

Influence of thermal treatment on the corrosion resistance of electrolytic Zn–Ni coatings

K. WYKPIŚ*, M. POPCZYK, J. NIEDBAŁA, A. BUDNIOK, E. ŁĄGIEWKA, B. BIERSKA-PIECH

University of Silesia, Institute of Materials Science, Bankowa 12, 40-007 Katowice, Poland

This study was undertaken in order to obtain and characterize the corrosion resistance of Zn–Ni coating. The process was carried out under galvanostatic conditions ($j = 50 \text{ mA}\cdot\text{cm}^{-2}$) chosen on the ground of an analysis of the deposition process in the Hull's cell. The Zn–Ni coatings were deposited on austenitic (OH18N9) steel substrate from the ammonia bath. Thermal treatment of Zn–Ni coating was carried out in argon atmosphere. Structural investigations were conducted by X-ray diffraction method. Surface morphology of the obtained coatings was determined using a scanning electron microscope (JEOL JSM-6480) with EDS attachment. The electrochemical corrosion resistance of the prepared Zn–Ni coatings, austenitic (OH18N9) and (St3S) steels, was defined. The studies of electrochemical corrosion resistance were carried out in 5 % NaCl, using potentiodynamic and electrochemical impedance spectroscopy (EIS) methods. Examinations of localized corrosion resistance were conducted using scanning vibrating electrode technique (SVET). On the grounds of these investigations it was found that Zn–Ni coating after thermal treatment was more corrosion resistant than the Zn–Ni coating before thermal treatment. The relatively good corrosion resistance of Zn–Ni coatings is not as high as the resistance of (OH18N9) steel substrate, but higher compared to (St3S) steel. Therefore, the Zn–Ni coatings may be regarded as a protective coating for St3S steel.

Keywords: *electrodeposition, corrosion, Zn–Ni coatings*

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1. Introduction

The use of zinc and zinc alloys to improve the corrosion resistance of coated steel sheets has been widely studied due to its importance in industrial applications. Zn–Ni electrodeposits offer a particularly promising alternative to pure Zn and galvanized steel, mainly in the automotive industry, due to their improved mechanical properties and corrosion resistance to sodium chloride in the atmospheric environment [1–3]. This alloy is also considered to be a viable alternative to cadmium [2]. The electrodeposition of zinc alloys with metals of iron group causes the anomalous codeposition phenomenon. This occurrence is very important in the zinc alloys electrodeposition. The effect of operating variables such as bath temperature and current density on grain size of electrodeposited Zn–Ni coatings was studied. According to the literature, the composition, structure, and porosity of electrodeposited Zn–Ni alloys also influence their corrosion behavior

[3–7]. The presence of Zn in Zn–Ni coatings provides cathodic protection of iron-based substrates while Ni increases corrosion resistance of the deposit. The beneficial influence of Ni is that it improves the protective characteristics of passive oxide films, and the alloy structure. The higher corrosion resistance of electrodeposited Zn–Ni coatings has been attributed to the predominant presence of crystallographic planes in the oxide layer with a higher packing density and hence, a more stable ionization in the environment [1, 3–7].

Classic electrochemical techniques provide average data (corrosion potential, corrosion current, polarization resistance) integrating over a large surface area of the studied material. The scanning vibrating electrode technique (SVET) is one of the most promising techniques. It provides the possibility to map variations in current densities at the microscale over metal surface by measuring potential gradients developed in the solution due to the ionic flow [8, 9].

The purpose of this work was to evaluate the ability of Zn–Ni coatings, before and after thermal treatment, as electrode materials, in corrosion re-

*E-mail: katarzyna.wykpis@us.edu.pl

sistance investigations in 5 % NaCl solution. The classic and localized corrosion resistance of Zn–Ni coating depending on thermal treatment, was determined.

2. Experimental

An electrolytic Zn–Ni coating was obtained from the ammonia bath of composition ($\text{g}\cdot\text{dm}^{-3}$): $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ – 50, $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ – 100, Na_2SO_4 – 75, $(\text{NH}_4)_2\text{SO}_4$ – 38, NH_4OH – 250 $\text{cm}^3\cdot\text{dm}^{-3}$. The temperature of the bath was 298 K; the pH was kept in the range of 9.6 to 10.4. The process was carried out in the galvanostatic conditions at a cathodic current density of $j = 50 \text{ mA}\cdot\text{cm}^{-2}$. The j value was selected on the basis of the deposition process in the Hull's cell.

The Zn–Ni coating was deposited on austenitic steel (OH18N9). The preparation of substrate surface consisted of the following steps: cleaning with a detergent solution, chemical treatment with HCl solution (1:1), rinsing in distilled water and degreasing. Prior to deposition, the steel substrate was activated in HCl solution, using a cathode current density of $j = 5 \text{ mA}\cdot\text{cm}^{-2}$, for 2 mins. The nickel underlayer, obtained from the bath containing 350 $\text{g}\cdot\text{dm}^{-3}$ $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and 111 $\text{cm}^3\cdot\text{dm}^{-3}$ HCl, was deposited before obtaining of Zn–Ni coating in order to assure adhesion of the Zn–Ni coating to the substrate.

The thermal treatment of the Zn–Ni coatings was carried out at a temperature of 593 K for 2 hours in protective gas atmosphere (argon).

The surface morphology and surface chemical composition of deposited coatings were studied using a scanning electron microscope (JEOL JSM-6480) with EDS attachment. The XRD patterns were measured using the Philips X'Pert PW 3040/60 X-ray diffractometer with copper radiation ($\lambda K\alpha = 1.54056 \text{ \AA}$). A graphite monochromator was used to select the $K\alpha$ radiation. The crystallite size and lattice strain were analyzed using the Williamson-Hall theory [10].

The electrochemical corrosion resistance of the prepared Zn–Ni coatings was defined and compared with the corrosion resistance of austenitic OH18N9 and St3S steel. The investigations of electrochemical corrosion resistance were conducted in a three-

electrode cell using potentiodynamic and electrochemical impedance spectroscopy (EIS) methods. These measurements were carried out in a 5 % NaCl solution, at a temperature of 293 K using AUTO-LAB® electrochemical system. The auxiliary electrode was a platinum mesh and the reference electrode was the saturated calomel electrode (SCE). The values of corrosion potential, corrosion current and polarization resistance were determined by the Stern method. The electrochemical impedance measurements were performed at the corrosion potential. In these measurements the amplitude of the ac signal was equal to 0.005 V. A frequency range from 10 kHz to 0.1 Hz was covered with ten points per decade.

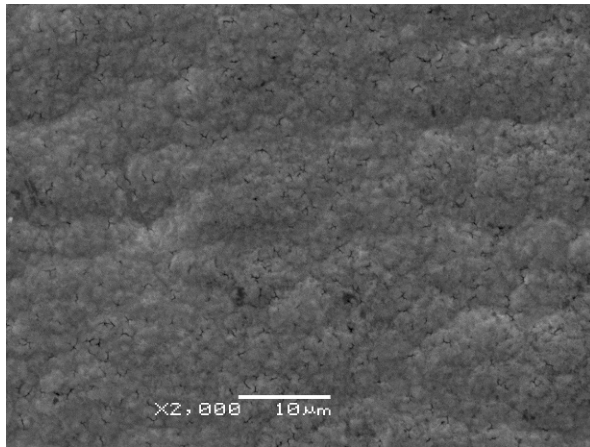
The SVET measurements were made using a Scanning Electrochemical Workstation Model 370 (Princeton Applied Research AMETEK). The SVET maps were registered at the potential of open circuit. A scan was made of $1000 \mu\text{m} \times 1000 \mu\text{m}$ surface area. The vibrating amplitudes of the scanning probe were adjusted to 30 μm . The values of registered potential difference were calculated on the basis of current density values obtained from a calibration potential-current curve which was determined for a 5 % NaCl water solution.

3. Results and discussion

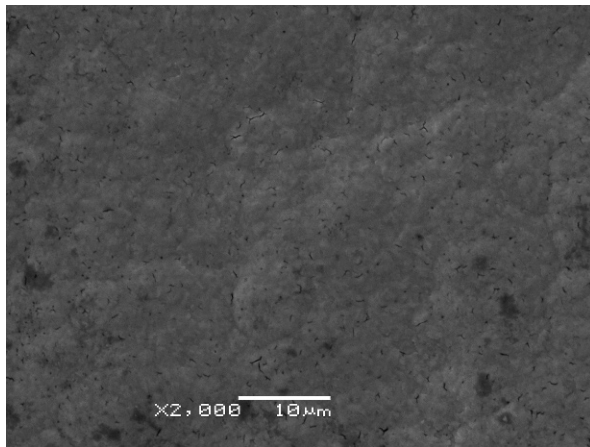
The Zn–Ni coatings, before and after thermal treatment, show good adhesion to the substrate. These coatings are characterized by smooth, matt and grey surface. After the thermal treatment a decrease in the surface development of Zn–Ni coating was observed (Fig. 1).

Surface chemical composition analysis was carried out using the scanning electron microscope and it was found that the Zn–Ni coating consists of $15.5 \% \pm 0.4 \% \text{ at. Ni}$ and $84.5 \% \pm 1.5 \% \text{ at. Zn}$.

Before and after annealing, the XRD patterns showed that the structure of electrodeposited coatings was diphasic: Ni(Zn) solid solution and $\text{Ni}_2\text{Zn}_{11}$ intermetallic phases. The amount of $\text{Ni}_2\text{Zn}_{11}$ intermetallic phase grew versus annealing temperature. The line broadening decreased after thermal treatment. The average Ni crystallite size was $\sim 250 \text{ \AA}$ before annealing and $\sim 700 \text{ \AA}$ after annealing. The



(a)

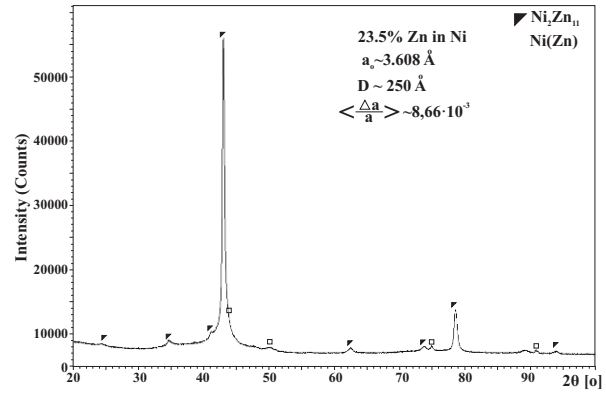


(b)

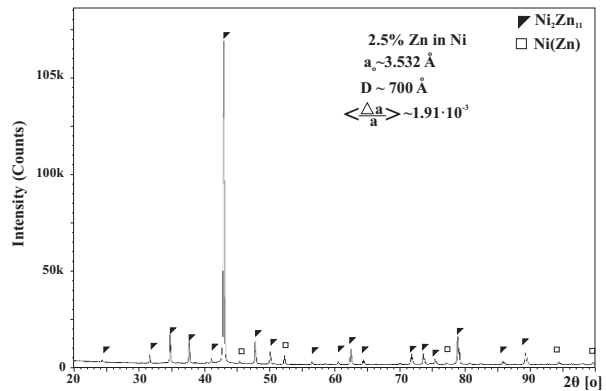
Fig. 1. Surface morphology of the Zn–Ni coating before (a) and after (b) thermal treatment.

lattice strain decreased from the value of $8.66 \cdot 10^{-3}$ for the samples before annealing to a value of $1.91 \cdot 10^{-3}$ for the samples after the thermal treatment (Fig. 2).

Open circuit potentials of the coatings were determined for 20 hours (Fig. 3). A range of ± 0.050 V was chosen from the determined value and a potentiodynamic curve was recorded with a rate of $v = 0.060$ V·min⁻¹. On the grounds of the obtained dependences $j = f(E)$, the values of corrosion parameters were determined. It was found that for the Zn–Ni coating after the thermal treatment, the value of corrosion current was lower and the value of corrosion potential was more positive in comparison with Zn–Ni coating before the thermal treatment



(a)



(b)

Fig. 2. XRD patterns of the Zn–Ni coating before (a) and after (b) thermal treatment.

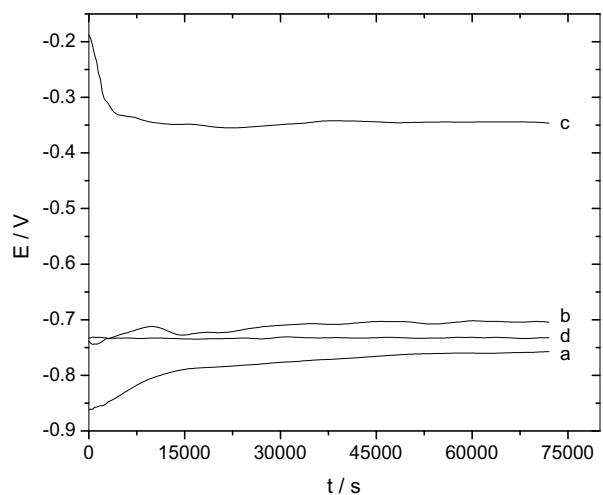


Fig. 3. Dependences of $E = f(t)$ for the Zn–Ni coating before (a) and after (b) thermal treatment and for OH18N9 (c) and St3S (d) steels.

Table 1. Corrosion parameters determined from potentiodynamic method.

Type of coatings	$E_{cor.}$ [V]	$j_{cor.}$ [$\mu\text{A}\cdot\text{cm}^{-2}$]	R_p [$\text{k}\Omega\cdot\text{cm}^2$]
Zn–Ni before thermal treatment	–0.755	0.81	8.45
Zn–Ni after thermal treatment	–0.712	0.71	11.88
OH18N9 steel	–0.354	0.15	67.92
St3S steel	–0.739	2.11	3.67

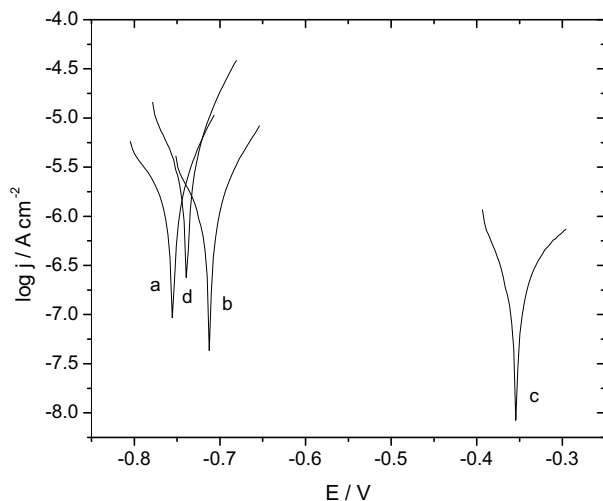


Fig. 4. Dependences of $\log j = f(E)$ for the Zn–Ni coating before (a) and after (b) thermal treatment and for OH18N9 (c) and St3S (d) steels.

(Tab. 1, Fig. 4). This coating was also characterized by a higher value of polarization resistance. It is suggested, that the Zn–Ni coating after thermal treatment is more corrosion resistant in a 5 % NaCl solution than the Zn–Ni coating before thermal treatment. These obtained parameters were compared with the corrosion parameters of austenitic OH18N9 and St3S steels.

It was ascertained that the corrosion potential of austenitic steel ($E_{cor.} = -0.354$ V) is more positive, corrosion current ($j_{cor.} = 0.15 \mu\text{A}\cdot\text{cm}^{-2}$) is lower and polarization resistance ($R_p = 67.92 \text{ k}\Omega\cdot\text{cm}^2$) is higher than for Zn–Ni coatings. This means that although Zn–Ni coatings after thermal treatment show a relatively good corrosion resistance, they are still less resistant to the aggressive environment of 5 % NaCl, compared with the austenitic steel substrate.

The corrosion resistance of (St3S) steel is the worst among the materials tested. The corrosion potential of this steel ($E_{cor.} = -0.739$ V) takes a more negative value compared to the heated Zn–Ni. The corrosion current ($j_{cor.} = 2.11 \mu\text{A}\cdot\text{cm}^{-2}$) is higher and polarization resistance ($R_p = 3.67 \text{ k}\Omega\cdot\text{cm}^2$) is lower, even compared to the as-deposited Zn–Ni coating. Therefore, the Zn–Ni coatings may be regarded as a protective coating for St3S steel (Tab. 1, Fig. 4).

Results of EIS investigations are submitted in the form of a Nyquist diagram [$Z'' = f(Z')$] (Fig. 5). These results were analyzed using a CNLS fitting program. It has been found that the impedance of obtained Zn–Ni coatings can be described by the CPE2 electrode model, which represents the solution resistance, R_s , in series with two parallel CPE – R_p elements (Fig. 6a), and explains the impedance behavior of the electrode containing pear-shape pores (R_{p1}, R_{p2} [$\Omega\cdot\text{cm}^2$] are the polarization resistances, CPE1, CPE2 are the constant phase elements, where $Z_{CPE} = 1/[T(j\omega)^\phi]$). This model produces two semicircles on the complex plane plots where the high-frequency semicircle is related to the surface porosity and the low-frequency semicircle is related to the electrode process [11, 12].

As a result of experimental data approximation, 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 ϕ_1, ϕ_2 are the CPE angles [11, 12] in the case of the CPE2 model. The sum of $R_{p1} + R_{p2}$ gives the total value of polarization resistance, which is higher after thermal treatment than before in the case of Zn–Ni coating (Tab. 2).

The results of electrochemical impedance investigation at the electrode-electrolyte interface show, that the ac behavior of austenitic OH18N9 and St3S

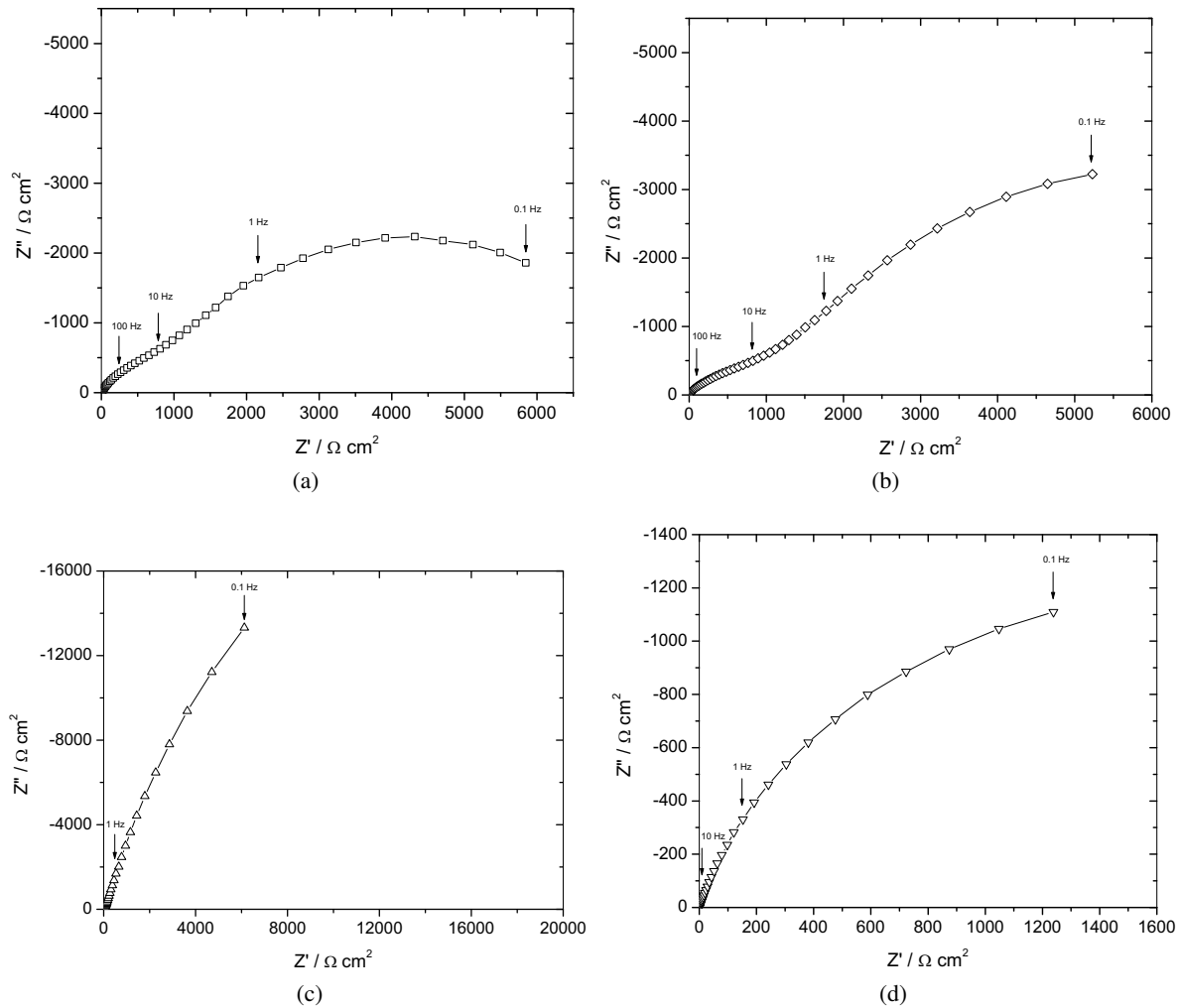


Fig. 5. Dependences of $Z'' = f(Z')$ for the Zn–Ni coating before (a) and after (b) thermal treatment and for OH18N9 (c) and St3S (d) steels.

steels can be described by the CPE1 model (Fig. 6b). This model consists of solution resistance R_s in series with a parallel connection of the CPE element and the charge-transfer resistance R_p .

As a result of approximation of the experimental data in the case of CPE1 model the following parameters could be obtained: R_s , R_p , T and ϕ . The model produces one semicircle on the complex plane plots in the whole frequency range [11, 12].

The values of R_p calculated using EIS method for all investigated materials are approximately comparable with the values of R_p obtained by potentiodynamic method and therefore the values obtained by the EIS method could be a measure of corrosion resistance of these materials.

These EIS results confirmed that Zn–Ni coatings both before and after thermal treatment are less corrosion resistant in a 5 % NaCl solution than austenitic steel. However, these Zn–Ni coatings exhibit higher corrosion resistance when compared to St3S steel.

The effect of thermal treatment on the localized corrosion resistance of Zn–Ni coatings was investigated by SVET technique in a 5 % NaCl solution. The obtained SVET maps (Fig. 7) show differences in the distribution of local current density. These differences concern the size and intensities of the anodic and cathodic sites on the surface of investigated coatings. The SVET map for as-deposited Zn–Ni coating shows a symmetric current distribution

Table 2. Corrosion parameters determined from EIS method for Zn–Ni coatings before and after thermal treatment.

Type of coatings	R_{p1} [kΩ·cm ²]	T_1	ϕ_1	R_{p2} [kΩ·cm ²]	T_2	ϕ_2	R_s [Ω·cm ²]
Zn–Ni before thermal treatment	1.56	0.0000584	0.59	7.01	0.0001037	0.65	0.68
Zn–Ni after thermal treatment	1.06	0.0000560	0.56	10.72	0.0002030	0.62	0.66

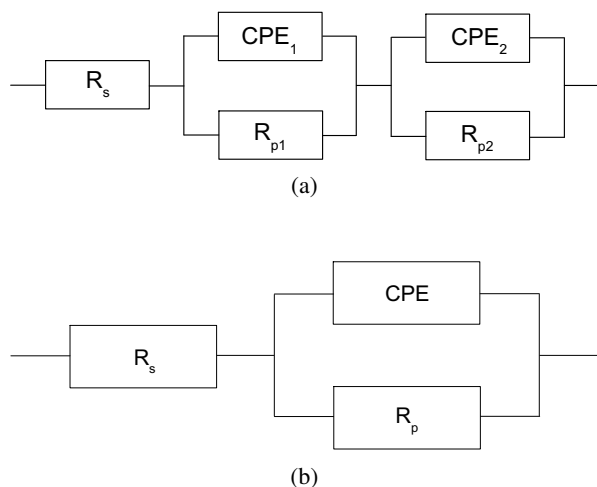


Fig. 6. Equivalent circuit schemes for the (a) CPE2, (b) CPE1 electrode model.

between anodic and cathodic sites. The map is characterized by considerably more sites with higher values of local current density compared with the map of the thermally treated Zn–Ni coating. The SVET analysis, with regard to the sites with a selected local current density of $6.0 \cdot 10^{-9} \text{ A} \cdot \text{cm}^{-2}$, indicates that most sites can be ascribed to as-deposited Zn–Ni coating on the SVET map (Fig. 7a). It means that the number of these sites slightly decreased after the thermal treatment of Zn–Ni coating. Thermal treatment limits the number of preferential centers of corrosion attack on the Zn–Ni coating surface. It was found that the Zn–Ni coating subjected to thermal treatment are characterized by lower local current densities than the as-deposited Zn–Ni coating. This indicates that thermal treatment improves both a total and local corrosion resistance of the Zn–Ni coating in a 5 % NaCl solution.

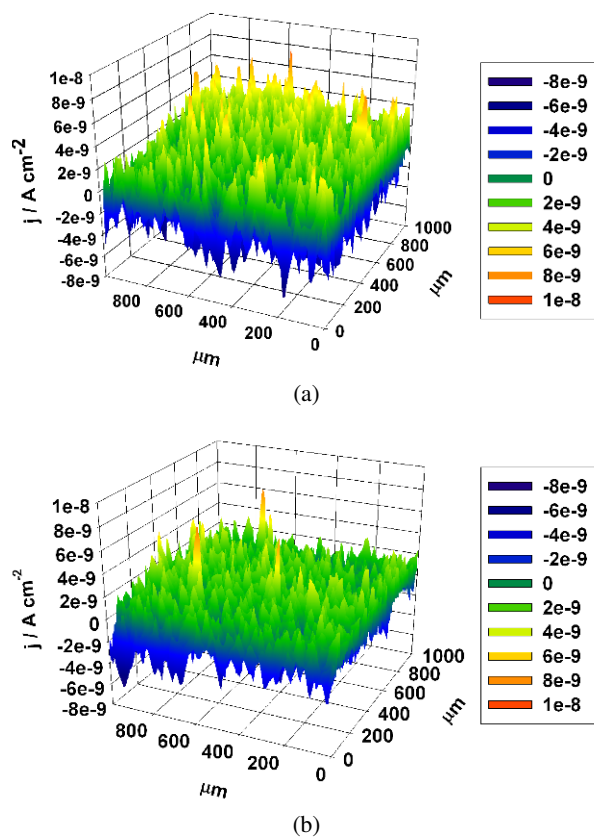


Fig. 7. SVET maps obtained for Zn–Ni coatings before (a) and after (b) thermal treatment.

4. Conclusions

Based on electrochemical investigations it was found that Zn–Ni coatings after thermal treatment are more corrosion resistant in a 5 % NaCl solution than Zn–Ni coatings before thermal treatment. More positive values of corrosion potential, lower value of corrosion current and also higher values of polarization resistance results from the above.

Table 3. Corrosion parameters determined from EIS method for OH18N9 and St3S steels.

Type of steel	R_p [k Ω ·cm ²]	T	ϕ	R_s [Ω ·cm ²]
OH18N9 steel	67.95	0.0000527	0.67	0.63
St3S steel	3.69	0.0032503	0.69	0.65

The relatively good corrosion resistance of Zn–Ni coatings is not as high as the corrosion resistance of (OH18N9) steel substrate but higher compared to (St3S) steel. Therefore, the Zn–Ni coatings may be regarded as a protective coating for St3S steel.

Moreover, it can be concluded, that the parameters calculated from EIS method could be a measure of the corrosion resistance of the coatings and confirm the results obtained from potentiodynamic method. The SVET analysis indicated that thermal treatment of Zn–Ni coating causes a decrease in the number of corrosion centers on their surface area. As a consequence of this decrease, the thermally treated Zn–Ni coatings are more resistant to corrosion than as-deposited ones.

Acknowledgements

This research was financed with Project PBZ-MNiSW-4/01/1/2007.

References

- [1] SOARES M.E., SOUZA C.A.C., KURI S.E., *Surf. Coat. Technol.*, 201(6) (2006), 2953.
- [2] ASHASSI-SORKHABI H., HAGRAH A., PARVINI-AHMADI N., MANZOORI J., *Surf. Coat. Technol.*, 140 (2001), 278.
- [3] LIN C.C., HUANG C.M., *J. Coat. Tech. Research.*, 3(2) (2006), 99.
- [4] LEHMBERG C.E., LEWIS D.B., MARSHALL G.W., *Surf. Coat. Technol.*, 192(2–3) (2005), 269.
- [5] RAMANAUSKAS R., GUDAVICIUTE L., KALNICENKO A., JUSKENAS R., *J. Solid State Electrochem.*, 9(12) (2005), 900.
- [6] BROOKS I., ERB U., *Scripta Materialia*, 44(5) (2001), 853.
- [7] FEI J., XICOX G.D., *Surf. Coat. Technol.*, 200(2–3) (2006), 3533.
- [8] IKEN H., BASSEGUY R., GUENBOUR A., BEN BACHIR A., *Electrochem. Acta.*, 52 (2007), 2580.
- [9] SIMOES A.M., BASTOS A.C., FERREIRA M.G., GONZALES-GARCIA Y., GONZALES S., SOUTTO R.M., *Corrosion Sci.*, 49 (2007) 726.
- [10] WILLIAMSON G.K., HALL W.H., *Acta Metallurgica*, 1 (1953), 22.
- [11] KARIMI-SHERVEDANI R., LASIA A., *J. Electrochem. Soc.*, 144(8) (1997), 2652.
- [12] KARIMI-SHERVEDANI R., LASIA A., *J. Electrochem. Soc.*, 145(7) (1998), 2219.

Received 02.03.2010

Accepted 25.11.2011