

## Electrolytic deposition and corrosion resistance of Zn–Ni coatings obtained from sulphate-chloride bath

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**Abstract.** Zn–Ni coatings were deposited under galvanostatic conditions on steel substrate (OH18N9). The influence of current density of deposition on the surface morphology, chemical and phase composition was investigated. The corrosion resistance of Zn–Ni coatings obtained at current density 10–25 mA cm<sup>-2</sup> are measured, and are compared with that of metallic cadmium coating. Structural investigations were performed by the X-ray diffraction (XRD) method. The surface morphology and chemical composition of deposited coatings were studied using a scanning electron microscope (JEOL JSM-6480) with EDS attachment. Studies of electrochemical corrosion resistance were carried out in the 5% NaCl, using potentiodynamic and electrochemical impedance spectroscopy (EIS) methods. On the ground of these research, the possibility of deposition of Zn–Ni coatings contained 24–26% at. Ni was exhibited. It was stated, that surface morphology, chemical and phase composition of these coatings are practically independent on current density of deposition. On the basis of electrochemical investigations it was found that corrosion resistance of these Zn–Ni coatings is also independent of current density. These coatings are more corrosion resistant in 5% NaCl solution than metallic cadmium. It was suggested that the Zn–Ni coating may be used as a substitute for toxic cadmium.

**Keywords.** Electrodeposition; corrosion; Zn–Ni coatings.

### 1. Introduction

Electroplating of Zn–Ni alloys has been applied to the production of highly corrosion resistant alloy plated steel. These alloys have been shown to be good substitutes for cadmium, which has fallen into disuse owing to its high toxicity (Abd el Rehim *et al* 1996; Fratesi and Roventi 1996; Bajat *et al* 2000; Gavrilă *et al* 2000; Ganesan *et al* 2007). The corrosion resistance of electrolytic Zn–Ni alloy depends practically on the percentage of Ni, morphology, structure, homogeneity in composition (Fratesi and Roventi 1996; Bajat *et al* 2000; Gavrilă *et al* 2000; Petrauskas *et al* 2005; Ganesan *et al* 2007). It was found that these properties of coating are formed in dependency on electrodeposition conditions (Gavrilă *et al* 2000; Petrauskas *et al* 2005).

Zn–Ni alloys can be electrodeposited from various types of baths, such as chloride containing ammonium chloride, sulphate containing boric acid, pyrophosphate and sulphate baths (Abd el Rehim *et al* 1996).

The electrodeposition of Zn–Ni coatings at higher values of cathodic current, is classified as an anomalous codeposition. Zinc, which is the less noble metal, is preferentially deposited and a higher percentage of Zn is present in the final deposit. Electrodeposition of Zn–Ni

coatings at lower values of cathodic current densities are not anomalous, and electrolytic coatings contain higher contents of Ni than Zn.

The purpose of this work was to evaluate the ability of Zn–Ni coatings obtained at the current densities from  $j = 10 \text{ mA cm}^{-2}$  to  $j = 25 \text{ mA cm}^{-2}$  as electrode materials in corrosion resistance investigations.

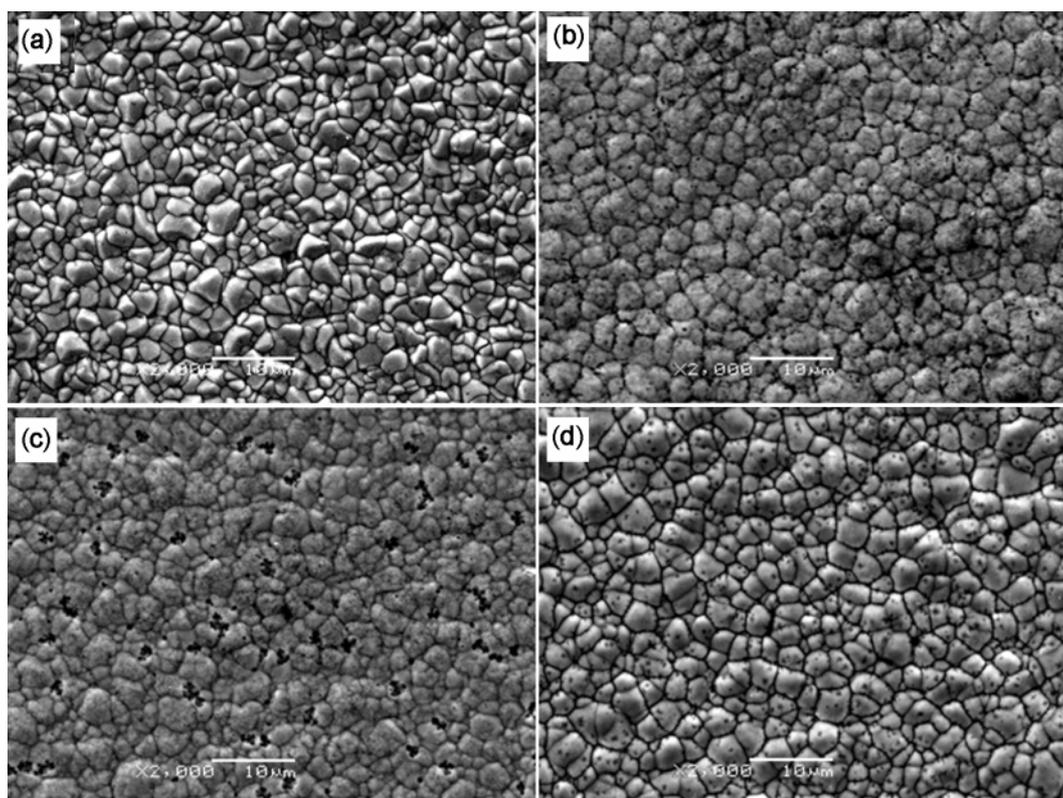
### 2. Experimental

Zn–Ni coatings were deposited on the austenitic steel (OH18N9). Preparation of substrate surface consisted of cleaning with a detergent solution, and then it was chemically treated with HCl solution (1 : 1), rinsed in distilled water and degreased. Prior to deposition, the steel substrate was activated in HCl solution, using cathode current density  $j = 5 \text{ mA cm}^{-2}$  during  $t = 2 \text{ min}$ .

Prior to the deposition of Zn–Ni coatings the thin Ni sublayer (1  $\mu\text{m}$ ) was plated on the substrate from the bath contained 350 g dm<sup>-3</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O and 111 cm<sup>3</sup> dm<sup>-3</sup> HCl, in order to ensure better adhesion of the deposit.

Electrolytic coatings were obtained from the following bath (concentration in g dm<sup>-3</sup>): NiSO<sub>4</sub>·7H<sub>2</sub>O – 160, NiCl<sub>2</sub>·6H<sub>2</sub>O – 24, H<sub>3</sub>BO<sub>3</sub> – 40, ZnCl<sub>2</sub> – 14, MgSO<sub>4</sub>·7H<sub>2</sub>O – 30 and 14 cm<sup>3</sup> dm<sup>-3</sup> XR. pH of the bath was kept in the range from 4.5 to 5.0. The process of deposition was carried out at the temperature of 298 K.

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**Figure 1.** Micrographs of surface of Zn–Ni coatings obtained for the following current densities: (a)  $10 \text{ mA cm}^{-2}$ ; (b)  $15 \text{ mA cm}^{-2}$ ; (c)  $20 \text{ mA cm}^{-2}$  and (d)  $25 \text{ mA cm}^{-2}$ .

The Zn–Ni coatings were deposited under galvanostatic conditions at current density  $j = 10\text{--}25 \text{ mA cm}^{-2}$ . Optimization for deposition current density range was done using Hull's cell.

Deposition time ranged from  $t = 39$  to 98 minutes, depending on the current density. One-sided geometric surface area of cathode was  $25 \text{ cm}^2$ . Sheet nickel served as anode. Electrodeposition of the Ni and Zn–Ni coatings was carried out using galvanic unit MAG (IMP-BUD 5, Poland).

Deposited coatings were subjected to a passivation treatment of 10 s duration in the following solution (concentration in  $\text{g dm}^{-3}$ ):  $\text{K}_2\text{Cr}_2\text{O}_7 - 70$ ,  $\text{H}_2\text{SO}_4 - 8$ .

The XRD patterns were measured using the Philips X'Pert PW 3040/60 X-ray diffractometer with the copper radiation ( $\lambda_{\text{K}\alpha} = 1.54056 \text{ \AA}$ ). A graphite monochromator was used to select the  $\text{K}\alpha$  radiation.

The surface morphology and surface chemical composition of deposited coatings were studied using a scanning electron microscope (JEOL JSM-6480) with EDS attachment.

Investigations of electrochemical corrosion resistance investigations were conducted in a three-electrode cell, using potentiodynamic and electrochemical impedance spectroscopy (EIS) methods. These measurements were carried out in 5% NaCl solution, at the temperature of

293 K, using AUTOLAB<sup>®</sup> electrochemical system. The auxiliary electrode was a platinum mesh and the reference electrode was the saturated calomel electrode (SCE). Values of corrosion potential, corrosion current and polarization resistance were determined by Stern method. The electrochemical impedance measurements were performed at the corrosion potential. In these measurements the amplitude of ac signal was equal 0.005 V. A frequency range from 10 kHz to 0.1 Hz was covered with ten points per decade.

### 3. Results and discussion

The obtained Zn–Ni coatings show good adhesion to the substrate. These coatings are characterized by grey and smooth surface. Generally, the surface morphology of obtained Zn–Ni coatings is independent of current density of deposition (figure 1).

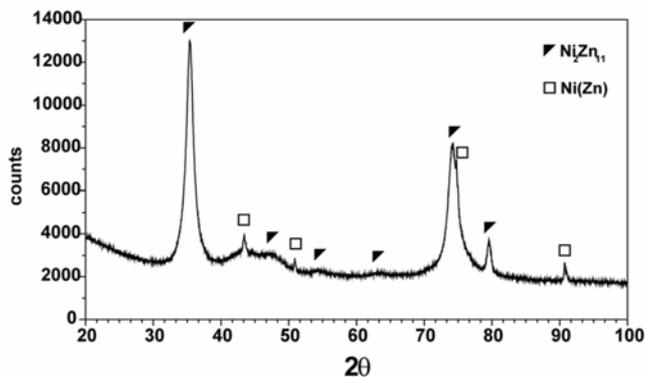
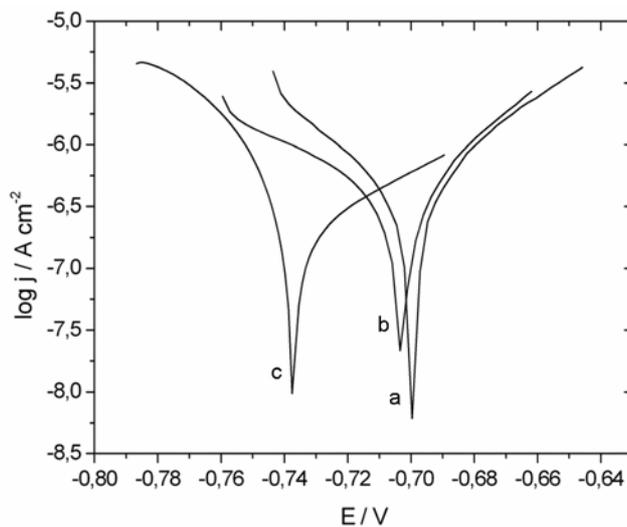
Surface chemical composition analysis appeared that the Zn–Ni coatings obtained at higher cathodic current density ( $j = 15\text{--}25 \text{ mA cm}^{-2}$ ) contained about 24% at. Ni. The Zn–Ni coating obtained at current density  $j = 10 \text{ mA cm}^{-2}$  contained slightly more Ni, i.e. about 26% at. (table 1). It is suggested that the chemical composition of obtained Zn–Ni coatings is practically also independent of current density of deposition.

**Table 1.** The surface local chemical composition of Zn–Ni coatings in dependence on deposition current density.

$j/\text{mA cm}^{-2}$	10	15	20	25
Ni (% at.)	$26.2 \pm 0.3\%$	$24.4 \pm 0.3\%$	$24.4 \pm 0.3\%$	$24.8 \pm 0.3\%$
Zn (% at.)	$73.8 \pm 0.3\%$	$75.6 \pm 0.3\%$	$75.6 \pm 0.3\%$	$75.2 \pm 0.3\%$

**Table 2.** Corrosion parameters for the Zn–Ni coatings, obtained at the current density of  $j = 10 \text{ mA cm}^{-2}$ ,  $j = 25 \text{ mA cm}^{-2}$  and for metallic cadmium, determined from potentiodynamic method.

Type of coatings	$E_{\text{cor}}$ (V)	$j_{\text{cor}}$ ( $\mu\text{A cm}^{-2}$ )	$R_p$ ( $\text{k}\Omega \text{ cm}^2$ )
Zn–Ni (obtained at the $j = 10 \text{ mA cm}^{-2}$ )	–0.699	0.27	27.56
Zn–Ni (obtained at the $j = 25 \text{ mA cm}^{-2}$ )	–0.703	0.31	27.12
Metallic cadmium	–0.737	1.93	25.80

**Figure 2.** X-ray diffraction patterns for Zn–Ni coating, obtained at the current density of  $j = 10 \text{ mA cm}^{-2}$ .**Figure 3.** Dependences of  $\log j = f(E)$  for the Zn–Ni coatings, obtained at the current density of  $j = 10 \text{ mA cm}^{-2}$  (a);  $j = 25 \text{ mA cm}^{-2}$  (b); and for the metallic cadmium (c).

Phase composition of Zn–Ni coatings is independent of applied current conditions. All X-ray diffraction patterns

show the presence of reflexes coming from solid solution of Zn in Ni and  $\text{Ni}_2\text{Zn}_{11}$  phases (figure 2).

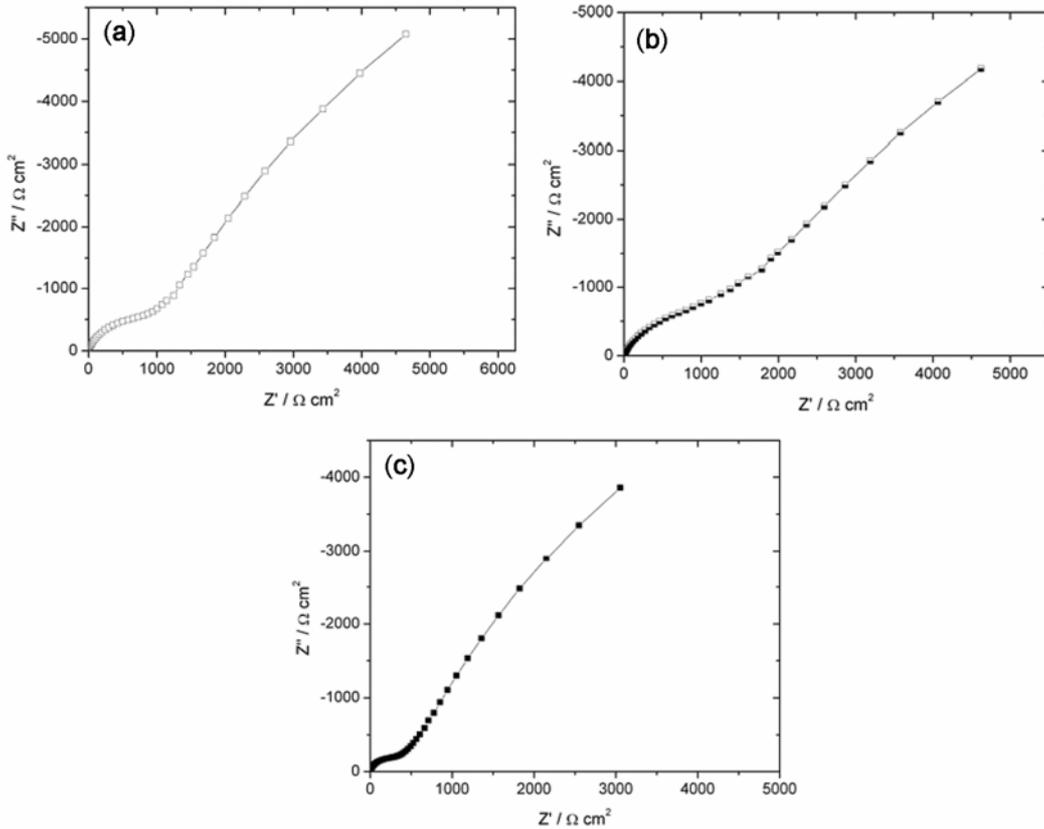
Investigations of corrosion resistance were made for Zn–Ni coatings, obtained at the current densities of  $j = 10\text{--}25 \text{ mA cm}^{-2}$ . Results of this investigations only for the coatings obtained at the extreme current densities  $j = 10$  and  $25 \text{ mA cm}^{-2}$  are presented in this work because corrosion resistance are independent of current density of deposition (as shown later in this work). Corrosion resistance of these coatings was compared with metallic cadmium one.

Open circuit potentials of coatings were determined after 20 h. It was chosen a range  $\pm 0.050 \text{ V}$  from determined value and recorded potentiodynamic curve with rate  $\nu = 0.060 \text{ V min}^{-1}$ . On the ground of the obtained dependences  $j = f(E)$ , values of corrosion parameters were determined. It was found that values of corrosion current are less and values of corrosion potential of the Zn–Ni coatings are more positive in comparison with metallic cadmium. Zn–Ni coatings also characterized by higher values of polarization resistance (table 2; figure 3). Average values of these corrosion parameters for Zn–Ni coatings, obtained at the current densities of  $j = 10\text{--}25 \text{ mA cm}^{-2}$  were equal:  $E_{\text{cor}} = -0.701 \pm 0.002 \text{ V}$ ,  $j_{\text{cor}} = 0.29 \pm 0.02 \mu\text{A cm}^{-2}$ ,  $R_p = 27.34 \pm 0.35 \text{ k}\Omega \text{ cm}^2$ . It is suggested that these coatings are more corrosion resistant in 5% NaCl solution than the metallic cadmium.

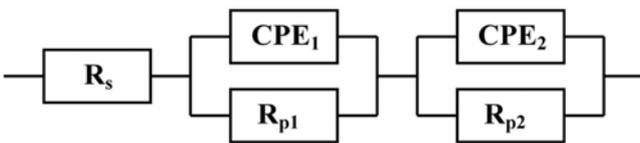
Additionally, corrosion resistance investigation of the Zn–Ni coatings and metallic cadmium by EIS method was made. Results of these investigations submitted in the form of Nyquist diagram ( $Z'' = f(Z')$ ) (figure 4). These results were analyzed using a CNLS fitting program. It has been found that the impedance of Zn–Ni coatings and metallic cadmium could be described by the two-CPE electrode model, which represented as the solution resistance,  $R_s$ , in series with two parallel CPE –  $R_p$  elements (figure 5), explains the impedance behaviour of the electrode containing pear-shape pores ( $R_{p1}$ ,  $R_{p2}$  [ $\Omega \text{ cm}^2$ ]) are the polarization resistances,  $\text{CPE}_1$ ,  $\text{CPE}_2$  are the

**Table 3.** Corrosion parameters of Zn–Ni coatings, obtained at the current density of  $j = 10 \text{ mA cm}^{-2}$ ,  $j = 25 \text{ mA cm}^{-2}$  and for metallic cadmium, determined from EIS method.

Type of coatings	$R_{p1}$ ( $\text{k}\Omega \text{ cm}^2$ )	$T_1$	$\phi_1$	$R_{p2}$ ( $\text{k}\Omega \text{ cm}^2$ )	$T_2$	$\phi_2$	$R_s$ ( $\Omega \text{ cm}^2$ )
Zn–Ni (obtained at the $j = 10 \text{ mA cm}^{-2}$ )	1.05	0.0000021	0.53	27.29	0.000052	0.71	0.39
Zn–Ni (obtained at the $j = 25 \text{ mA cm}^{-2}$ )	1.02	0.0000016	0.51	26.74	0.000055	0.72	0.36
Metallic cadmium	0.43	0.0000019	0.52	26.07	0.000061	0.71	0.37



**Figure 4.** Dependences of  $Z'' = f(Z')$  for the Zn–Ni coatings obtained at the current density of  $j = 10 \text{ mA cm}^{-2}$  (a);  $j = 25 \text{ mA cm}^{-2}$  (b); and metallic cadmium (c).



**Figure 5.** Equivalent circuit scheme for the two-CPE electrode model.

constant phase elements, where  $Z_{CPE} = 1/[T(j\omega)^\phi]$  (Karimi-Shervedani and Lasia 1997, 1998).

As a result of approximation of experimental data in the case of two-CPE model the following parameters could be obtained:  $R_{p1}$ ,  $T_1$ ,  $\phi_1$ ,  $R_{p2}$ ,  $T_2$ ,  $\phi_2$  and  $R_s$ , where  $T_1$ ,  $T_2$  are the capacity parameters and  $\phi_1$ ,  $\phi_2$  are the CPE angles. The total values of  $R_p$  calculated from EIS method

are approximately comparable with values of  $R_p$  obtained with potentiodynamic method and therefore also could be a measure of corrosion resistance of Zn–Ni coatings and metallic cadmium (table 3).

#### 4. Conclusions

On the basis on this research, the possibility of deposition of Zn–Ni coatings contained 24–26% at. Ni was exhibited. It was stated that surface morphology, chemical and phase composition of obtained Zn–Ni coatings are practically independent of current density of deposition.

On the basis of electrochemical investigations it was found that corrosion resistance of Zn–Ni coatings is independent of current density. These coatings are more

corrosion resistant in 5% NaCl solution than the metallic cadmium. The less value of corrosion current, more positive values of corrosion potential and also higher value of polarization resistance results from above. It was suggested that Zn–Ni coatings may be used as a substitute for toxic cadmium.

It could be concluded, that parameters calculated from EIS method could be a measure of corrosion resistance of Zn–Ni coatings and metallic cadmium and confirmed results obtained from potentiodynamic method.

#### Acknowledgement

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#### References

- Abd el Rehim S S, Fouad E E, Abd el Wahab S M and Hassan H H 1996 *Electrochem. Acta* **41** 1413
- Bajat J B, Kačarević-Popović Z, Mišković-Stanković V B and Maksimović M D 2000 *Prog. Org. Coat.* **39** 127
- Fratesi R and Roventi G 1996 *Surf. Coat. Technol.* **82** 158
- Ganesan P, Kumaraguru S P and Popov B N 2007 *Surf. Coat. Technol.* **201** 7896
- Gavrila M, Millet J P, Mazile H, Marchandise D and Cuntz J M 2000 *Surf. Coat. Technol.* **123** 164
- Karimi-Shervedani R and Lasia A 1997 *J. Electrochem. Soc.* **144** 2652
- Karimi-Shervedani R and Lasia A 1998 *J. Electrochem. Soc.* **145** 2219
- Petrauskas A, Grincevičienė L, Češūnienė A and Matulionis E 2005 *Surf. Coat. Technol.* **192** 299