Ternary Zn–Ni–Co alloy: anomalous codeposition and corrosion stability

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Abstract: Electrochemically deposited Zn–Ni–Co alloys under various deposition conditions were investigated using atomic absorption spectroscopy for the determination of the chemical composition, atomic force microscopy for surface morphology analysis, and electrochemical impedance spectroscopy for determination of corrosion properties. The influence of the ratio of the alloying elements, $[Co^{2+}]/[Ni^{2+}]$, in a chloride deposition solution, as well as the deposition current density, on the chemical content, morphology and corrosion properties of the ternary alloys was studied. The plating solutions used were with the same overall metal concentration, free of additives and the deposition was realized at room temperature. It was shown that the deposition of the ternary alloy coatings was of anomalous type and that the ratio of nickel to cobalt ions in the plating solution, as well as the deposition current density, had a significant influence on the chemical composition and corrosion stability of these coatings. The presence of both Ni and Co was beneficial for their corrosion stability. It was shown that morphology and porosity were important factors in the corrosion stability of these coatings. The coating deposited from the solution with higher $[Co^{2+}]/[Ni^{2+}]$ ratio at 8 A dm^{-2} was made up of the smallest crystalline aggregates, had a small surface roughness and porosity, and was with quite uniform distribution of agglomerates and it exhibited the best corrosion stability.

Keywords: electrodeposition; ternary alloy coatings; corrosion; EIS; AFM.

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INTRODUCTION

Alloy electrodeposition is widely used in the production of new materials that require some particular mechanical, chemical and physical properties. It was shown that zinc alloys could provide improved corrosion resistance compared to pure zinc in the protection of ferrous-based metals. The most common zinc alloys are zinc–nickel,[1–3] zinc–cobalt[4–6] and zinc–iron.[7,8] Compared with Zn the Zn–Ni and Zn–Co binary alloys give corrosion protection and physical properties significantly superior to those obtained with pure zinc deposits. However, the binary Zn alloys, that provide good alloy properties, often have a rough, non-uniform and unattractive finish, so additives often have to be used in the plating solutions.

Therefore, it would be interesting to combine the properties of Zn–Ni and Zn–Co alloys in one alloy, which could be accomplished *via* the electrodeposition of ternary Zn–Ni–Co alloys. There are several literature data on Zn–Ni–Co ternary alloys. Younan[9] and Eliaz *et al.*[10] studied the deposition of such ternary alloys in the presence of additives (sodium dodecyl sulfate,[9] sulphanilic acid[10] and gelatine[10]) and showed the increased corrosion stability with respect to the corresponding binary alloys: the corrosion rates of Zn–Ni–Co coatings were 7–10 times lower than binary Zn–Co and Zn–Ni alloys. Younan showed that the increased corrosion stability of Zn–Ni–Co deposits is not only due to the formation of a high nickel γ-alloy phase, but also to the codeposition of Co, which caused a change in a crystal orientation and resulted in a finer grain size.[9] Namely, Zn–Ni alloy coatings with 13–17.8 % Ni were a γ-phase $Zn_{21}Ni_5$ solid solution with (330) and (411) crystal orientation. Upon incorporation of Co, the crystal orientation of the γ-phase changed to (442) and (600), and with increasing Co content, ε-$Zn(OH)_2$ was also formed.

Higher corrosion resistance of ternary alloys was also determined by other authors,[11–14] for alloy coatings deposited from sulfate solutions, mainly at high temperatures. Since it was shown in previous work[15,16] that Zn–Ni and Zn–Co alloys deposited from sulfate plating baths had lower corrosion stability as compared to binary alloys deposited from chloride bath, the aim of this work was to investigate Zn–Ni–Co codeposition from a simple chloride plating solution. Different ratios of alloying elements were tested in order to determine whether greater Ni or Co contents in the alloy coatings would be beneficial for better corrosion protection. The plating baths used were free of additives and deposition was performed at room temperature since the aim of the work was to investigate only the influence of different cobalt to nickel ratios in the solution.

EXPERIMENTAL

Electrodeposition of Zn–Ni–Co alloys

The Zn–Ni–Co alloys were deposited galvanostatically, at various current densities, from chloride baths of the following composition (pH 4.5±0.1): 0.38 mol dm^{-3} ZnCl$_2$; 0.24 mol dm^{-3}

H_3BO_3; 3.85 mol dm^{-3} KCl and either 0.34 mol dm^{-3} $NiCl_2 \cdot 6H_2O$ and 0.04 mol dm^{-3} $CoCl_2 \cdot 6H_2O$, or 0.20 mol dm^{-3} $NiCl_2 \cdot 6H_2O$ and 0.18 mol dm^{-3} $CoCl_2 \cdot 6H_2O$, at 25 °C. The employed electrolytes were prepared using p.a. chemicals and double distilled water.

The working electrodes were Zn–Ni–Co alloys deposited on: *i*) steel panel (20 mm×20 mm×0.25 mm), for electrochemical measurements: electrochemical impedance spectroscopy (EIS) and open circuit potential (E_{ocp}) measurements and atomic force microscopy (AFM) analysis and *ii*) Pt panel for determination of the chemical composition.

Prior to each electrodeposition the steel substrates were pretreated by mechanical cleaning (polishing successively with emery papers of the following grades: 280, 360, 800 and 1000) and then degreased in a saturated solution of sodium hydroxide in ethanol, pickled with a 1:1 hydrochloric acid solution for 30 s and finally rinsed with distilled water. The Pt panel was pretreated by mechanical polishing with a polishing cloth (Buehler Ltd.), impregnated with a water suspension of alumina powder (0.3 μm grade) and then rinsed with pure water in an ultrasonic bath.

The counter electrodes were: *i*) a zinc panel, placed parallel to a steel panel and *ii*) a Pt spiral wire for the EIS measurements.

The reference electrode used in all experiments was a saturated calomel electrode (SCE).

Chemical composition and surface morphology

The chemical compositions of the Zn–Ni–Co alloys were determined by atomic absorption spectrometry (AAS-PYE Unicam SP9, Philips).

The structural characterization was performed by atomic force microscopy, with a NanoScope 3D (Veeco, USA) microscope operated in the tapping mode under ambient conditions. Etched silicon probes with a spring constant 20–80 N m^{-1} were used.

Electrochemical measurements

The electrochemical measurements were performed in 3 % aqueous NaCl solution using a Gamry Reference 600 potentiostat/galvanostat/ZRA. A classic three-electrode cell arrangement was used. The working electrode was a coated steel panel situated in a special holder. The counter electrode was a platinum mesh with a surface area considerably greater than that of the working electrode. The reference electrode was a saturated calomel electrode (SCE). The cell assembly was located at a Faraday cage to prevent electrical interferences. The electrochemical impedance spectroscopy measurements were performed at the open-circuit potential (OCP), over a frequency range from 100 kHz to 10 mHz, using a 10 mV amplitude sinusoidal voltage. The impedance spectra were analyzed using the Gamry Elchem Analyst fitting procedure. The corrosion stability was also evaluated by determining the time to the appearance of red rust. The plated specimens (10 μm thick) were immersed in a 3 % aqueous NaCl solution and the open circuit potential was measured daily.

RESULTS AND DISCUSSION

Chemical composition of Zn–Ni–Co alloys

In order to define the composition of ternary alloys, three variables of composition should be fixed. The manner in which the composition of the plating solution is varied is very important.[17] The most convenient way is to keep the total metal content of the solution and one of the metal-percentages constant. In this manner, the chemical content of a ternary alloy then becomes a function of the metal percentage of one of the other two metals in the solution.[17] In this work

the Zn content was held constant in both the examined plating solutions and the ratio of two alloying elements, Co and Ni, was varied. The influence of the deposition current density on the chemical content of Co, Ni and Zn in the Zn–Ni–Co alloys, determined by AAS, is shown in Figs. 1 and 2 for alloys deposited from plating solutions with different Co^{2+} to Ni^{2+} ratios. It can be seen that chemical content of the alloying elements depends on both the ion ratio in the plating solution and the deposition current density. Namely, the alloys deposited from a solution with $[Co^{2+}]/[Ni^{2+}] = 0.12$ contained a significantly greater amount of Ni as compared to Co (Fig. 1), whereas the differences among contents of Co and Ni were smaller for the alloys deposited from a solution with $[Co^{2+}]/[Ni^{2+}] = 0.90$ (Fig. 2). The total content of alloying elements, Ni and Co, was greater for alloy coatings deposited from the bath with higher cobalt to nickel ion ratio and it varied depending on the deposition current density. Namely, in this plating solution, the Co content in the alloy deposit increased with increasing deposition current density until 5 A dm^{-2} but a further increase in current density resulted in a decreased Co content (Fig. 2).
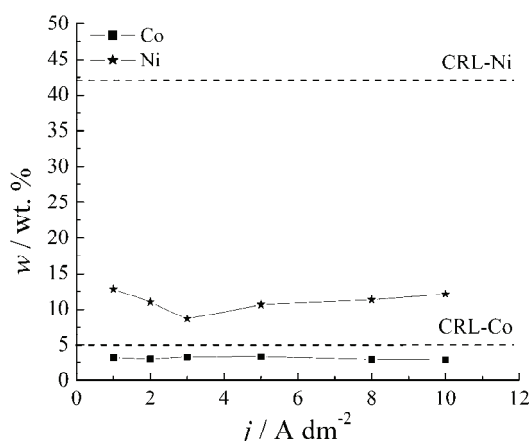

Fig. 1. Dependence of the Co and Ni contents in Zn–Ni–Co alloys on the deposition current density for alloys deposited from the solution with $[Co^{2+}]/[Ni^{2+}] = 0.12$.

The ratio of each alloying element to the total amount of metal cations in the plating solution is shown in Figs. 1 and 2 by composition reference lines (CRL) for both Co and Ni. Brenner[17] classified the electrodeposition of Zn with elements of the iron group as anomalous, when zinc, which is the less noble metal, deposits preferentially and the content of alloying element in the deposit is smaller than in the plating solution. The amount of Zn in ternary alloys does not change much with the deposition current density and in both plating solutions it was well above the CRL lines, which being ≈52 %, suggesting preferential Zn deposition (see Fig. S-1a and b in the Supplementary material to this paper).
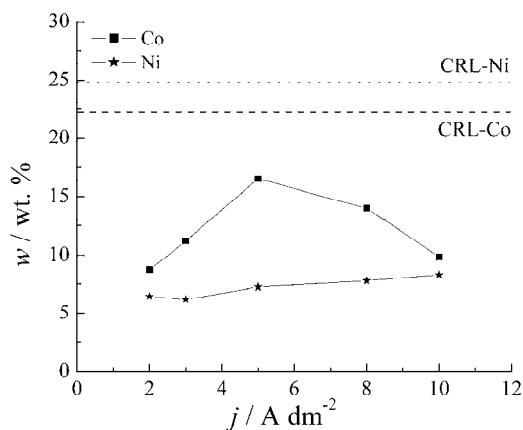
Fig. 2. Dependence of the Co and Ni contents in Zn–Ni–Co alloys on the deposition current density for alloys deposited from the solution with $[Co^{2+}]/[Ni^{2+}] = 0.90$.

Since the contents of both Co and Ni were below their corresponding composition reference lines and the zinc content was considerably above its CRL, and bearing in mind that Zn is less noble than both Co and Ni, it could be concluded that the two alloying elements form an anomalous plating system with Zn.

In one plating solution the ratio of the alloying elements, Co and Ni ions, was 0.12, whereas the ratios of these metals in the deposits were in the range 0.25–0.38, depending on the deposition current density. In the other plating solution, where ratio of the alloying elements was 0.90, their ratio in the deposit was even higher, ranging from 1.2 (at low and high current densities) to 2.3 (at intermediate current densities). In both cases, the ratio of Co and Ni in the deposit was much higher than their ratio in the plating solution, suggesting that these elements could have a synergistic beneficial effect in their codeposition and incorporation in a deposit. Eliaz *et al.* studied partial current densities for the deposition of Zn–Ni–Co alloys in the presence of gelatine and evidenced a mutual synergistic catalytic effect of Ni on Co.[10]

Corrosion protection

Since Zn alloys are mainly used in corrosion protection, their corrosion stability was determined by electrochemical measurements. The results of electrochemical impedance spectroscopy, a technique commonly used in corrosion testing of Zn alloy coatings,[1,10,18,19] are shown in Fig. 3a and b. Nyquist plots for the impedance of the Zn–Ni–Co deposits obtained from the solution with higher ratio of alloying elements, at different current densities, after 60 min of exposure to 3 % NaCl solution are shown in Fig. 3a. All EIS plots were characterized by two semicircles. According to the literature,[10,19,20] the time constant in the high frequency range relates to the presence of a porous oxide layer, while the second time constant, in the lower frequency range, accounts for a pseudo--barrier layer of alloy coating. The smallest impedance values, suggesting the
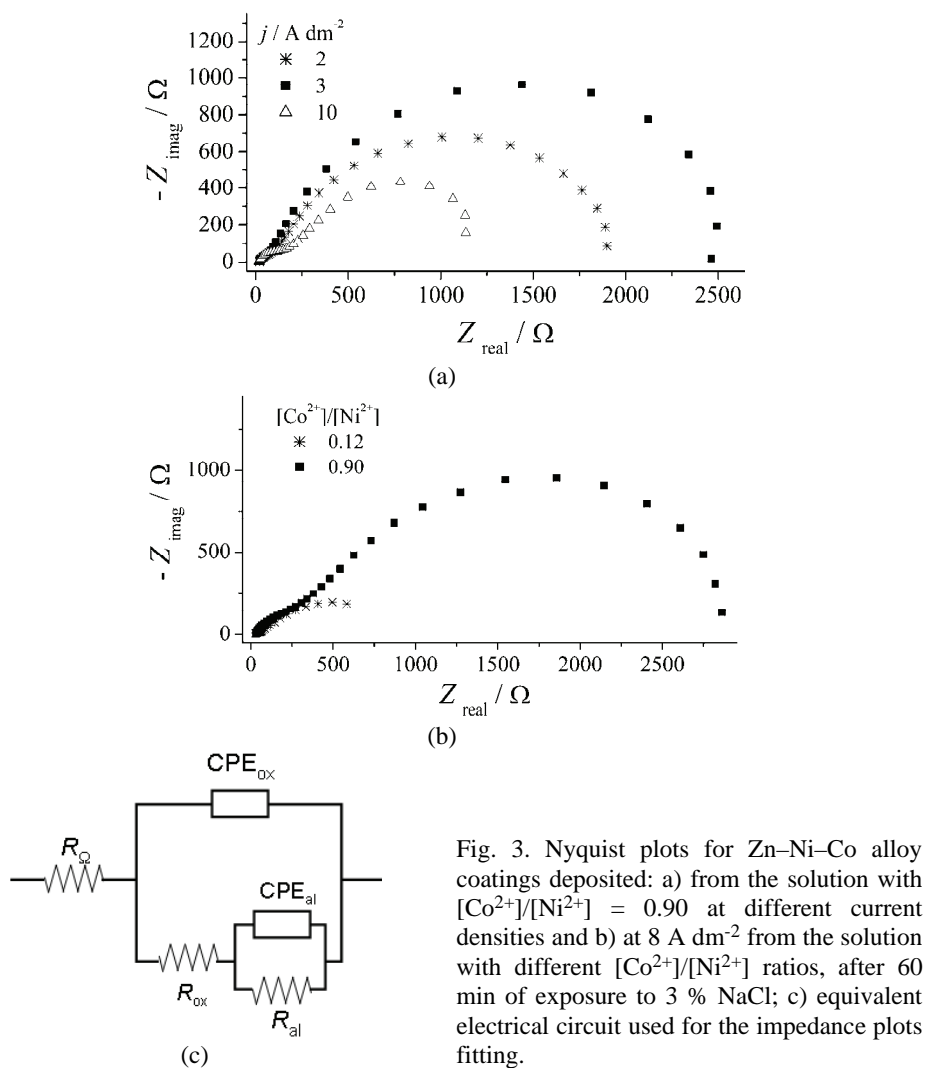
Fig. 3. Nyquist plots for Zn–Ni–Co alloy coatings deposited: a) from the solution with $[Co^{2+}]/[Ni^{2+}] = 0.90$ at different current densities and b) at 8 A dm^{-2} from the solution with different $[Co^{2+}]/[Ni^{2+}]$ ratios, after 60 min of exposure to 3 % NaCl; c) equivalent electrical circuit used for the impedance plots fitting.

smallest resistance, were obtained for the Zn–Ni–Co alloy coating deposited at the highest current, 10 A dm^{-2}, having 9.8 % Co and 8.3 % Ni. Higher impedance was determined for coatings deposited at smaller current densities. The overall impedance of the alloy coating deposited at 3 A dm^{-2} (with 11.2 % Co and 6.2 % Ni) was two times greater than that for the coating deposited at 10 A dm^{-2} with a smaller Co content and a higher Ni content.

The influence of the $[Co^{2+}]/[Ni^{2+}]$ ratio in the plating solution on the corrosion stability of Zn–Ni–Co alloys is shown in Fig. 3b, for coatings deposited at 8 A dm^{-2}. As can be seen, the differences in the corrosion stability were more dependent on the plating solution composition than on the current density. Depo-

sition from the solution with higher ratio of the alloying elements, with 14 % Co and 7.8 % Ni, resulted in the almost three-fold increase in the overall impedance, as compared to the alloy with only 2.9 % Co and 11.3 % Ni. This could be the result of the differences in the chemical composition of the alloy coatings deposited from the different plating solutions. Namely, the overall content of the alloying elements in the deposits were greater when they were obtained from the solution with their higher ion ratio, as well as greater Co content.

The corrosion protection was analyzed by electrochemical impedance spectroscopy and the EIS data were fitted by the appropriate equivalent electrical circuit (Fig. 3c), having two time constants, (R_{ox}, C_{ox}) and (R_{al}, C_{al}). The elements of the equivalent electrical circuit are: R_Ω – the electrolyte resistance, R_{ox} – the oxide layer resistance, R_{al} – the resistance of the alloy coating with corrosion products, and CPE_{ox} and CPE_{al} are the constant phase elements, which are related to the capacitance of the oxide layer and alloy coating with corrosion products, respectively. The time constant related to the charge-transfer resistance and double layer capacitance (R_{ct}, C_{dl}) were not used in the equivalent electrical circuit. This time constant indicates that the corrosion processes on the steel substrate on initial exposure to a corrosive agent was negligible compared to the time constant related to the alloy coating, (R_{al}, C_{al}). Thus, the whole corrosion process, at this early stage, was characterized by the properties of the alloy coating and the time constant (R_{al}, C_{al}), and the oxide layer. The fitting of experimental data enabled the determination of R_{ox}, C_{ox}, R_{al} and C_{al} for the alloy coatings and the results are shown in Figs. 4 and 5. The capacitance C_{al} was determined in the Gamry Instruments Echem Analyst and also calculated using the proposed method from the literature.[21]

As can be seen from Figs. 3 and 4, the impedance of the thin, porous oxide layer was significantly smaller than the impedance of the inner pseudo-barrier layer on the alloy surface. The R_{al} values of the Zn–Ni–Co alloys deposited from the solution with low $[Co^{2+}]/[Ni^{2+}]$ ratio, with around 3 % Co and 9–13 % Ni, were up to six times lower (indicating lower corrosion stability) than the alloy coatings deposited from the other plating solution, which containing a greater amount of Co and a smaller amount of Ni (9–16.5 % Co and 6–8 % Ni).

For the alloy coatings deposited from the solution with the low ratio of the alloying elements, the highest alloy coating resistance was determined for the ones with the same chemical content (2.9 % Co and 12 % Ni) deposited at 8 and 10 A dm^{-2} (822 and 905 Ω cm^2), while much higher resistances were found for alloy coatings deposited from the solution with high ion ratio at 3 and 8 A dm^{-2}, having greater Co and smaller Ni amounts (11.2 % Co, 6.2 % Ni and 14 % Co, 8.3 % Ni, respectively) (2640 and 2710 Ω cm^2).

The resistances of the corresponding binary alloy coatings were 800 Ω cm^2 for Zn–Ni (with 12.0 % Ni) and 450 Ω cm^2 for Zn–Co (11.3 % Co), deposited at

8 A dm^{-2} from the plating solutions free of one of the alloying element (Co and Ni, respectively). Hence, the ternary alloy coatings provided either comparable or greater corrosion stability, depending on both the deposition current density and the deposition solution.
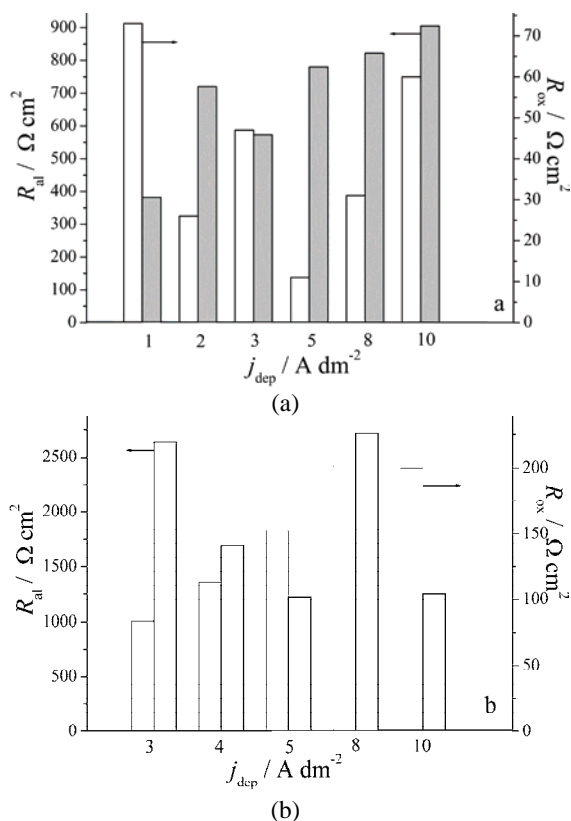

Fig. 4. The values of R_{ox} and R_{al} for the Zn–Ni–Co alloys deposited at different deposition current densities from the solution with [Co^{2+}]/ /[Ni^{2+}]: a) 0.12 and b) 0.90.

The values of alloy coating capacitances, C_{al}, are shown in Fig. 5. One to two order of magnitude higher C_{al} values were determined for alloy coatings deposited from the solution with the lower alloying ion ratio, having a smaller Co content. The smallest capacitances were determined for coatings deposited at 3 and 8 A dm^{-2} from the solution with [Co^{2+}]/[Ni^{2+}] = 0.90, suggesting they were less porous. The capacitances of the corresponding binary alloy coatings were 20 μF cm^{-2} and 310 μF cm^{-2} for Zn–Ni and Zn–Co alloys, respectively.

Based on the EIS plots and results shown in Figs. 4 and 5, it could be concluded that the higher content of either of the alloying element was not solely responsible for providing higher corrosion stability, as indicated by the high R_{al} and low C_{al} values, for coatings deposited from both the plating solutions. The highest corrosion stability (highest R_{al} and lowest C_{al} values) was observed for

the Zn–Ni–Co (14 % Co, 8.3 % Ni) alloy deposited at 8 A dm^{-2} from the bath with a high [Co^{2+}]/[Ni^{2+}] ratio.
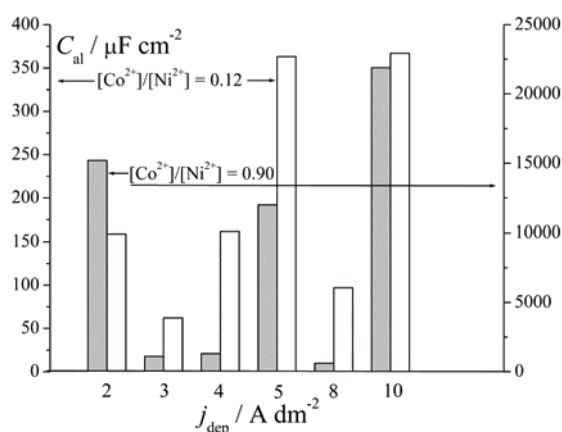

Fig. 5. The values of C_{al} for the Zn–Ni–Co alloys deposited at different deposition current densities from the solution with [Co^{2+}]/[Ni^{2+}]: 0.12 and 0.90.

The long-term protection was evaluated by following the change in the open circuit potential with time of exposure to a 3 % NaCl solution. The time dependence of E_{ocp} for steel coated by Zn–Ni–Co alloys deposited from different plating solutions at different current densities was analyzed (see Fig. S-2 of the Supplementary material). The potentials of all the Zn–Ni–Co alloys were more negative than the E_{ocp} value of the steel base; hence, these ternary alloy deposits offered sacrificial cathodic protection. The open circuit potentials of the alloys deposited from the solution with [Co^{2+}]/[Ni^{2+}] = 0.12 were more negative (lower than –1020 mV *vs*. SCE) as compared to those deposited from the solution with the higher ion ratio (–720 mV *vs*. SCE). The alloy coatings deposited from the latter solution have greater overall amounts of alloying elements and, consequently, a nobler E_{ocp}. The E_{ocp} values of steel coated with Zn–Ni–Co alloys increased with time of immersion and eventually reached the steel E_{ocp}, which represents loss of the deposit and the start of a steel corrosion process. Deposits obtained from the solution with the lower ion ratio reached the steel E_{ocp} more rapidly. The alloy coating deposited at 1 A dm^{-2} (3.2 % Co, 12.8 % Ni) reached the steel E_{ocp} already after 3 days, whereas the ones deposited at 3, 5 and 8 A dm^{-2} (≈3 % Co, 10.5–12 % Ni) lasted longer, 7–9 days. Among the coatings obtained from the solution with [Co^{2+}]/[Ni^{2+}] = 0.90, red rust appeared first on the alloy deposited at 10 A dm^{-2} (9 days). The longest time to red rust appearance (24 days), indicating the best corrosion stability, was observed for the Zn–Ni–Co alloy deposited from this plating solution at 8 A dm^{-2}.

The differences in corrosion stability among coatings could be the due to the greater overall content of the alloying elements, as well as the greater Co content, in deposits obtained from the solution with their higher ion ratio. It was shown

that the chemical content of all the alloy coatings analyzed in this work was sufficient to provide better corrosion protection with respect to the protection offered by binary coatings. However, the results shown so far suggest that the chemical content of the alloys was not the only factor governing good corrosion stability.

Surface morphology

Homogenous and coherent coatings were obtained from both plating solutions up to a current density 10 A dm^{-2}. Already at 12 A dm^{-2}, the deposits were not so uniform and powdery at the edges. The differences in surface morphology of some of the electrodeposited Zn–Ni–Co alloys could be seen from the atomic force microscopy (AFM) images shown in Figs. 6 and 7. A large crystal agglomeration of hexagonal type, ranging from 900–1500 nm, could be seen in Fig. 6a for the deposit obtained from the plating solution with $[Co^{2+}]/[Ni^{2+}] = 0.12$ at 5 A dm^{-2}. A larger Co content in the plating solution, at the same current density, resulted in a deposit having a different shape of crystal agglomerations (Fig. 6b). They were smaller (500–700 nm), more narrow and flat and thus, more densely packed.
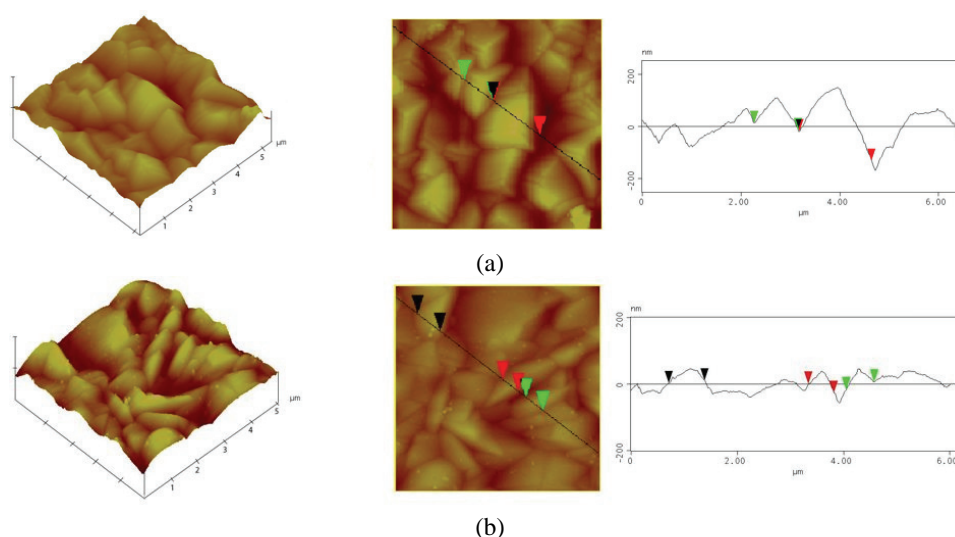

(a)

(b)

Fig. 6. 3D and 2D AFM images and height profiles of the Zn–Ni–Co alloy deposited at 5 A dm^{-2} from the solution with $[Co^{2+}]/[Ni^{2+}]$: a) 0.12 and b) 0.90.

Higher current densities modified the morphology of the alloys, decreasing the surface roughness, in both plating solutions. A smooth surface with large agglomerations, ranging from 1.3–1.7 μm, could be seen in Fig. 7a for the alloy deposited at 8 A dm^{-2} from the solution with the smaller Co to Ni ratio. Large

agglomerations with high roughness no longer existed, suggesting the inhibition of vertical agglomeration growth on the surface. The deposit was composed of large, flat agglomerates that are not closely packed and hence, it does not seem very compact. The surface morphology of alloy deposited at 8 A dm^{-2} from the plating solution with $[Co^{2+}]/[Ni^{2+}] = 0.90$ was more compact and smoother, as can be seen in Fig. 7b, with agglomerates of smaller size, *i.e.*, 750–800 nm.

(a)

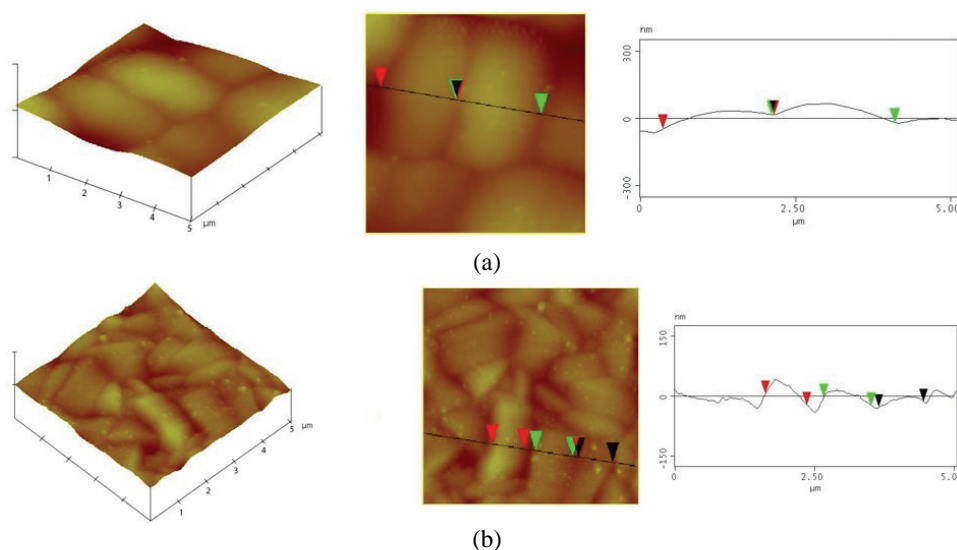(b)

Fig. 7. 3D and 2D AFM images and height profiles of the Zn–Ni–Co alloy deposited at 8 A dm^{-2} from the solution with $[Co^{2+}]/[Ni^{2+}]$: a) 0.12 and b) 0.90.

The distribution of sizes of the agglomerates, determined from AFM images (not shown), indicated that the average agglomerate size of all deposits varied greatly with the $[Co^{2+}]/[Ni^{2+}]$ ratio in the plating bath. Smaller agglomerates were observed for the alloy coatings deposited from the solution with the greater ion ratio and greater overall amounts of alloying elements. In addition, the homogeneity of agglomerates size distribution for these samples was also greater.

It is well known that Zn alloys corrode preferentially, thus providing sacrificial protection of steel. The protection mechanism for both Zn–Ni and Zn–Co alloy coatings was suggested by Lambert and confirmed by Short.[22,23] Namely, at the beginning of exposure to a corrosive agent, *i.e.*, during the early stage of corrosion, zinc, as a less noble metal, dissolves preferentially, providing galvanic protection of steel. Consequently, a dezincification process occurs, resulting in enrichment of the alloy surface layer with alloying elements. The dezincification of the Zn–alloy coating leads to an improved barrier layer, which reduces the corrosion rate. This, in turn, leads to a shift in the corrosion potential to more noble values. With further exposure to a corrosive agent, a layer of corrosion

products forms on the surface that acts as a protective, barrier layer. It was shown that the layer of corrosion products on Zn-alloys in a chloride-containing environment is mainly made up of zinc hydroxychloride, $Zn_5(OH)_8Cl_2$.[4,25,26] It has a very low solubility, $10^{-14.2}$,[27] providing a pseudo-passive layer that enables high protective ability. If porosity of this pseudo-barrier layer were smaller, the corrosion protection would be improved.

The more densely packed morphology of the alloy coatings obtained from the plating solution with greater $Co^{2+}]/[Ni^{2+}]$ ratio, with a greater amount of Co and considerably smaller crystal agglomerates, resulted in a less porous deposit. The smaller porosity was indicated by AFM images and confirmed by the at least order of magnitude smaller capacitances (Fig. 6). Eliaz *et al.*[10] also found that the minimal corrosion rates of Zn–Ni–Co alloy coatings neither corresponded to the highest content of the more noble element (iron-group metal) in the coating nor to the highest thickness of the coatings. They showed that the coatings with the lower corrosion resistance were those with a higher degree of porosity. Hence, the chemical content was not the sole factor determining the corrosion stability of the ternary alloy coatings examined in this work.

Hence, it could be concluded that the chemical content and surface properties, such as homogeneity, agglomeration size and their distribution, depend on the plating solution, as well as on deposition current density. The agglomerates obtained from the plating solution with a smaller ion ratio were larger, with considerable differences in size, with respect to the ones deposited from the plating solution with the higher ion ratio. More compact alloy coatings, with a uniform distribution of agglomerates, are deposited from the solution with the higher ion ratio, especially at 8 A dm^{-2}. Hence, the pseudo-passive layer of the corrosion products formed on the surface of this alloy was more compact, with a higher resistivity and a smaller permeability (reflected by the smaller capacitance values), which, in turn, resulted in improved corrosion stability.

CONCLUSION

Ternary Zn–Ni–Co alloy coatings were successfully deposited from chloride, additive free, plating solutions. Based on the presented results, it could be concluded that the ratio of nickel to cobalt ions in the plating solution and deposition current density had a significant influence on the chemical composition, morphology and corrosion stability of Zn–Ni–Co electrodeposited alloys.

The contents of both Co and Ni are below their corresponding composition reference lines and the zinc content is considerably above its CRL, so the two alloying elements form an anomalous plating system with Zn. The ratio of Co and Ni is much higher than their ratio in the plating solution, in all examined deposits, suggesting that these elements could have a beneficial synergistic effect in their codeposition and incorporation in a deposit.

It was shown that the ternary alloy coatings provide either comparable or greater corrosion stability, depending both on the deposition current density and the deposition solution. A higher impedance of the ternary alloys deposited from the solution with the greater $[Co^{2+}]/[Ni^{2+}]$ ratio was determined. These deposits also showed significantly smaller capacitances, suggesting improved corrosion stability. The longest time to red rust appearance, indicating the best corrosion stability, was observed for the Zn–Ni–Co alloy deposited from this plating solution at 8 A dm^{-2}.

Homogenous and coherent coatings were obtained from both plating solutions up to a current density of 10 A dm^{-2}. Smaller crystalline aggregates were formed by deposition from the solution with the higher $[Co^{2+}]/[Ni^{2+}]$ ratio, *i.e.*, in deposits with the greater Co content. In addition, the homogeneity of the size distribution of the agglomerates for these samples was also greater and the corresponding corrosion stability was higher. It is assumed that more compact alloy coatings with uniform distribution of agglomerates, which were deposited from the solution with the higher ion ratio, especially at 8 A dm^{-2}, resulted in an improved corrosion stability.

SUPPLEMENTARY MATERIAL

Figures S-1 and S-2 along with corresponding discussion are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

ТРОЈНЕ Zn–Ni–Co ЛЕГУРЕ: АНОМАЛНО ТАЛОЖЕЊЕ И КОРОЗИОНА СТАБИЛНОСТ

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У овом раду су проучаване Zn–Ni–Co легуре електрохемијски таложене под различитим условима. Хемијски састав је одређиван AAS техником, морфологија AFM анализом а корозиона стабилност применом EIS. Испитиван је утицај односа легирајућих елемената, $[Co^{2+}]/[Ni^{2+}]$, у хлоридном раствору за таложење, као и густине струје таложења, на хемијски састав, морфологију и корозиону постојаност легура. Коришћени су раствори са истим укупним садржајем метала, без додатака, и таложење је вршено на собној температури. Показано је да је таложење тројних легура аномално и да однос јона никла и кобалта у раствору за таложење, као и густина струје таложења, имају зна-

чајан утицај на хемијски састав и корозиону стабилност ових легура. Заједничко при-суство Ni и Co је имало повољан утицај на корозиону постојаност легура. Показано је да су морфологија и порозност превлака легура веома важни фактори који утичу на њи-хову корозиону стабилност. Превлака добијена таложењем из раствора са већим одно-сом јона легирајућих елемената густином струје од 8 A dm^{-2} се састојала од мањих агре-гата кристалних зрна, била је мање храпавости и порозности и показала је највећу коро-зиону стабилност.

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