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CLASSIC AND LOCAL CORROSION RESISTANCE OF ELECTROLYTIC Zn-Ni LAYERS

**Katarzyna Wykpiś, Antoni Budniok,
Julian Kubiształ, Eugeniusz Łągiewka**

Summary

The Zn-Ni layers were obtained by electrolytic method in the conditions of pulse current. The austenitic steel (X5CrNi18-10) was used as the cathode. Surface morphology, phase and surface chemical composition, were defined. Structural investigations were conducted by X-ray diffraction method using Philips diffractometer and $\text{CuK}\alpha$ radiation. Surface morphology of the obtained layers was determined by scanning electron microscope (JEOL JSM-6480). Classic corrosion resistance investigations were conducted using potentiodynamic and electrochemical impedance spectroscopy methods. Localized corrosion resistance investigations were conducted using scanning vibrating electrode technique (SVET). Classic corrosion resistance investigations showed that passivation and heat treatment improved the corrosion resistance of Zn-Ni layers in 5% NaCl solution. Higher corrosion resistance of heated Zn-Ni layers is caused by the creation of $\text{Ni}_5\text{Zn}_{21}$ intermetallic phase. Moreover the heated Zn-Ni layers are characterized by slightly higher corrosion resistance compared with metallic Cd. The SVET analysis indicated that the passivation and heat treatment of Zn-Ni layers cause a decrease in number of corrosion centers on their surface area.

Keywords: alloys electrodeposition, Zn-Ni alloys, corrosion resistance, SVET

Ogólna i zlokalizowana odporność korozyjna elektrolitycznych warstw stopowych Zn-Ni

Streszczenie

Elektrolityczne warstwy stopowe Zn-Ni wytwarzano metodą osadzania pulsowego na podłożu stali austenitycznej (X5CrNi18-10). Określono skład fazowy oraz powierzchniowy skład chemiczny. Badania strukturalne wykonano metodą dyfrakcji promieni rentgenowskich, stosując dyfraktometr firmy Philips oraz promieniowanie lampy $\text{CuK}\alpha$. Obrazy powierzchni warstw uzyskano za pomocą mikroskopu skaningowego JOEL JSH-6480. Badania ogólnej odporności korozyjnej prowadzono klasyczną metodą Sterna oraz metodą spektroskopii impedancyjnej. Odporność korozyjną zlokalizowaną określono za pomocą techniki skaningowej elektrody wibrującej (SVET). Badania odporności korozyjnej wykazały, że pasywacja i obróbka cieplna poprawiają odporność na korozję warstwy stopowej Zn-Ni w 5% wodnym roztworze NaCl. Przyczyną lepszej odporności jest utworzenie fazy międzymetalicznej niklu z cynkiem – $\text{Ni}_5\text{Zn}_{21}$. Stwierdzono, że warstwy stopowe Zn-Ni poddane obróbce cieplnej charakteryzują się lepszą odpornością korozyjną w porównaniu z metalicznym kadmem. Analiza SVET wykazała, że pasywacja i obróbka cieplna elektrolitycznych warstw Zn-Ni zmniejszają gęstość lokalnych ognisk korozyjnych na ich powierzchni.

Słowa kluczowe: elektroosadzanie stopów, stopy Zn-Ni, odporność korozyjna, SVET

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Introduction

Interest in zinc and its alloys [1-4] results from good corrosive resistance of these materials and search for a suitable alternative of toxic cadmium coatings.

Electrolytic co-deposition of Zn with iron group of metals (Ni, Co and Fe) from acid and weak- acid baths is classified as anomalous [5]. This phenomenon consist in preferentially depositing of, a less noble metal on a cathode.

Electrolytic Zn-Ni alloys are characterized by occurrence of wider range of different phases. Corrosion resistance of these alloys is conditioned by their structure and surface morphology [6-9]. It was stated that independent of kind of substrate, nickel is dominant in an alloys layer adjacent to the substrate. Depending on deposition current density, zinc in nickel solid solution (α -phase) is formed [10]. Unlike in equilibrium metallurgical alloy, α and β phases are not formed in electrolytic Zn-Ni alloy. Using potentiodynamic stripping method, potential values of current peaks were attributed to the values of selective dissolution of particular phases [11]. In this way, the creation of γ -phase i.e. $\text{Ni}_5\text{Zn}_{21}$ and η -phase being 1% nickel in zinc solid solution was indicated. On the basis on electrochemical investigations it was found that the γ -phase is very chemically active by the selective dissolution of zinc. A high corrosion resistance and good mechanical properties of Zn-Ni layers are connected with the presence of the γ -phase, i.e. $\text{Ni}_5\text{Zn}_{21}$.

The corrosion resistance research were conducted most often by classic Stern and electrochemical impedance spectroscopy (EIS) methods. These techniques enable to evaluate total corrosion resistance of a coating.

These techniques provide only average values of corrosion parameters such as corrosion potential, corrosion current density and polarization resistance. However, sometimes it is necessary to measure the local current connected with local corrosion.

In these cases, the scanning vibrating electrode technique (SVET) may be used [12, 13]. SVET offer the possibility of mapping variations in current densities at the microscale over metal surface by measuring potential gradients developed in the solution due to the ionic flow.

The aim of present work was to determine the parameters of classic and local corrosion resistance of Zn-Ni layer in dependence on passivation and heat treatment. The obtained results are compared with corrosion resistance of metallic cadmium.

Experimental

The Zn-Ni layers were deposited on the austenitic steel (X5CrNi18-10). Preparation of substrate surface consisted of purifying with a detergent solution, and 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 $i = 5 \text{ mA}\cdot\text{cm}^{-2}$, during 2 min.

As to assure the adhesion of Zn-Ni layers to the substrate, nickel underlayer from bath containing $350 \text{ g/dm}^3 \text{ NiCl}_2\cdot 6\text{H}_2\text{O}$ and $111 \text{ cm}^3/\text{dm}^3 \text{ HCl}$, was deposited, before obtaining Zn-Ni layer. The thickness of the nickel layers was about $1 \mu\text{m}$.

Electrolytic layers were obtained from the following bath (concentration in $\text{g}\cdot\text{dm}^{-3}$): $\text{NiSO}_4\cdot 7\text{H}_2\text{O} - 225$, $\text{ZnSO}_4\cdot 7\text{H}_2\text{O} - 144$, $\text{CH}_3\text{COONa} - 41$, $\text{Na}_2\text{SO}_4 - 161$. pH of the bath was kept in range from 3.5 to 4.5. The process of deposition was carried out at the temperature of 298 K.

The Zn-Ni layers were obtained by electrolytic method in the conditions of pulse current with symmetric current pause. The time of the cathodic pulse ($t_{\text{on}} = 2 \text{ ms}$) was equal the time between pulses t_{off} . The layers were deposited at cathodic current densities $i_c = 20 \text{ mA}\cdot\text{cm}^2$. The time of deposition ($t = 49 \text{ min.}$) ensured obtaining Zn-Ni layer with thickness $10 \mu\text{m}$. One-sided geometric surface area of cathode was 25 cm^2 . The sheet nickel served as anode.

Electrodeposition of the Ni and Zn-Ni layers was carried out using galvanic unit MAG.

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

Heat treatment of the layers was carried out at a temperature of 320°C , during 4 hours in argon atmosphere.

Phase composition investigation was conducted by the X-ray diffraction (XRD) method using a Philips diffractometer and the CuK_α radiation. Diffraction patterns were recorded in the 2θ range of $10-100^\circ$. Phase identification was carried out on the base of ICDD cards.

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

Electrochemical corrosion resistance investigations on the prepared layers were conducted in a three-electrode cell containing 5% NaCl solution. The platinum counter electrode and the saturated calomel reference electrode (NEK), were used.

Classic corrosion research contained potential of open circuit measurement and recording of potentiodynamic curve in the range of $\pm 0.05 \text{ V}$ to the potential.

These curves were recorded with rate $v = 0.050 \text{ V}\cdot\text{min}^{-1}$. On the base of the obtained results, the corrosion potential – E_{cor} , corrosion current density – i_{cor} and the polarization resistance – R_p were determined by Stern method.

The electrochemical impedance measurements were performed at the corrosion potential. In these measurements the amplitude of ac signal was 0.005 V . A frequency range from 10 kHz to 0.1 Hz was covered with ten points

per decade. Results of impedance investigations were presented on the Bode log $|Z| = f(\log\omega)$ and $\phi = f(\log\omega)$ diagrams.

Potentiodynamic and electrochemical impedance spectroscopy measurements were carried out using AUTOLAB[®] electrochemical system.

The SVET measurements were performed using a Scanning Electrochemical Workstation Model 370 (Princeton Applied Research AMETEK). The SVET maps were registered at a potential of open circuit. The vibrating probe was placed above the surface of the substrate at a height of about 100 μm . A scan was made at a 1000 $\mu\text{m} \times 1000 \mu\text{m}$ area. The vibrating amplitudes of the scanning probe were adjusted to 30 μm . Registered potential difference values were calculated on current density values using a calibration potential-current curve, obtained for 5% NaCl water solution.

Results and discussion

The obtained Zn-Ni layers have a mat and homogeneous surface both before and after thermal treatment. These layers are characterized by good adhesion to the substrate and lack of cracks (Fig. 1). After thermal treatment a decrease in development of Zn-Ni layer surface was observed.

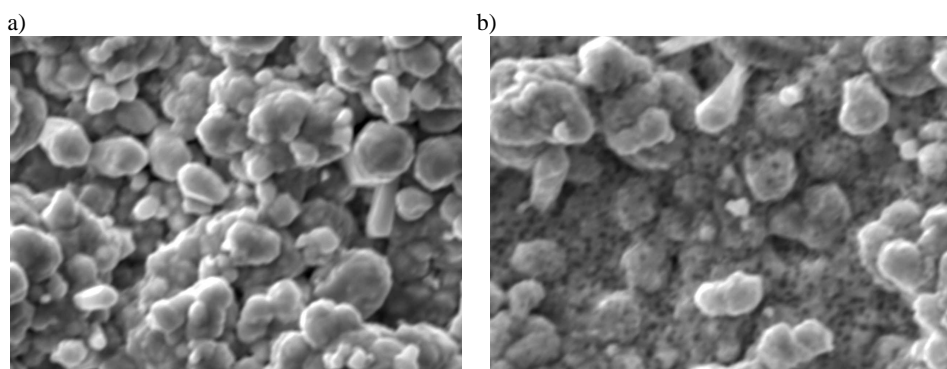


Fig. 1. Surface morphology of electrolytic Zn-Ni layer: a) as-deposited, b) after passivation and thermal treatment

The results of surface chemical composition analysis carried out using the scanning electron microscope show, that Zn-Ni layer contains 19.2 ± 0.4 % at. Ni and 81 ± 1.4 % at. Zn.

X-ray diffraction pattern recorded before thermal treatment, show the presence of reflexes from Zn solid solution of Zn in Ni and ZnO phases (Fig. 2a). Thermal treatment of Zn-Ni layer causes partial decomposition of the solid

solution of Zn in Ni and of intermetallic compound $\text{Ni}_5\text{Zn}_{21}$. These phase coexists with the Zn and ZnO phases (Fig. 2b).

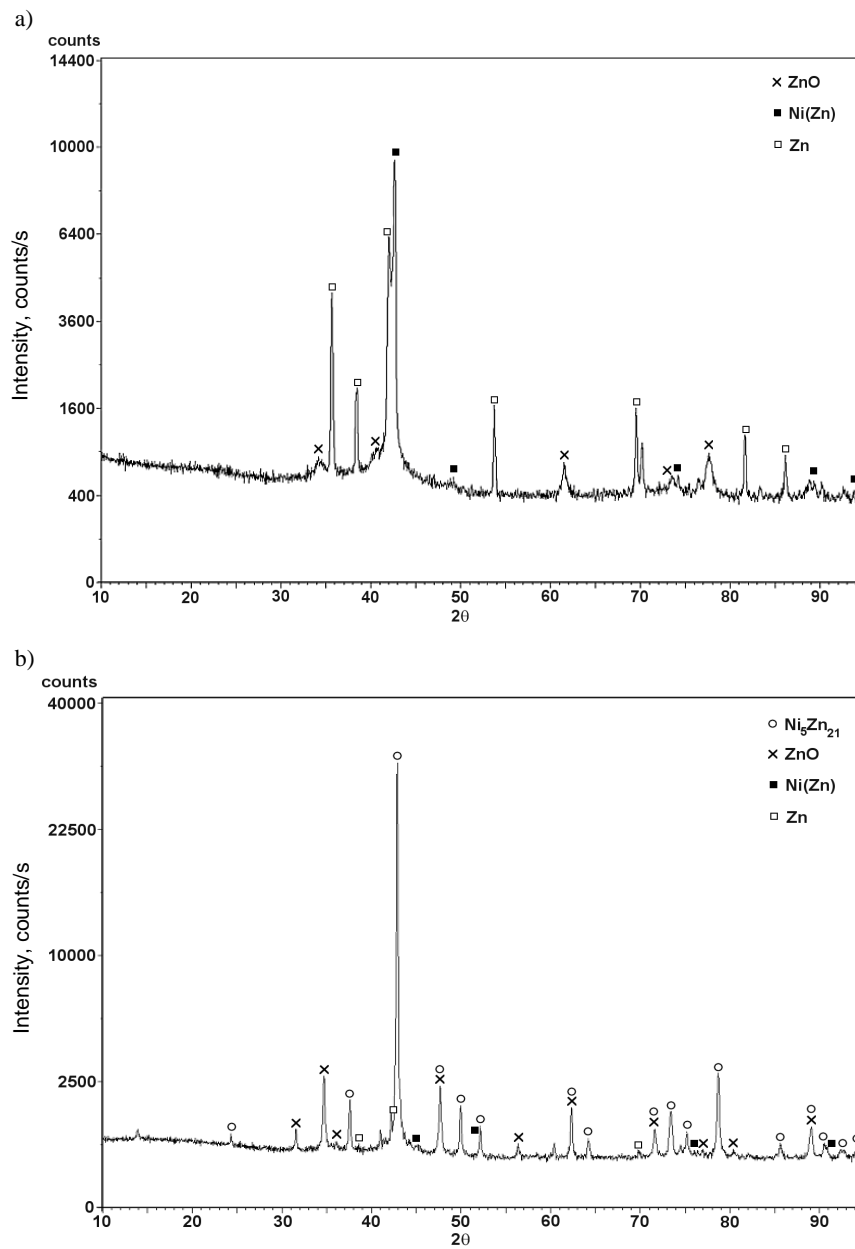


Fig. 2. X-ray diffraction patterns for Zn-Ni layers deposited by pulse current method ($j_c = 20 \text{ mA}\cdot\text{cm}^{-2}$) before (a) and after (b) thermal treatment

The presence of ZnO phase is probably due to passivation treatment of Zn-Ni layer. No reflexes coming from compounds of Cr with the alloys elements, as products of passivation treatment, were showed.

On the basis of the dependences $j = f(E)$ recorded in the range of ± 0.05 V to the potential of open circuit (Fig. 3), the corrosion parameters of as-deposited Zn-Ni layer, the layers after passivation and after thermal treatment, were determined and compared with corresponding parameters for cadmium (Tab. 1).

Table 1. Corrosion parameters determined by Stern method [14]

Kind of layers	E_{cor} V	j_{cor} A/cm ²	R_p Ωcm^2
As-deposited Zn-Ni	-1.025	$1.15 \cdot 10^{-5}$	$7.41 \cdot 10^2$
Zn-Ni after passivation	-1.014	$6.24 \cdot 10^{-6}$	$4.25 \cdot 10^3$
Zn-Ni after passivation and thermal treatment	-0.711	$6.22 \cdot 10^{-7}$	$1.99 \cdot 10^4$
Cd	-0.740	$1.93 \cdot 10^{-6}$	$2.58 \cdot 10^4$

It was found that passivation treatment leads to a decrease in a corrosion current values and increase in a polarization resistance. Thermal treatment additionally improves values of these parameters. Thermal treatment causes a shift of corrosion potential in a more positive direction by about 300 mV. thanks to that Zn-Ni layers could be an alternative of toxic cadmium coatings.

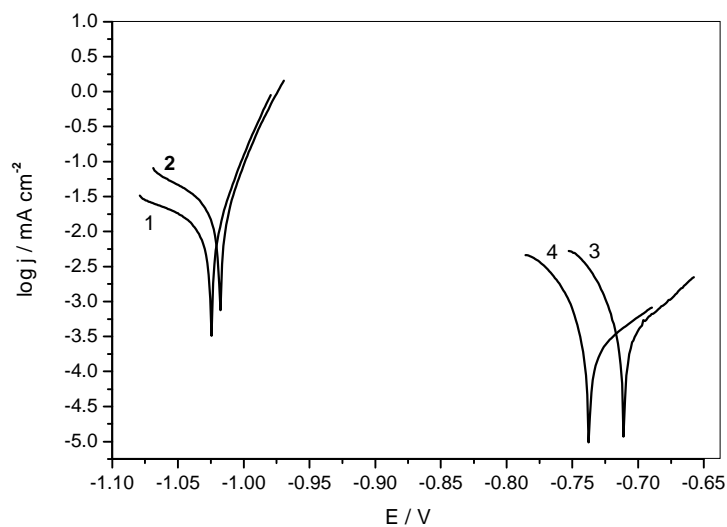


Fig. 3. Log $j = f(E)$ dependences determined by Stern method for Zn-Ni as-deposited (curve 1), Zn-Ni after passivation (curve 2), Zn-Ni after passivation and thermal treatment (curve 3) and metallic Cd (curve 4)

On the basis the Bode $\log |Z| = f(\log \omega)$ diagrams it was found that the thermally treated Zn-Ni layers are characterized by a higher value of the impedance module than these before thermal treatment and a lower value than cadmium (Fig. 4). It suggests that thermal treatment of the Zn-Ni layer improves their corrosion resistance in 5% NaCl solution. The corrosion resistance is similar to the cadmium one.

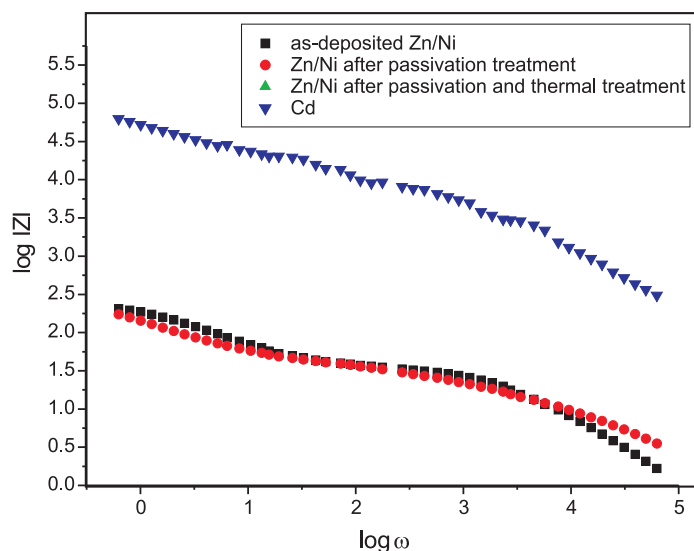


Fig. 4. EIS Bode $\log |Z| = f(\log \omega)$ plots obtained for the Zn-Ni layer depending on passivation and thermal treatment and for metallic cadmium

Moreover, the phase angle versus the logarithm of angular frequency dependencies (Fig. 5) for the heated Zn-Ni layer and metallic cadmium are very similar. These $\phi = f(\log \omega)$ show a considerably wider range of independence of the phase angle value the logarithm of angular frequency compared to the as-deposited Zn-Ni layer. Moreover, the dependencies $\phi = f(\log \omega)$ for the heated Zn-Ni layer and cadmium show no maximum, which are visible on these diagram for Zn-Ni layers before thermal treatment. It indicates that some processes characterized by phase angle value at low frequencies were inhibited as a results from passivation and thermal treatment of Zn-Ni layer. Consequently, corrosion resistance of the Zn-Ni layer after thermal treatment increases. Such course of Bode diagrams confirmed a higher corrosion resistance of Zn-Ni layer after passivation and thermal treatment than as-deposited one. The corrosion resistance of heated Zn-Ni layer is similar to cadmium.

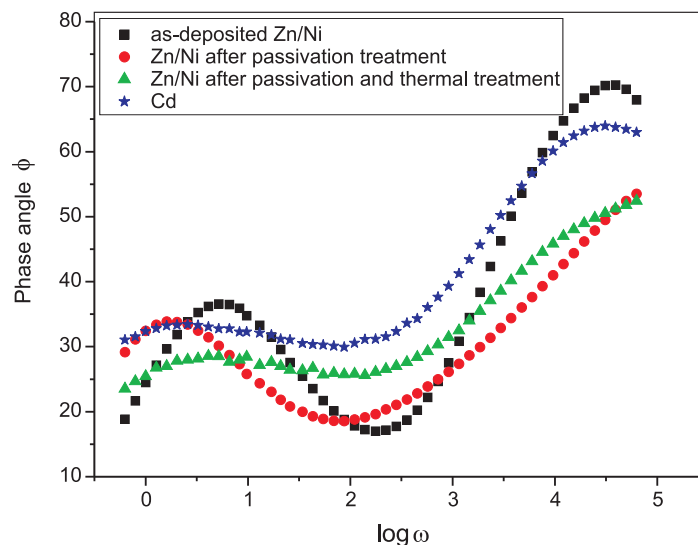


Fig. 5. EIS Bode $\phi = f(\log \omega)$ plots obtained for the Zn-Ni layer depending on passivation and thermal treatment and for metallic cadmium

The localized corrosion research by SVET technique were carried out in 5% NaCl solution for electrolytic Zn-Ni layer in dependence on passivation and heat treatment and for metallic cadmium. SVET maps (Fig. 6) show differences in local current density distribution. These differences concern sizes and intensities of the anodic and cathodic sites on the surface of investigated layers.

SVET map for as-deposited Zn-Ni layer shows symmetric current distribution of anodic and cathodic sites and more sites with higher values of local current density compared with the maps of other investigated layers.

The SVET analysis in respect to sites with selected local current density $1.0 \cdot 10^{-8} \text{ A}\cdot\text{cm}^{-2}$ indicated that most at these sites are on the SVET map for Zn-Ni layer before passivation and thermal treatment (Fig. 6a). Number of these sites slightly decreased after the passivation treatment (Fig. 6b). Least of these sites was observed for the Zn-Ni-layer after thermal treatment. It means, that passivation and particularly thermal treatment limit a number of preferential centers of corrosion attack on the Zn-Ni layer surface. The number of local corrosion centers for heated Zn-Ni layer (Fig. 6c) is comparable with metallic cadmium (Fig. 6d).

It was found that Zn-Ni layers subjected to passivation and thermal treatment are characterized by the least local current densities out of the investigated layers and symmetric distribution of the anodic and cathodic sites on the substrate (Fig. 6c). Passivation and thermal treatment improve local corrosion resistance of the Zn-Ni layer in 5% NaCl solution.

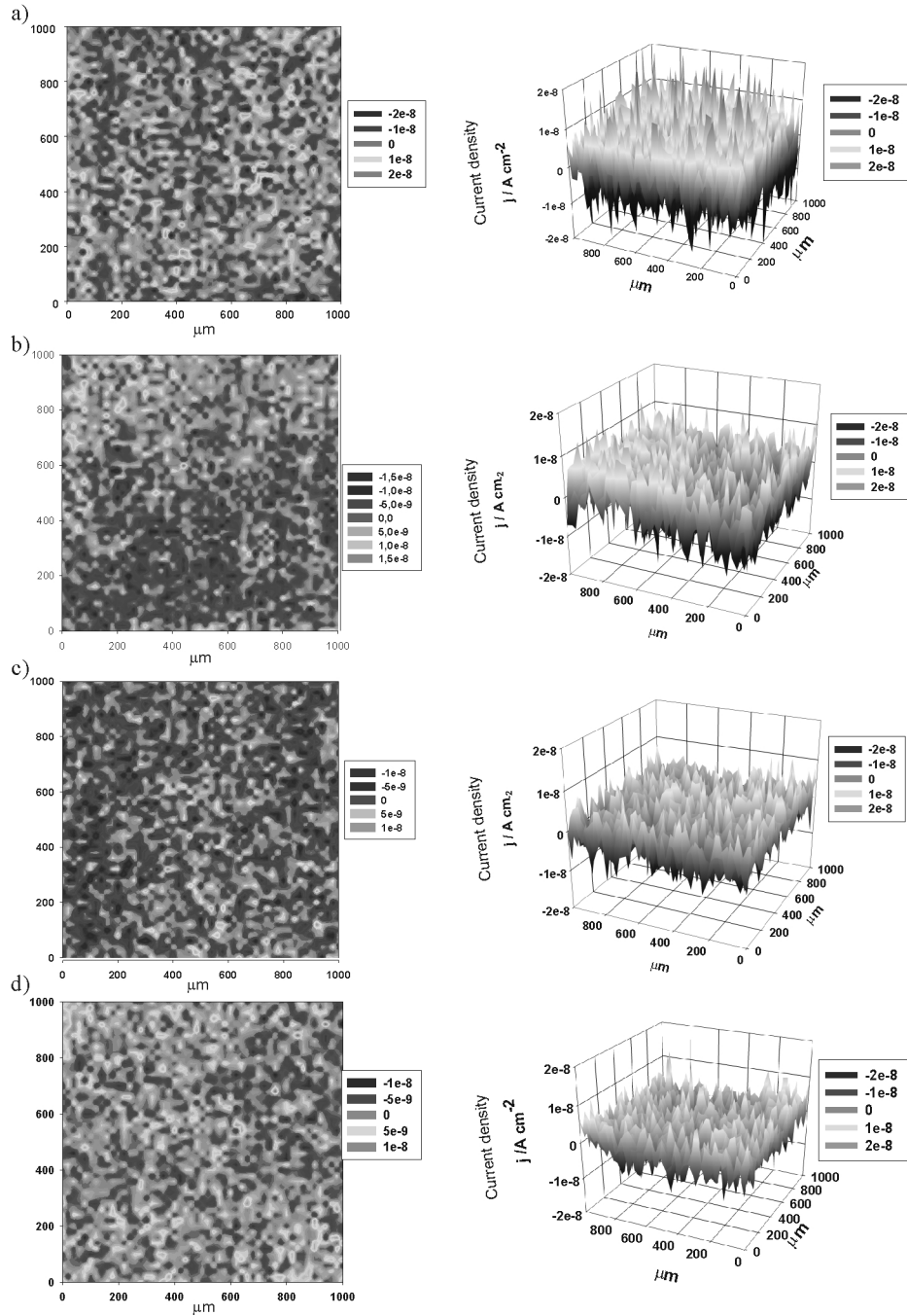


Fig. 6. SVET maps (2D i 3D) obtained for Zn-Ni: a) as-deposited, b) after passivation treatment, c) after passivation and thermal treatment and d) metallic Cd

Conclusion

On the basis on this study it was stated, that both passivation and thermal treatment improved the corrosion resistance of Zn-Ni layers in 5% NaCl solution. Higher corrosion resistance of heated Zn-Ni layers is caused by the creation of Ni₅Zn₂₁ intermetallic phase. The low values of local cathodic and anodic current density (order of magnitude 10⁻⁸ A·cm⁻²) suggests that the heated Zn-Ni layer are characterized by slightly higher corrosion resistance compared with metallic cadmium.

The SVET analysis indicated that the passivation and heat treatment of Zn-Ni layers caused a decrease in the number of corrosion centers on their surface area.

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