G. NAWRAT*, J. PIOTROWSKI*, A. MACIEJ*, W. SIMKA*, Ł. NIEUŻYŁA*

# INFLUENCE OF PARAMETERS OF ELECTRODEPOSITION Zn – Ni COATINGS ON THEIR STRUCTURE AND COMPOSITION

## WPŁYW PARAMETRÓW ELEKTROOSADZANIA POWŁOK Zn – Ni NA ICH STRUKTURĘ I SKŁAD CHEMICZNY

Coatings which are anodic covers have had great significance in anticorrosion protection of steel and they are commonly used for a long time. Because of relatively low price of zinc, it's the most widespread metal protecting steel elements from corrosion. However, in some cases, for the sake of rugged conditions of exploitation, application of zinc coatings is limited, e.g. in automotive and aircraft industry. So far in that instances, they are substituted with success by the cadmium layers, which are characterized by good anticorrosive properties. But due to their toxic peculiarities there exists the tendency to replace them by alloy coatings, e.g. Ni – Zn [1].

Electrodepositing of zinc- nickel alloy coatings can be realized both by using alkaline or acid baths. As soon the largest significance found slightly acid chloride baths and minor sulfuric baths. The coatings deposited from acid baths exhibit the greatest anticorrosion resistance in the range of 10 – 15% of nickel in the alloy. Application of alkaline baths permit to receive layer with similar corrosion resistance, but with lower content of Ni (6 - 10%) [2, 3]. It was also found that the coatings exhibit several times better anticorrosive properties than pure zinc layers. [4]. However, during corrosion process zinc undergo preferential digestion, what causing enrichment the layer with nickel, what in consequence lead to increasing corrosion potential in the direction more positive values [2].

In this paper the investigations of electrodeposition of Zn – Ni alloy layers from chloride baths on common steel St3S substrate were presented. The influence of bath composition and cathodic current density on the chemical composition and structure obtained coatings was determinated. The Zn – Ni layers were put to the microhardness tests and corrosion resistance examinations in 5% NaCl solution. There was found that content of alloy-creating metal ions in bath and their mutual molar ratio considerably influence on surface morphology of obtained coatings, effect of used current density is smaller. The content of Ni in layer increases with decreasing of $[Zn^{2+}]/[Ni^{2+}]$ ratio in the bath. The hardness of obtained alloy layers is considerably higher that hardness of the substrate (St3S steel) and distinctly depends on amount of nickel in the layer. It was also found that in the range of 13 – 16% at. of nickel content in alloy the best corrosion resistance of layer was obtained.

*Keywords*: electrodeposition, alloy coatings, Zn – Ni alloys, SEM, EDS

W ochronie antykorozyjnej stali od dawna bardzo duże znaczenie mają powłoki stanowiące zabezpieczenie o charakterze anodowym. Ze względu na relatywnie niską cenę cynku, jest on najbardziej rozpowszechnionym metalem zabezpieczającym elementy stalowe przed korozją. Jednak w niektórych przypadkach, ze względu na trudne warunki pracy, stosowanie powłok cynkowych jest ograniczone, np. w przemyśle motoryzacyjnym i lotniczym. Dotychczas w takich przypadkach z sukcesem zastępowały je powłoki kadmowe, które charakteryzują się bardzo dobrymi właściwościami antykorozyjnymi. Jednak ze względu na ich toksyczne właściwości istnieje tendencja do zastępowania ich powłokami stopowymi, np. Zn – Ni [1].

Elektrolityczne osadzanie powłok stopowych cynk – nikiel można realizować zarówno przy użyciu kąpieli alkalicznych, jak i kwaśnych. Jak dotąd największe znaczenie znajdują słabokwaśne kąpiele chlorkowe oraz w mniejszym stopniu siarcza-nowe. Powłoki osadzane z kąpieli kwaśnych wykazują największą odporność na korozję przy zawartości niklu od 10 do 15 %. Zastosowanie kąpieli alkalicznych pozwala na otrzymanie powłok o podobnej odporności korozyjnej, jednak o mniejszej zawartości Ni (6 – 10 %) [2, 3]. Stwierdzono również, że powłoki tego typu wykazują kilkukrotnie lepsze właściwości antyko-rozyjne w stosunku do powłok cynkowych [4]. Podczas przebiegu procesu korozji powłoki cynk ulega jednak preferencyjnemu roztwarzaniu, powodując wzbogacanie powłoki w nikiel, co w konsekwencji prowadzi do wzrostu potencjału korozyjnego w kierunku wartości dodatnich [2].

W pracy przedstawiono badania procesu elektroosadzania powłok stopowych cynk – nikiel z kąpieli chlorkowych na stali niestopowej St3S. Określono wpływ składu kąpieli oraz katodowej gęstości prądu na skład chemiczny i strukturę otrzymanych powłok. Powłoki Zn – Ni poddano badaniom mikrotwardości oraz odporności korozyjnej w 5% roztworze NaCl. Stwierdzono, że zawartość jonów metali powłokotwórczych w kąpieli oraz ich wzajemny stosunek molowy istotnie wpływa na morfologię

* DEPARTAMENT OF INORGANIC CHEMISTRY, TECHNOLOGY AND FUELS, FACULTY OF CHEMISTRY, SILESIAN UNIVERSITY OF TECHNOLOGY, B. KRZYWOUSTEGO 6, 44-100, GLIWICE, POLAND

powierzchni powstałej powłoki, mniejszą rolę odgrywa zaś zastosowana gęstość prądu. Zawartość Ni w powłoce wzrasta wraz ze zmniejszeniem stosunku [Zn²⁺]/[Ni²⁺] w kąpieli. Twardość powstałych powłok stopowych jest zdecydowanie większa od twardości podłoża (stali St3S) i wyraźnie zależy od zawartości niklu w powłoce. Stwierdzono, że przy zawartości 13 – 16% at. niklu w stopie uzyskuje się najlepszą odporność powłok na korozję.

## 1. Introduction

Coatings which are anodic covers have had great significance in anticorrosion protection of steel and they are commonly used for a long time. Because of relatively low price of zinc, it's the most widespread metal protecting steel elements from corrosion. However, in some cases, for the sake of rugged conditions of exploitation, application of zinc coatings is limited, e.g. in automotive and aircraft industry. So far in that instances, they are substituted with success by the cadmium layers, which are characterized by good anticorrosion properties. But due to their toxic peculiarities there exists the tendency to replace them by alloy coatings, e.g. Zn – Ni [1 – 3].

Electrodepositing of zinc – nickel alloy coatings can be realized both by using alkaline [4] or acid baths [5–7]. Studies of receiving the Zn – Ni coatings from non-aqueous (methanol) bath are also reported [8]. As soon the largest significance found slightly acid chloride baths and minor sulfuric baths. The coatings deposited from acid baths exhibit the greatest anticorrosion resistance in the range of 10 – 15 % of nickel in the alloy. Application of alkaline baths permit to receive layer with similar corrosion resistance, but with lower content of Ni (5-10%) [4]. It was also found that the coatings exhibit several times better anticorrosion properties than pure zinc layers. [7, 9]. Commonly obtained Zn - Ni coatings are less active than pure zinc and are characterized by lesser corrosion rate. However, during corrosion process zinc undergo preferential digestion, what causing enrichment the layer with nickel, what in consequence lead to increasing corrosion potential in the direction more positive values [6, 10].

It's commonly known that electrodeposition of Zn – Ni alloy layers proceeds in anomalous way. It means that, privileged deposition of zinc, which is less noble ($E^O_{Zn2+/Zn}$ = -0,76 V) than nickel ($E^O_{Ni2+/Ni}$ = -0,25 V) is observed in wide range of parameters using during electroplating process. Mechanism of this phenomena hasn't been exactly known yet, but the hypothesis assuming inhibition deposition of nickel by hydroxy-compounds of zinc is the most widespread [8, 11].

The aim of this study was to determine the effect of bath composition and cathodic current density on chemical composition and structure of obtained layers and also define their anticorrosion properties and hardness.

## 2. Experimental

Samples used to the investigations were steel bars with 6 mm diameter and 80 mm length. The substrate material was St3S steel, which composition is showed in table 1. An anode was made from zinc sheet with 2 mm thickness.

TABLE 1

Chemical composition of St3S steel, wt.%

| C max | Mn max | Si max | P max | S max | Cr max | Ni max | Cu max | Al all | Fe |
|-------|--------|--------|-------|-------|--------|--------|--------|--------|------|
| 0.22 | 1,10 | 0,35 | 0,05 | 0,05 | 0,30 | 0,30 | 0,30 | 0,02 | rest |

Electrodeposition of Zn – Ni alloy coatings was realized in thermostatical, cylindrical glass electrolysis cell with 70 mm diameter. Steel cathode was put along its axis, whereas the zinc anode adhered to its side wall. Electroplating was carried out in 25°C. Qualitative composition all of used baths was the same, but the solutions differed from each other in total concentration of $Zn^{2+}$ and $Ni^{2+}$ ions and in ratio of those ions concentrations. Total contents of alloy-creating ions amounted to 0,5; 1,0 and 1,5 mol/dm³ whereas concentrations ratios of zinc to nickel ions were 0,5; 2,0 and 8,0. The composition of the baths is presented in table 2. Content of $NH_4Cl$ and $H_3BO_3$ was constant in all baths and amounts to 240g/dm³ and 20 g/dm³ respectively. All the solutions were prepared using pure grade reagents from POCh Gliwice.

TABLE 2

Chemical composition of baths; constant ingredients concentration: $NH_4Cl = 240g/dm^3$, $H_3BO_3 = 20g/dm^3$

| Bath symbol | A1 | A2 | A3 | B1 | B2 | B3 | C1 | C2 | C3 |
|---|---|---|---|---|---|---|---|---|---|
| $[Zn^{2+}]+[Ni^{2+}]$ | 0,5 mol/dm³ | | | 1 mol/dm³ | | | 1,5 mol/dm³ | | |
| $[Zn^{2+}]/[Ni^{2+}]$ | 0,5 | 2 | 8 | 0,5 | 2 | 8 | 0,5 | 2 | 8 |
| $ZnCl_2$ [mol/dm³] | 0,167 | 0,333 | 0,444 | 0,333 | 0,667 | 0,889 | 0,500 | 1,000 | 1,333 |
| $NiCl_2*6H_2O$ [mol/dm³] | 0,333 | 0,167 | 0,056 | 0,667 | 0,333 | 0,111 | 1,000 | 0,500 | 0,167 |

Because of using only zinc digesting electrode, the bath was enriching with ions of that metal insignificantly – because zinc is main coating component. For the sake of those changes in bath composition, it was replaced on fresh bath every time. Electrodeposition process was carried out three current density, i.e. 100 A/m², 400 A/m² and 800 A/m².

Morphology and chemical composition of obtained coatings were was analyzed by means of Hitachi S-3400N scanning electron microscope equipped with the system of X-ray microanalysis (EDS) of the firm Thermo Noran, provided with the software System Six.

Investigations of corrosion resistance was carried out in 5% NaCl solution using AUTOLAB PGSTAT 30 potentiostat (EcoChemie), controlled by means of the software GPES (General Purpose Electrochemical System). Basing on the obtained results the corrosive potential ($E_{corr}$, V) was determined as well as the density of the corrosive current ($j_{corr}$, A/cm²) and the polarization resistance ($R_p$, Ω· m). Hardness of the coatings was determinated by Mitutoyo HM-112 Vickers microhardness tester, using load of indenter equal 0,2 kG (1,9614 N). In order to define thickness of those Dualscope MP20E-S thickness gauge of the firm Fisher was exploited. It was equipped with EGAB1.3 sonde, which works on principle of rotary currents.

## 3. Results and discussion

During analyzing of results particular attention was directed on influence of bath composition and current density on chemical composition of obtained coatings and their structure.
It was observed that in series of trials performed in the baths with identical composition the content of nickel in the alloys diminishes with decreasing of current density in a majority of cases. Best of all it's showed in case, in which the values of nickel content in alloys are the largest and considerably differ from each other (the differences to 3%). Such coatings were obtained in bath C1 (Fig. 1).There's no such relationship merely in two cases. For the sake of relatively close contents of nickel

it could be state that current density exert less influence on Ni content in alloy than quantitative bath composition. Moreover, special regularity was observed during compare content of nickel in layers, which were obtained in the same current conditions, in baths with constant total ion amount of alloy-creating metals but with different ratios of those ions to each other. In all series it's noticed that content of nickel in coating increase with increasing its content in bath, regardless of total metal ions in the bath (Fig. 2 a-c). There's no deviations in the tendency in the range of used parameters.
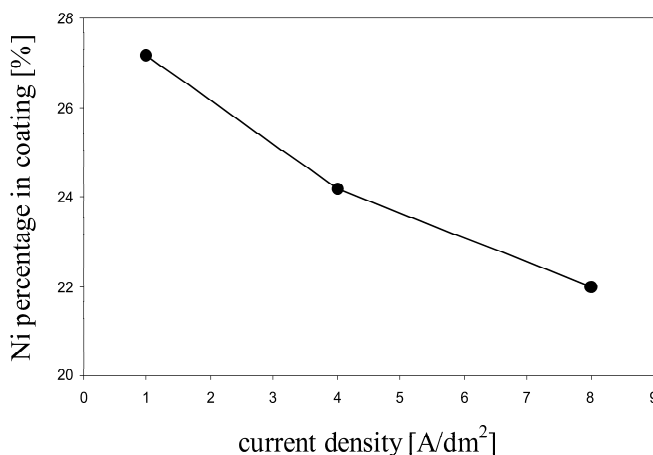


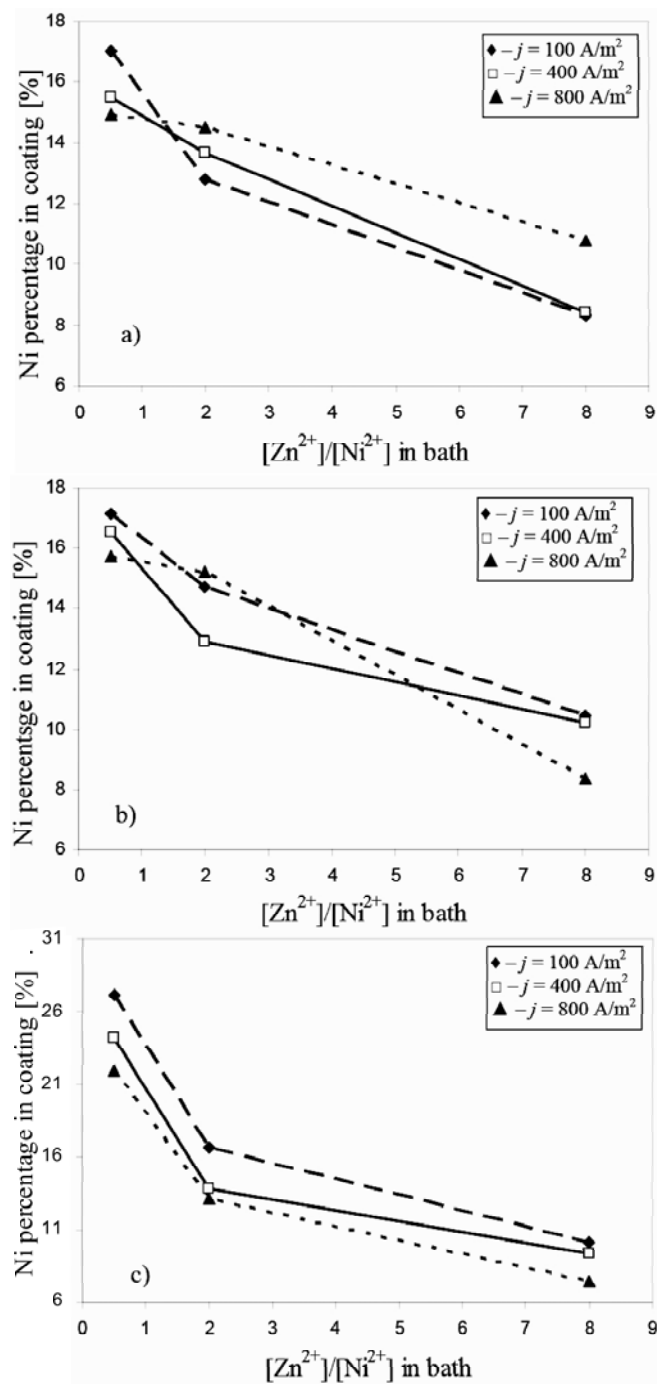Fig. 1. Influence of current density on nickel content in coating bath C1

Fig. 2. Relationship of nickel content in coating and ratio of concentrations zinc ions to nickel ions in the bath; total concentration of alloy-creating ions in the bath $[Zn^{2+}]+[Ni^{2+}]$: a) 0,5 mol/dm$^3$, b) 1,0 mol/dm$^3$, c) 1,5 mol/dm$^3$

pyramidal crystallites with size to 3 μm (Fig. 3 a). Such coatings are homogeneous enough and they practically haven't gaps and holes, what is presented in other cases. When the content of nickel in alloy decreases (about 16 - 17% at.) the characteristic structure begin to lose. The crystals are worse shaped, there form polyhedrons with vary size or pyramids with cut top (Fig. 3 b). Nodular grains with cauliflower structure are observed for layers with 11 – 15% at. of nickel (Fig. 3 c). There are often rare-packed and their size clearly depends on applying current density. For example the coatings performed in bath A2, in lower value of that parameter (j = 100 A/m$^2$) the formed grains have size 4 – 5 μm, in 400 A/m$^2$ the size is 2 – 3 μm, while in 800 A/m$^2$ it's about 1 μm. The contents of nickel in the coating obtained in the same bath and differ current density are very similar and amount to 14,29% at., 13,98% at. and 13,25% at., respectively. The coatings with the smallest quantity of Ni (8 – 10% at.) most often are characterized by nodular shape of grains but in some cases they exhibit tendency to forming dendritic structures. That situation take place during electrodepositing of coatings in current density equal 400 A/m$^2$ in bath with the largest total content alloy-creating metals (1,5 mol/dm$^3$) and with the most zinc ions content. Big cauliflower-shaped grains with 10 m size, which are built of smaller grains are apparent in scanning micrographs (Fig. 3 d). They are initial forms of stanchion accretions (Fig. 3 e ). It could supposing that presence of nickel ions in bath not only has an influence on forming respective grain forms but also it can determinate forming of dendritic structures. Besides, creation of the structures can be caused by high concentration of alloy-creating metal ions in bath. It's worth to say that some part of obtained coatings wasn't absolutely hermetic, even in spite of close-packed grains. The gaps (rarely) and holes formed as a result of hydrogen evolution (more often) were observed on their surface. No operations were taken to limit adhesion hydrogen bubbles to sample surface, e.g. using surface-active substance or cathode movement.
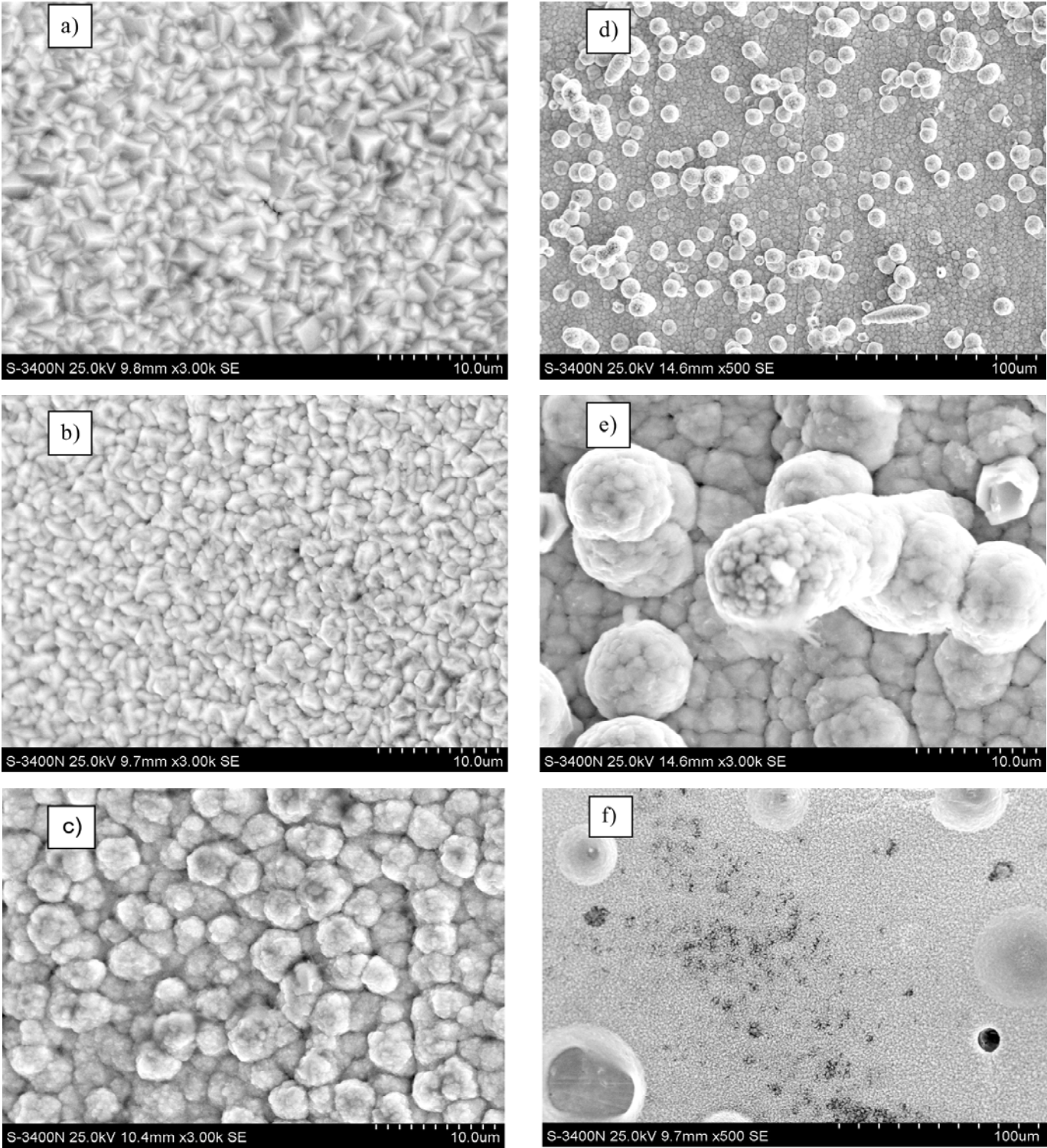
The SEM micrographs present morphology of obtained layers. In dependence on applying bath and current density, structure of their surface changes drastically. Content of metal components have an large effect on layer appearance, undoubtedly. Alloys containing >20% at., like those performed in bath C1 and vary current density are characterized by well shaped and tight packed

Fig. 3. SEM image of selected samples surface: a) bath C1, j = 400 A/m²; b) bath B2, j =100 A/m²; c) bath B2, j = 100 A/m²; d, e) bath B3, j = 400 A/m²; f) bath B2, j = 400 A/m²

Studying alloy coatings can be use in potentially wide gamut of applications, so the mechanical properties are very important. For the sake of that, hardness of the layers was also determined by Vickers method. The

measurements were performed in accordance with EN ISO 4516:2002 European Standard. The average of five hardness measurements was quoted as the hardness value. In comparison with hardness of steel substrate (St3S),

for which it amounts to 161HV0,2; the coatings exhibit larger hardness, in all cases. Distinct influence of nickel content in layer on its hardness is also visible in that issue. Hardness of the coatings increase with increasing content of nickel in obtained alloy (Fig. 4). For coatings with the smallest nickel percentage (near 9%) it's about 200HV0,2, whereas in nickel-rich layers (>20%) exhibit hardness above 350HV0,2, that is over two times greater than applied grade of steel. Alteration of the property can be connected with the phase composition. It is report-ed that Ni − Zn coatings with nearly 20% of Ni create $\gamma$-$Ni_5Zn_{21}$ phase [5]. Stoichiometric amount of Ni in the phase is 19,2% at. Some sources reports that there's present maximum of hardness in Zn-Ni alloy with about 20% of nickel. Received results might confirm that but there is no enough data to state it unequivocally. A larger majority of obtained coatings contain more quantity of zinc, which create solid solutions. Increasing of quantity of zinc is a reason for the hardness decline.
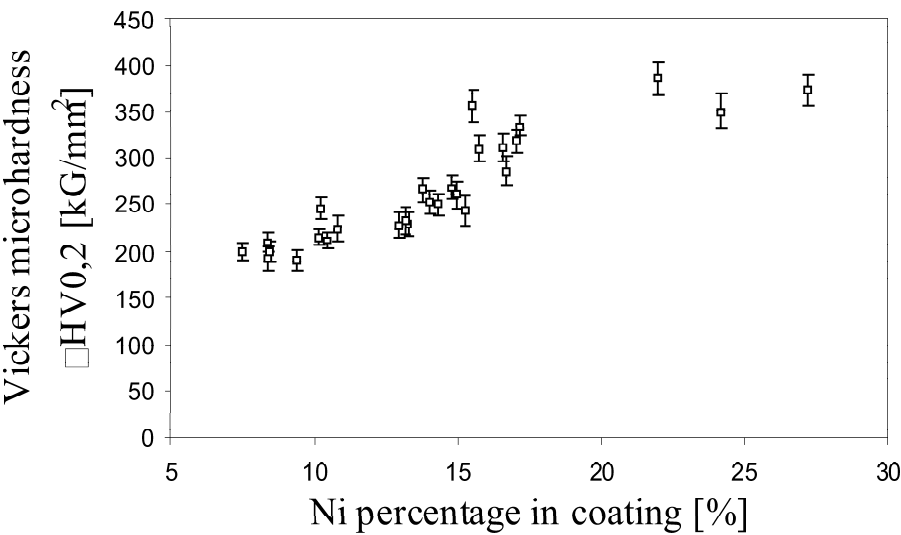


Fig. 4. Relationship between Vickers microhardness and nickel content in coatings

Determination of effect of composition and alloy structure on anticorrosion properties was also undertaken. Potentiodynamic investigations in 5% sodium chloride were carried out and as the results voltamograms with picks in corrosion potentials were obtained. On the basis of Stern-Geary equation the corrosion values were obtained, which are included in table 3. Value of the potential changes in wide range, i.e. from -0,60 V (vs. SCE) for 27% Ni in alloys to -1,04 V for coatings with little Ni content (8 − 9%) in alloy. Received results confirm existence of corrosion resistance maximum of Ni − Zn alloy coatings in the cases of layers with 13 − 16% at. Ni. Samples from that range exhibit the largest corrosion resistance. It's clearly shown by means of obtained values of linear corrosion rate, which attain the minimum in the range (Fig. 5). The alloy coatings containing about 15% at of nickel point out the corrosion rate $10^{-3}$ mm/year dimensionality. Reason of the phenomena may be similar to that, which has been shown previous-ly, i.e. that's connected with the phase composition − formation of $Zn_5Ni_{21}$ phase. Presence of homogeneous structure (single phase) is connected with high corrosion resistance. Existence of heterogeneous structure, which may occur via change of composition, cause extension of local corrosion by galvanic coupling of phases.

Few of obtained results making a little concession from that tendency. The alloys with similar quantitative composition but with differ surface morphology exhibit small difference in corrosion resistance level. Homogeneous layers with close-packed grains reveal better anticorrosion properties than inhomogeneous layers with gaps, holes and dendritic structures. It's suggests that not only ratio of metals contents in alloy has an effect on the corrosion resistance but also structure of layer can affect it. But it's worth to remember that Ni - Zn coatings have anodic character and during corrosion process they do corrode and the corrosion products plug the pores and holes inhibiting electrolyte (water) penetration.

TABLE 3

Results of corrosion investigation

| Sample | Bath | $j_{cath.}$ [A/m$^2$] | Ni percentage in coating [%] | $j_{corr}$ [mA/cm$^2$] | $E_{corr}$ [V] | $r_{corr}$ [mm/y] |
|---|---|---|---|---|---|---|
| 1 | | 100 | 17,03 | $1,38 \cdot 10^{-3}$ | -0,726 | 0,020 |
| 2 | A1 | 400 | 15,51 | $0,79 \cdot 10^{-3}$ | -0,771 | 0,011 |
| 3 | | 800 | 14,95 | $0,14 \cdot 10^{-3}$ | -0,904 | 0,002 |
| 4 | | 100 | 17,10 | $1,55 \cdot 10^{-3}$ | -0,679 | 0,022 |
| 5 | B1 | 400 | 16,53 | $1,14 \cdot 10^{-3}$ | -0,852 | 0,016 |
| 6 | | 800 | 15,74 | $0,18 \cdot 10^{-3}$ | -0,704 | 0,002 |
| 7 | | 100 | 27,19 | $3,21 \cdot 10^{-3}$ | -0,601 | 0,044 |
| 8 | C1 | 400 | 24,17 | $1,86 \cdot 10^{-3}$ | -0,699 | 0,026 |
| 9 | | 800 | 21,97 | $2,62 \cdot 10^{-3}$ | -0,683 | 0,036 |
| 10 | | 100 | 14,29 | $0,16 \cdot 10^{-3}$ | -0,866 | 0,002 |
| 11 | A2 | 400 | 13,98 | $0,13 \cdot 10^{-3}$ | -0,961 | 0,002 |
| 12 | | 800 | 13,25 | $0,12 \cdot 10^{-3}$ | -0,959 | 0,002 |
| 13 | | 100 | 14,73 | $3,58 \cdot 10^{-3}$ | -0,981 | 0,005 |
| 14 | B2 | 400 | 12,90 | $1,70 \cdot 10^{-3}$ | -0,962 | 0,024 |
| 15 | | 800 | 15,22 | $1,16 \cdot 10^{-3}$ | -0,869 | 0,016 |
| 16 | | 100 | 16,66 | $1,85 \cdot 10^{-3}$ | -0,864 | 0,026 |
| 17 | C2 | 400 | 13,14 | $1,31 \cdot 10^{-3}$ | -1,015 | 0,019 |
| 18 | | 800 | 13,76 | $0,57 \cdot 10^{-3}$ | -0,955 | 0,008 |
| 19 | | 100 | 8,34 | $5,18 \cdot 10^{-3}$ | -1,026 | 0,075 |
| 20 | A3 | 400 | 8,42 | $3,02 \cdot 10^{-3}$ | -1,042 | 0,044 |
| 21 | | 800 | 10,79 | $2,43 \cdot 10^{-3}$ | -1,016 | 0,035 |
| 22 | | 100 | 10,44 | $2,99 \cdot 10^{-3}$ | -1,034 | 0,043 |
| 23 | B3 | 400 | 10,21 | $1,70 \cdot 10^{-3}$ | -1,035 | 0,023 |
| 24 | | 800 | 8,27 | $3,66 \cdot 10^{-3}$ | -1,013 | 0,053 |
| 25 | | 100 | 10,13 | $4,32 \cdot 10^{-3}$ | -0,976 | 0,062 |
| 26 | C3 | 400 | 9,38 | $5,74 \cdot 10^{-3}$ | -0,989 | 0,083 |
| 27 | | 800 | 7,47 | $3,92 \cdot 10^{-3}$ | -0,958 | 0,057 |
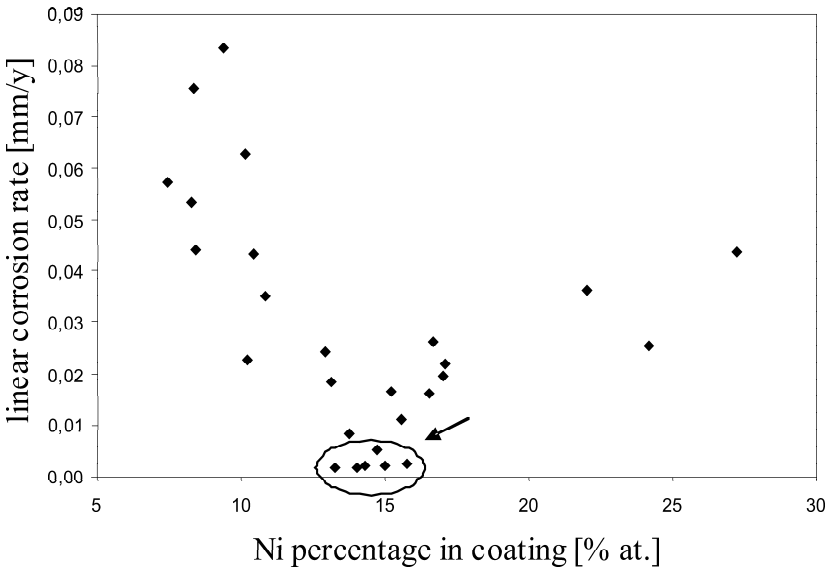


Fig. 5. Relationship of Ni percentage in coating and linear corrosion rate

Measurements of obtained coatings thickness were also enclosed in the investigations. Results indicates that the alloy coatings are relatively homogeneous in respect of thickness in all used parameters. The thickness of received coatings equals $20\pm2\mu$m.

## 4. Conclusions

1. The composition of Ni – Zn coating is directly connected with content of alloy-creating metal ions in bath. Increasing of amount of the nickel in bath cause rise the nickel percentage in bath, regardless of total concentration alloy-creating metal ions in the bath.

2. Escalation of galvanic current density cause decreasing of Ni content in the coating. Alteration of cathodic current density exert lesser influence on changes of Ni contain in comparison to chemical composition of bath.

3. Morphology of Ni – Zn alloy layers essentially depends on content of metals forming the layer, which is connected with bath composition. Cathodic current density of electrodeposition process have also effect on the structure – smaller grains are obtained in higher value of the parameter.

4. The hardness of coating increases with increasing nickel content in the layer, to about 20% at. Ni and probably attain the maximum. It arises from forming $\gamma$-Ni$_5$Zn$_{21}$ phase, which stoichiometric Ni amount equals 19,2% at.

5. The best anticorrosion properties exhibits the alloy coatings with nickel content in the range of 13 – 16% at., which is connected with nearly homogeneous structure. Presence of pores doesn't discredit the coatings from usage because of their anodic character.

### REFERENCES

[1] M. S o a r e s, C. S o u z a, S. K u r i, Mater. Sci. Eng. **402**, 16 (2005).

[2] M. A b l u - K r i s h a, F. A s s a i, A. T o g h a n, J. Solid State Elect. **11**, 244 (2007).

[3] D. C r o t t y, Met. Finish. **9**, 54 (1996).

[4] H. L e e, S. K i m, Surf. Coat. Tech. **135**, 69 (2000).

[5] A. P e t r a u s k a s, L. G r i n c e v i č i e n ė, A. Č e š ū n i e n ė, R. J u š k ė n a s, Electrochim. Acta **50**, 1189 (2005).

[6] R. F r a t e s i, G. R o v e n t i, Surf. Coat. Tech. **82**, 158 (1996).

[7] M. H e y d a r z a d e h S o h i, M. J a l a l i, J. Mater. Process. Tech. **138**, 63 (2003).

[8] T. T s u r u, S. K o b a y a s h i, T. A k i y a m a, H. F u k u s h i m a, S. G o g i a, R. K a m m e l, J. Appl. Electrochem. **27**, 209 (1997).

[9] D. E. H a l l, Plat Surf. Finish. **70**, 59 (1983).

[10] P. O z g a, E. B i e l a ń s k a, Mater. Chem. Phys. **81**, 562 (2003).

[11] A. B r e n n e r, Electrodeposition of Alloys **2**, Academic Press, New York; 194 (1963).