Advanced Composite Materials

ISSN: 0924-3046 (Print) 1568-5519 (Online) Journal homepage: http://www.tandfonline.com/loi/tacm20

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

Katarzyna Wykpis, Magdalena Popczyk, Jolanta Niedbała, Bożena Bierska-Piech, Antoni Budniok & Eugeniusz Łągiewka

To cite this article: Katarzyna Wykpis, Magdalena Popczyk, Jolanta Niedbała, Bożena Bierska-Piech, Antoni Budniok & Eugeniusz Łągiewka (2015) Influence of thermal treatment on the corrosion resistance of electrolytic Zn–Ni+Ni composite coatings, Advanced Composite Materials, 24:5, 431-438, DOI: 10.1080/09243046.2014.901471

To link to this article: http://dx.doi.org/10.1080/09243046.2014.901471

Published online: 26 Mar 2014.

Advanced Composite Materials, 2015
Vol. 24, No. 5, 431–438, http://dx.doi.org/10.1080/09243046.2014.901471

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

Katarzyna Wykpis*, Magdalena Popczyk, Jolanta Niedbała, Bożena Bierska-Piech, Antoni Budniok and Eugeniusz Łągiewka

Institute of Materials Science, University of Silesia, 75 Pułku Piechoty 1A, 41-500 Chorzów, Poland

(*Received 26 April 2013; accepted 4 March 2014*)

This study was undertaken in order to obtain and characterize the corrosion resistance of Zn–Ni+Ni composite coatings. The influence of thermal treatment on surface morphology, phase composition, and corrosion resistance of Zn–Ni+Ni coating was investigated. The Zn–Ni+Ni coating was deposited under galvanostatic conditions ($j = 40$ mA cm^{-2}). Thermal treatment was carried out in argon atmosphere. The surface morphology of Zn–Ni+Ni coatings was carried using a scanning electron microscope (JEOL JSM-6480) and the surface chemical composition was determined by the EDS method. Structural investigations were conducted by X-ray diffraction method. The studies of electrochemical corrosion resistance were carried out in a 5% NaCl solution, using potentiodynamic and scanning vibrating electrode (SVET) methods. On the grounds of corrosion investigations, it was stated that thermal treatment improves both total and localized corrosion resistance of Zn–Ni+Ni coating in a 5% NaCl water solution. The higher corrosion resistance of the thermally treated Zn–Ni+Ni coating could be attributed to the increase in the amount of zinc bonded to nickel in the form of Ni_2Zn_{11} and Ni_5Zn_{21} intermetallic phases. The SVET analysis indicated that thermal treatment of Zn–Ni+Ni coating causes a decrease in the number of corrosion centers on their surface area.

Keywords: composite coatings; thermal treatment; corrosion resistance

1. Introduction

The interest in zinc and its alloys [1–6] results from good corrosive resistance of these materials and a search of an alternative to toxic and high-cost cadmium coatings. Among those materials, zinc–nickel coatings are considered because of their better corrosion resistance and improved mechanical properties (hardness, stamping) in comparison with pure zinc. Thus, the Zn–Ni coatings have been applied in the automotive, the electronic, and the aeronautical industries.[5–7]

Zn–Ni alloy deposition is an anomalous codeposition [7,8] which results in a high content of zinc. As the zinc could be leached out in aggressive environment, the Zn–Ni coatings could exhibit a decreased corrosion resistance. Reduction of anomalous deposition effect and an increase in the nickel content in the Zn–Ni coating can be obtained by an addition of nickel powder to a galvanic bath. In this way, composite coatings containing nickel powder incorporated into the Zn–Ni matrix may be obtained.

*Corresponding author. Email: katarzyna.wykpis@us.edu.pl

The composite materials could exhibit properties which are not only a combination of characteristics of its individual components, but also arise from their interaction on interfacial borders. Additionally, thermal treatment of such obtained coatings may leads to the homogenization of their components through the creation of intermetallic compounds or solid solutions. Composite materials characterized by various properties such as dispersion hardening, high temperature oxidation resistance, excellent wear resistance, and corrosion resistance. Thus, the composite coatings find use in tribology and as electrode materials for catalysis of electrochemical reactions and for corrosion protection.

The corrosion resistance research is conducted most often by the classic Stern method. This method enables to evaluate total corrosion resistance of coatings and provides only surface-average values of corrosion parameters such as the corrosion potential, corrosion current density, and the polarization resistance.

The surface of composite coatings is heterogenous. Hence, these corrosion parameters determined for macro- and micro-surface area of the coatings may be different. Therefore, the Scanning vibrating electrode (SVET) method is one of the most promising techniques.[9,10] SVET offers the possibility of mapping variations in current densities at the micro-scale over metal surface by measuring potential gradients developed in the solution due to the ionic flow.

The purpose of this work was to determine an influence of thermal treatment on morphology, phase composition, and corrosion resistance of Zn–Ni+Ni composite coating.

2. Experimental

The Zn–Ni+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 (at current density $j = 0.1\ \mathrm{A\ cm^{-2}}$ in the hot solution containing 0.8 M $C_6H_{11}O_7Na$ and 4.3 M NaOH).

Prior to deposition, the steel substrate was activated in HCl solution, using cathode current density $j = 5\ \mathrm{mA\ cm^{-2}}$, for 2 min. The nickel underlayer, obtained from the bath containing $350\ \mathrm{g\ dm^{-3}}$ $NiCl_2 \cdot 6H_2O$ and $111\ \mathrm{cm^3\ dm^{-3}}$ HCl, was deposited before obtaining of Zn–Ni+Ni coating in order to assure adhesion on the Zn–Ni+Ni coating to the substrate.

Electrolytic Zn–Ni+Ni coating was obtained from the bath of composition ($\mathrm{g\ dm^{-3}}$): $NiSO_4 \cdot 7H_2O$ – 50, $ZnSO_4 \cdot 7H_2O$ – 100, Na_2SO_4 – 75, $(NH_4)_2SO_4$ – 38 + $250\ \mathrm{cm^3\ dm^{-3}}$ NH_4OH + nickel powder (APS 3–7 micron, 99.9% Ni, Alfa Aesar) – 4. The temperature of the bath was 298 K; the pH was kept in the range of 9.6–10.4. The galvanic bath was mechanically stirred ($400\ \mathrm{rpm\ min^{-1}}$) during the deposition.

Zn–Ni+Ni coating was deposited under galvanostatic conditions at the current density $j = 40\ \mathrm{mA\ cm^{-2}}$. On the ground of preliminary investigations, it was found that this j value ensured deposition of the coating with good adhesion to the substrate and lack of cracks.

The coating was deposited on the two-sided cathode. Total geometric surface area of cathode was $50\ \mathrm{cm^2}$. A sheet nickel served as anode.

Electrodeposition of the nickel sublayer and Zn–Ni+Ni coating was carried out using a MAG (IMP-BUD 5, Poland) galvanic unit.

The deposited Zn–Ni+Ni coating was passivated in the solution of composition: $K_2Cr_2O_7$ – 70 g dm^{-3}, H_2SO_4 – 8 g dm^{-3}, for 10 s.

The thermal treatment of the Zn–Ni+Ni coatings was carried out at a temperature of 593 K for 4 h in protective gas atmosphere (argon).

The surface morphology of Zn–Ni+Ni coatings was carried using a scanning electron microscope (JEOL JSM-6480) and the surface chemical composition was determined by the EDS method.

The XRD patterns were measured using the Philips X′Pert PW 3040/60 X-ray diffractometer with the copper radiation ($\lambda K_\alpha = 1.54056$ Å). A graphite monochromator was used to select the K_α radiation. The content of zinc in nickel in the Ni(Zn) solid solution was calculated from the Vegard law – where the lattice parameter of the solution is directly proportional to the atomic percent solute present. Deformation of the random substitutional solid solution of B and A may be accompanied by either an increase or a decrease in cell volume depending on whether the B atom is larger or smaller than the A atom.[11]

The investigations of electrochemical corrosion resistance on the prepared coatings were carried out at a temperature of 293 K, in 5% NaCl solution potentiodynamic method. Open-circuit potentials of ad-deposited and annealed Zn–Ni+Ni coatings were determined for 20 h. A three-electrode electrochemical cell was used. The counter electrode was a Pt gauze. The reference electrode was the saturated calomel electrode. The working electrode had the surface area of 1 cm^2. The values of corrosion potential, corrosion current and polarization resistance were determined on the grounds of the obtained dependences $j = f(E)$ by the Stern method. The potentiodynamic polarization curve was registered with rate $v = 0.060$ V min^{-1}, in the potential range ± 0.050 V from open circuit potential. These measurements were performed using an Autolab® 20 Potentiostat/Galvanostat.

The SVET and SKP 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. 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.

To investigate the corrosion resistance of the coatings, the salt-spray test was also applied in 5% NaCl solution at a temperature of 308 K for 96 h (according to PN-EN ISO 9227), using KOHLER HK 400 salt-spray chamber.

3. Results and discussion

The Zn–Ni+Ni coating shows good adhesion to the substrate and a lack of cracks, both before and after thermal treatment. The coating has a rough metallic surface with visible grains of incorporated nickel powder. The tendency to agglomeration of nickel grains is observed (Figure 1). Additionally, a decrease in surface development of Zn–Ni+Ni coating is observed after thermal treatment.

The analysis of surface chemical composition shows that the Zn–Ni+Ni coating consists of 17.6 ± 0.4% at. Ni and 82.4 ± 1.4% at. Zn.

Before annealing, the XRD pattern showed that the structure of the electrodeposited coating was diphase: Ni(Zn) solid solution and Ni_2Zn_{11} intermetallic phases (Figure 2).

X-ray diffraction patterns recorded after thermal treatment show the presence of diffraction peaks corresponding to Ni_2Zn_{11} intermetallic and Ni(Zn) solid solution phases.

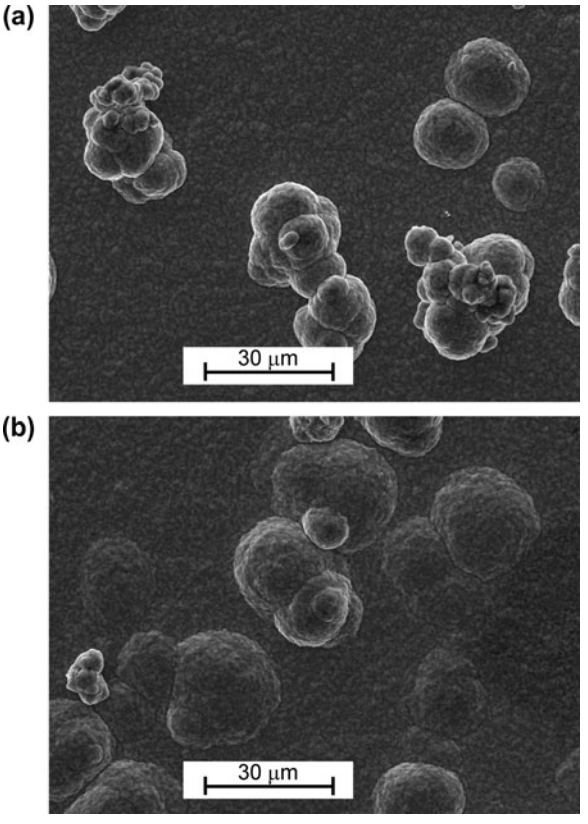

Figure 1. Surface morphology of the Zn–Ni+Ni coating before (a) and after (b) thermal treatment.

However, the zinc content of nickel in the case of Ni(Zn) solid solution (determined on the basis of the Vegard law) decreases after thermal treatment from about 15 to 1%. Moreover, the presence of Ni_5Zn_{21} intermetallic phase as a result of the partial decomposition of the Ni(Zn) solid solution is stated (Figure 2(b)).

These findings suggest that the thermal treatment causes an increase in the amount of zinc bonded with nickel into intermetallic phase forms.

These phase differences may be the reason for differences of corrosion resistance of the composite Zn–Ni+Ni coating, as in the case of Zn–Ni coatings.[6,9]

On the grounds of the obtained dependences $j = f(E)$, the values of corrosion parameters, i.e. corrosion current (j_{cor}), corrosion potential (E_{cor}), and polarization resistance (R_p) were determined (Figure 3, Table 1).

It was found that for the annealed Zn–Ni+Ni coating, the value of corrosion current does not changes but the values of polarization resistance is higher and the corrosion potential is more positive in comparison with the as-deposited Zn–Ni+Ni coating. It is suggested that the Zn–Ni+Ni coating after thermal treatment is more corrosion resistant in a 5% NaCl solution than the Zn–Ni+Ni coating before thermal treatment.

Comparing the corrosion parameters determined for Zn–Ni+Ni composite coatings and Zn–Ni matrix coatings [12], it is noted that the Zn–Ni+Ni composite coating is more corrosion resistant than the Zn–Ni coating, even without thermal treatment.

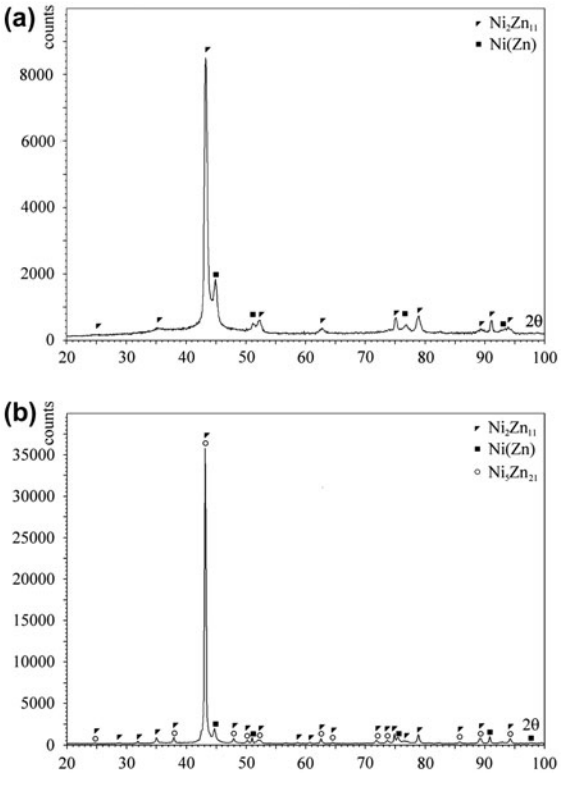

Figure 2. X-ray diffraction patterns of Zn–Ni+Ni coating before (a) and after (b) thermal treatment.

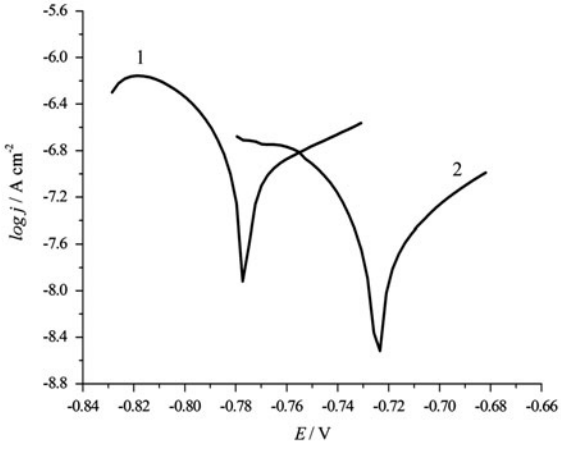

Figure 3. Dependences of $\log j = f(E)$ for the Zn–Ni+Ni coating before (curve 1) and after (curve 2) thermal treatment.

Table 1. Corrosion parameters determined from potentiodynamic method.

Kind of coatings	E_{cor}/[V]	j_{cor}/[μA cm^{-2}]	R_p/[kΩ cm^2]
Zn–Ni+Ni before thermal treatment	−0.777	0.02	68.20
Zn–Ni+Ni after thermal treatment	−0.725	0.02	338.80

The effect of thermal treatment on the localized corrosion resistance of Zn–Ni+Ni coating was investigated by SVET technique in a 5% NaCl solution. The obtained SVET maps (Figure 4) 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.

It was found that the surface of the Zn–Ni+Ni coating after thermal treatment characterized by smaller values of local current density and a more symmetric current distribution between cathodic and anodic sites in comparison with the as-deposited coating. It means that thermal treatment limits number of preferential centers of corrosion attack on the Zn–Ni+Ni coating surface. Thus thermal treatment improves local corrosion resistance through the reduction of the local corrosion centers.

On the basis of the computer calculation of topography maps obtained by a Kelvin probe (not presented here), the surface roughness was estimated as ratio of real surface area of electrode to the geometric one.[13] The ratio is 1.2 and 1.0 for Zn–Ni+Ni

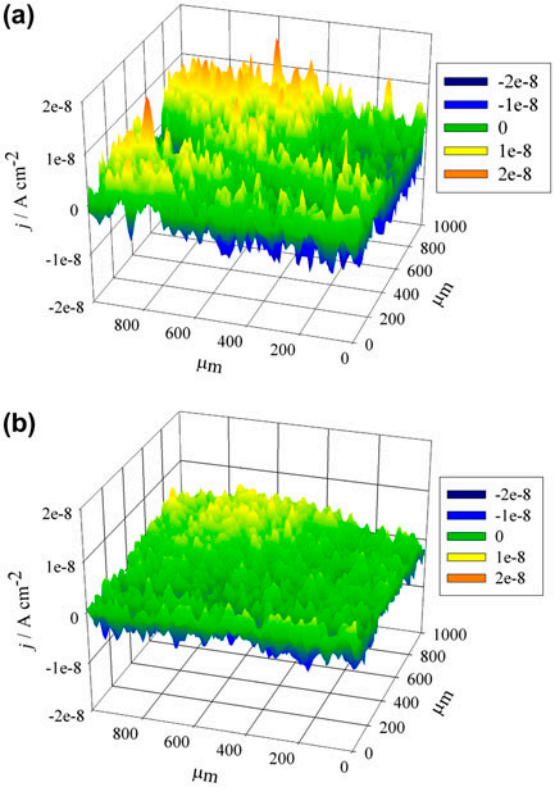

Figure 4. SVET maps of the Zn–Ni+Ni coating before (a) and after (b) thermal treatment.

coatings before and after thermal treatment, respectively. This may mean that the thermal treatment causes a decrease in surface roughness of the Zn–Ni+Ni coatings.

The results of salt-spray test (Figure 5) exhibit the appearance of white rust corrosion, which is characteristic for zinc oxidation process. The Zn–Ni+Ni coatings (Figure 5(b)) are covered with a relatively small amount of the corrosion products. The corrosion of steel substrate was not observed. Therefore, the salt-spray test confirms the good corrosion resistance of the thermally treated Zn–Ni+Ni coating. However, it is worth noting that the process of corrosion proceeds in a similar way as in the case of the Zn–Ni+Ni coatings without thermal treatment.[13]

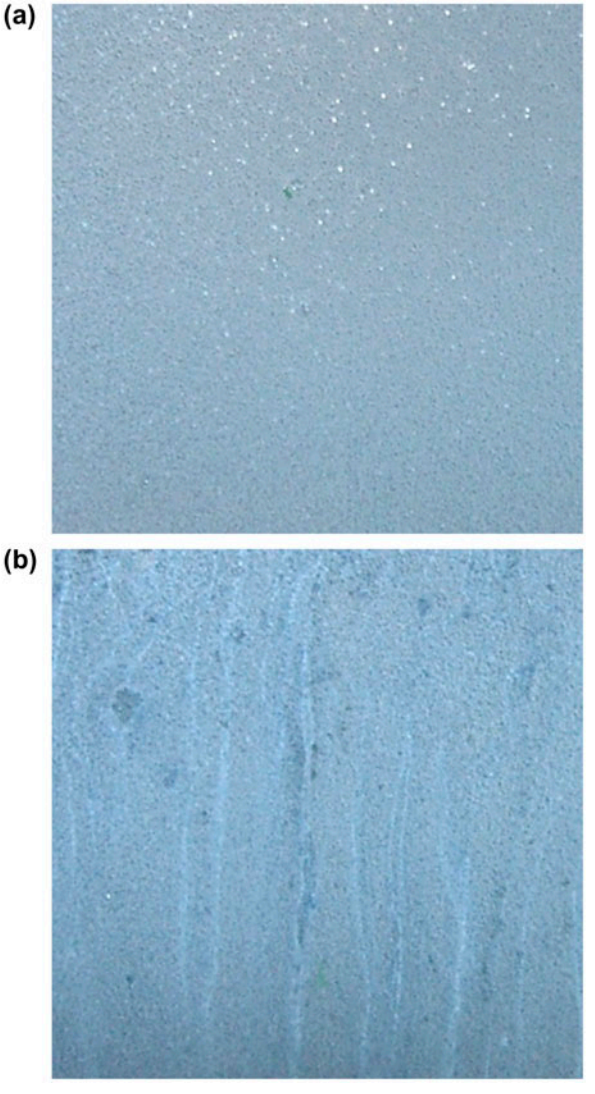

Figure 5. Surface of the thermal-treated Zn–Ni+Ni coating before (a) and after (b) exposure to the salt spray.

4. Conclusion

Based on this research, the possibility of incorporation of nickel powder to the Zn–Ni matrix from a suspension bath during galvanostatic deposition was demonstrated.

On the grounds of corrosion investigations, it was stated that thermal treatment improves both total and localized corrosion resistance of Zn–Ni+Ni coating in a 5% NaCl water solution.

The higher corrosion resistance of the thermally treated Zn–Ni+Ni coating could be attributed to the increase in the amount of zinc bonded to nickel in the form of Ni_2Zn_{11} and Ni_5Zn_{21} intermetallic phases. As a consequence of this, a decrease in surface development of Zn–Ni+Ni coating is observed after thermal treatment.

The SVET analysis indicated that thermal treatment of Zn–Ni+Ni causes a decrease in the number of corrosion centers on their surface. Thus, the thermally treated Zn–Ni+Ni coatings are more resistant to corrosion than as deposited one.

Acknowledgment

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

References

[1] Conde A, Arenas MA, Demborenea JJ. Electrodeposition of Zn-Ni coatings as Cd replacement for corrosion protection of high strength steel. Corros. Sci. 2011;53:1489–1497.
[2] Szczygieł B, Laszczyńska A, Tylus W. Influence of molybdenum on properties of Zn-Ni and Zn-Co alloy coatings. Surf. Coat. Technol. 2010;204:1438–1444.
[3] Fratesi R, Roventi G. Corrosion resistance of Zn-Ni alloy coatings in industrial production. Surf. Coat. Technol. 1996;82:158–164.
[4] Bajat JB, Mišković-Stankovic VB, Maksimović MD, Dražić DM, Zec S. Electrochemical deposition and characterization of Zn-Co alloys and corrosion protection by electrodeposited epoxy coating on Zn-Co alloy. Electrochim. Acta. 2002;47:4101–4112.
[5] Ganesan P, Kumaraguru SP, Popov BN. Development of compositionally modulated multilayer Zn-Ni deposits as replacement for cadmium. Surf. Coat. Technol. 2007;201:7896–7904.
[6] Gavrila M, Millet JP, Mazille H, Marchandise D, Cuntz JM. Corrosion behaviour of zinc-nickel coatings, electrodeposited on steel. Surf. Coat. Technol. 2000;123:164–172.
[7] Soares ME, Souza CAC, Kuri SE. Corrosion resistance of a Zn-Ni electrodeposited alloy obtained with a controlled electrolyte flow and gelatin additive. Surf. Coat. Technol. 2006;201:2953–2959.
[8] Petrauskas A, Grincevičienė L, Češūnienė A, Juškėnas R. Studies of phase composition of Zn-Ni alloy obtained in acetate-chloride electrolyte by using XRD and potentiodynamic stripping. Electrochim. Acta. 2005;50:1189–1196.
[9] Iken H, Basseguy R, Guenbour A, Ben Bachir A. Classic and local analysis of corrosion behaviour of graphite and stainless steel in polluted phosphoric acid. Electrochim. Acta. 2007;52:2580–2587.
[10] Montemor MF, Ferreira MGS. Electrochemical study of modified bis-[triethoxysilylpropyl] tetrasulfide silane films applied on the AZ31 Mg alloy. Electrochim. Acta. 2007;52:7486–7495.
[11] Cullity BD, Stock SR. Elements of X-ray diffraction. New Jersey: Prentice Hall; 2001.
[12] Wykpis K, Popczyk M, Niedbała J, Budniok A, Łągiewka E, Bierska-Piech B. Influence of the thermal treatment on the corrosion resistance of electrolytic Zn-Ni coating. Mater. Sci.-Poland. 2011;29:177–183.
[13] Wykpis K, Niedbała J, Popczyk M, Budniok A, Łągiewka E. The electrodeposition and properties of Zn-Ni+Ni composite coatings. Russ. J. Electrochem. 2012;48:1123–1129.