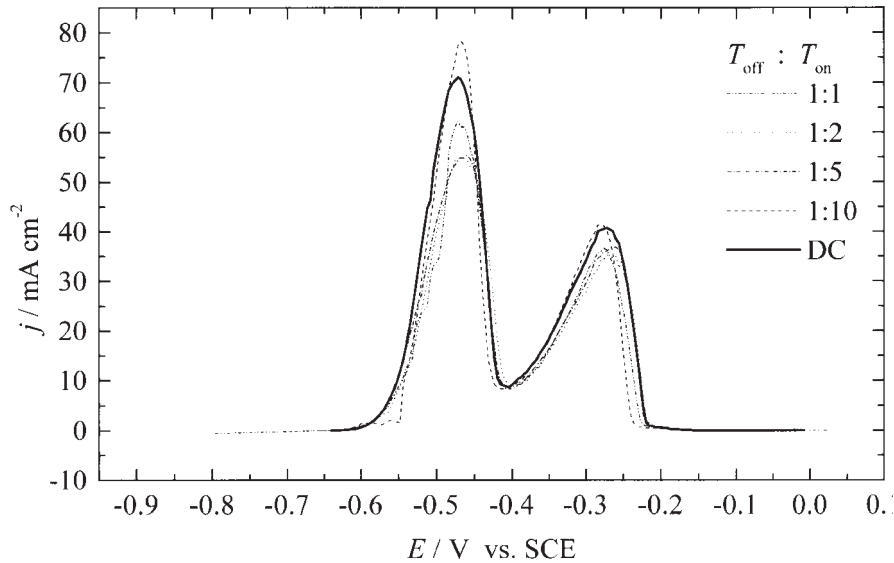
Fig. 5. ALSVs in Na_2SO_4 + EDTA solution of the dissolution of Zn-Ni alloys deposited by DC and PC with T_{on} = 1 ms and different ratio of T_{off}: T_{on}.

Fig. 6. ALSVs in Na_2SO_4 + EDTA solution of the dissolution of Zn-Ni alloys deposited by DC and PC with T_{on} = 0.1 ms and different ratio of T_{off}: T_{on}.

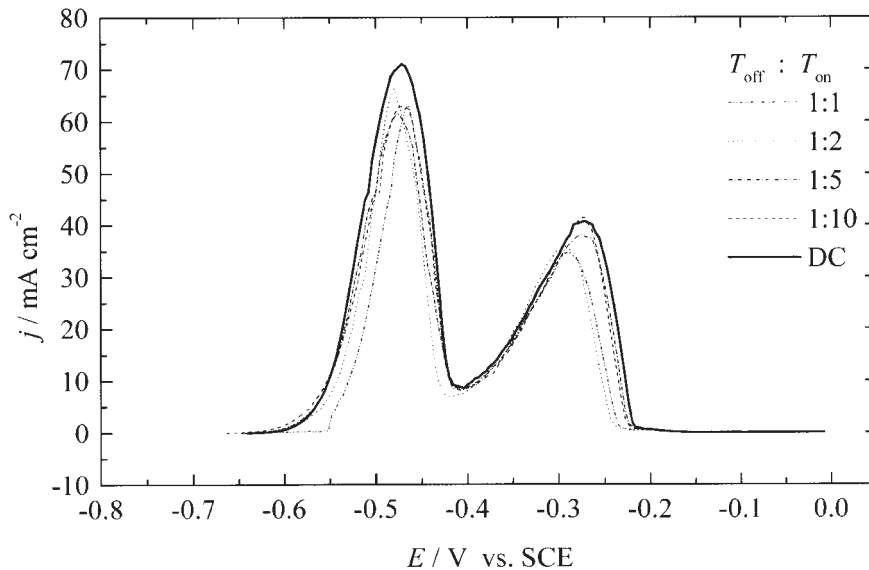were 1:1, 1:2, 1:5 and 1:10. The anodic linear sweep voltammograms obtained (Figs. 3–6) show the phase structures of the Zn-Ni alloys deposited at constant and pulse current density with different pulse plating parameters. As can be seen, there are two dissolution peaks on all the ALSVs, indicating the presence of two different phase structures. For all the ex-
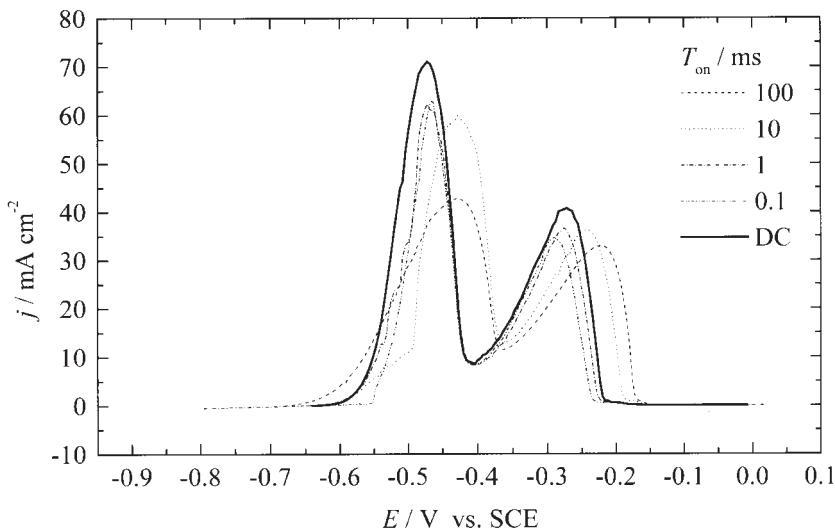
Fig. 7. ALSVs in Na_2SO_4 + EDTA solution of the dissolution of Zn-Ni alloys deposited by DC and PC with $T_{off} : T_{on} = 1$ and different values of T_{on}.

amined cases, the peak current corresponding to the less noble peak potential is higher than that of the other current peak and the charge under this peak exceeds the charge under the other peak. Increasing the pause-to-pulse ratio causes the potentials to shift to less noble values, although for cathodic times of 0.1 and 1 ms there is only a slight shift of the peak potential (Figs. 5 and 6). This is in agreement with previously shown dependence of Ni content on the T_{off}/T_{on} ratio, where it was shown that an increase of this ratio results in a decrease of the Ni content in the alloy (Fig. 2). Since it is assumed that the greater the amount of the more noble metal, Ni, in a deposit, the more noble will be the dissolution potential, it could be expected that increasing the pause-to-pulse ratio, which causes an decrease in the Ni content, would induce a shift of the current peaks in the ALSVs in a negative direction.

The influence of the cathodic time on the phase structures of Zn-Ni alloys obtained by PC with a constant pause-to-pulse ratio of 1 : 1, as well the phase structure for a Zn-Ni alloy obtained by DC is shown in Fig. 7. It can be seen that with decreasing pulse time the ALSVs of the deposits obtained by PC approach the ALSV of the deposit obtained by DC.

The amounts of each alloy phase, corresponding to the area under each current peak, obtained by integrating the peaks in Figs. 3–6, are presented by the anodic charge, along with the portion of each phase in the Zn-Ni deposits are shown in Table I. It can be seen that for cathodic times of 100 and 10 ms the amount of dissolution charge corresponding to the current peak with the less noble peak potential (denoted as Q (I) in Tab. I) changes with pause-to-pulse ratio, reaching a maximum value for a ratio of 1 : 5. For cathodic times of 1 and 0.1 ms, there is a small change of the anodic charge with different pause-to-pulse ratios for both current peaks, and the portion of the two alloy phases depends neither on the pause-to-pulse ratio nor on the duration of the cathodic time.

The peak height on ALSV of the Zn-Ni alloy deposited by DC exceeds the current peaks corresponding to the dissolution of the Zn-Ni alloys deposited by PC (Fig. 7) and the

charge under the voltammetric peaks, *i.e.*, the amount of each alloy phase, are greater with the deposit obtained by DC than that obtained by PC, which is in agreement with the literature data which shows that the current efficiency for Zn-Ni alloys obtained by DC range from 70–95 % while it is just over 50 % in PC.[8]

TABLE I. The anodic dissolution charges and fractions of phases in Zn-Ni alloys obtained by plating with different cathodic times and pause-to-pulse ratios.

T_{on} / ms	T_{off} / T_{on}	Q (I) /C cm^{-2}	Q (II) /C cm^{-2}	Q (I) / ΣQ	Q (II) / ΣQ
100	1	6.19	4.37	0.59	0.41
	2	6.80	4.03	0.63	0.37
	5	8.22	3.05	0.73	0.27
	10	7.83	3.89	0.67	0.33
10	1	6.28	4.19	0.60	0.40
	2	5.56	4.36	0.56	0.44
	5	7.27	3.98	0.65	0.35
	10	6.65	3.53	0.65	0.35
1	1	5.05	3.74	0.57	0.43
	2	5.17	3.99	0.56	0.44
	5	5.23	4.05	0.56	0.44
	10	5.47	4.05	0.57	0.43
0.1	1	4.32	3.47	0.55	0.45
	2	4.60	3.55	0.56	0.44
	5	5.24	4.15	0.56	0.44
	10	5.51	4.08	0.57	0.43

On the basis of the ALSVs, the chemical composition and equilibrium phase diagram of the Zn-Ni system,[12] an identification of the phase structures present in the Zn-Ni alloys obtained by DC and PC was made. The Zn-Ni alloy consists of several intermediate phases and/or intermetallic compounds of different crystallographic orientations. The homogeneous range between 76–77 mol.% Zn corresponds to the γ_1-phase, the Zn content of 82–86 mol.% corresponds to the γ-phase, and 89 mol.% Zn to the δ-phase. According to some authors,[13] there is also a η-phase, which is a solid solution of Ni in Zn, with up to 1 mol.% Ni.

It is well known that deposition of Zn-Ni alloys is anomalous from most plating baths[14] which is why it is possible to acquire Zn-rich deposits, in which the γ (γ_1) and δ-phase prevail. On the basis of the ALSVs, it was shown that all the investigated alloys dissolve under two voltammetric peaks, indicating the presence of two different alloy phases. If it is assumed that the peak potential is more noble for the phase with the higher Ni content, then it could be proposed that the first ALSV peak corresponds to the δ-phase, or Ni$_3$Zn$_{22}$. The second ALSV peak, with a more positive dissolution potential, corre-

sponds to the γ-phase, or Ni$_5$Zn$_{21}$. This presumption is in accordance with the results of the determination of the chemical composition of the Zn-Ni deposits shown earlier (Figs. 1 and 2), where it was shown that the Ni content of all the investigated alloys was in the range of 10–13 wt. %. In addition, it is also in agreement with X-ray analysis from our earlier work[6] which showed the presence of both the δ- and γ-phase in Zn-Ni alloys deposited from a chloride bath (of the same composition) at 20 mA cm^{-2}.

Corrosion properties of the Zn-Ni alloys

Zn-Ni alloys were electrodeposited on steel panels by PC with different pause-to-pause ratios and different cathodic times, as well as by DC ($j = 20$ mA cm^{-2}), as a reference. The average current density in PC was the same for all the deposits, 20 mA cm^{-2}, the cathodic times were: 0.1, 1, 10, 100 and 1000 ms and the pause-to-pulse ratios were 1:1, 1:2, 1:5 and 1:10. The thickness of the deposits was 5 μm. The plated specimens were immersed in a 3 % aqueous NaCl solution and the open circuit potential (E_{ocp}) was measured daily, in order to investigate the corrosion resistance of the Zn-Ni deposits. The time dependence of E_{ocp} for steel plated with Zn-Ni alloys deposited by both constant current and pulse current deposition are shown in Fig. 8. The open circuit potential of a bare steel surface in 3 % NaCl was –640 mV *vs*. SCE which is marked with a line in Fig. 8. The potentials of the Zn-Ni alloys are more negative than the E_{ocp} of the steel base, so the Zn-Ni deposits offer sacrificial cathodic protection. It can be seen from Fig. 8 that at the beginning of exposure to 3 % NaCl the E_{ocp} values of the deposits differ a little but then, with time of immersion and after some time they reach the E_{ocp} of steel, which represents the loss of deposit and the start of corrosion processes. The results of the visually observed alloy destruction in 3 % NaCl solution, or the appearance of red rust on the steel base, are presented in Table II.
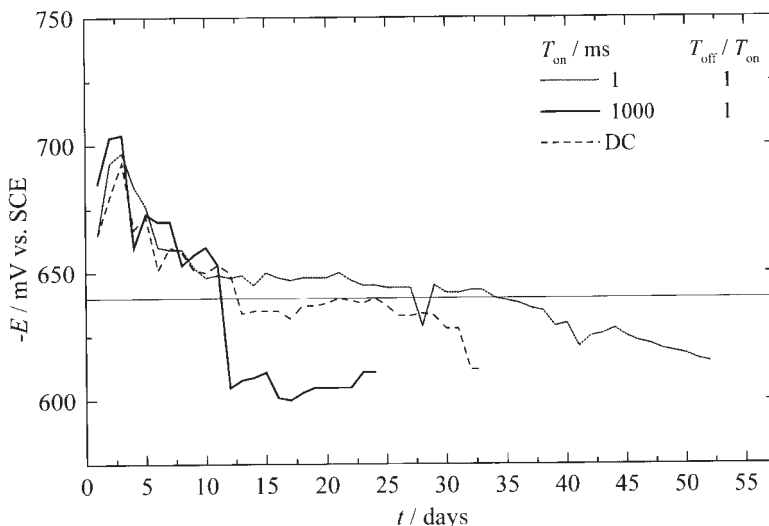

Fig. 8. The dependence of E_{ocp} for Zn-Ni alloys deposited on steel by PC with different cathodic times and different pause-to-pulse ratios.

TABLE II. The time to the appearance of red rust

Deposition parameters	t/h
$T_{on} = 100$ ms, $T_{off}/T_{on} = 1$	1008
$T_{on} = 100$ ms, $T_{off}/T_{on} = 2$	1248
$T_{on} = 100$ ms, $T_{off}/T_{on} = 5$	912
$T_{on} = 100$ ms, $T_{off}/T_{on} = 10$	1080
$T_{on} = 10$ ms, $T_{off}/T_{on} = 1$	840
$T_{on} = 1$ ms, $T_{off}/T_{on} = 1$	1248
$T_{on} = 0.1$ ms, $T_{off}/T_{on} = 1$	744
$T_{on} = 1$ s, $T_{off}/T_{on} = 1$	576
Constant current	792

The corrosion results indicate that the Ni content of the alloy is not the only factor responsible for good corrosion protection, since the Ni content of the deposits investigated here was the highest in the case of DC plating, and this deposit showed poor corrosion protection. Different surface morphology, obtained by different deposition parameters, also influences the corrosion properties of the deposits. It was shown that the deposits obtained by PC with $T_{on} = 1$ ms and a pause-to-pulse ratio of 1 and $T_{on} = 100$ ms and a pause-to-pulse ratio of 2 lasted the longest (1248 hours). Since the deposit roughness is enhanced with increasing T_{on},[4] it could be concluded that among all the deposits investigated in this work, the one obtained with $T_{on} = 1$ ms and a pause-to-pulse ratio of 1, showed the best properties.

CONCLUSIONS

On the basis of the obtained results it was shown that the on-time did not affect the Ni content of Zn-Ni deposits obtained by PC.

All the Zn-Ni alloys investigated in this work dissolve under two voltammetric peaks, indicating the presence of two different phase structures in these alloys. Increasing the pause-to-pulse ratio causes the peak potentials to shift to negative values, especially for cathodic times of 10 and 100 ms. This is a consequence of the lower Ni content at higher T_{off}/T_{on} ratios, since alloys with a greater Ni content dissolve at more noble potentials.

With decreasing pulse time (T_{on}), for a 1 : 1 pause-to-pulse ratio, the ALSVs of the deposits obtained by PC approach those of a deposit obtained by DC.

The Zn-Ni alloy deposited with $T_{on} = 1$ ms and a pause-to-pulse ratio of 1 : 1 showed the best corrosion properties, since the red rust appeared after the longest exposure time to 3 % NaCl (1248 h) and the T_{on} applied provides smooth deposits.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ТАЛОЖЕЊЕ И КАРАКТЕРИЗАЦИЈА ЛЕГУРА ЦИНК-НИКАЛ ДОБИЈЕНИХ КОНСТАНТНОМ И ПУЛСИРАЈУЋОМ СТРУЈОМ

ЈЕЛЕНА Б. БАЈАТ, МИОДРАГ Д. МАКСИМОВИЋ и ГОРАН Р. РАДОВИЋ

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Испитивани су хемијски састав и фазна структура легура Zn-Ni добијених применом различитих параметара електрохемијског таложења. Легуре су таложене из хлоридног раствора на ротирајућој диск електроди и на челичним плочицама константном и пулсирајућом струјом. Испитивани су параметри пулсирајућег таложења (катодног времена, времена паузе и односа паузе и катодног времена) на састав, фазну структуру и корозионе особине легура. Показано је да фазни састав утиче на антикорозионе особине Zn-Ni легура током излагања дејству раствора 3 % NaCl. Легура Zn-Ni добијена пулсирајућим таложењем са катодним временом од 1 ms и односом паузе и пулса од 1 има најбоље корозионе особине.

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