

Ewa OSUCHOWSKA¹, Zofia BUCZKO², Klaudia OLKOWICZ³

¹The Łukasiewicz Research Network – Institute for Engineering of Polymer Materials and Dyes (Sieć Badawcza Łukasiewicz – Instytut Inżynierii Materiałów Polimerowych i Barwników)

²The Łukasiewicz Research Network – Institute of Precision Mechanics (Sieć Badawcza Łukasiewicz – Instytut Mechaniki Precyzyjnej)

³Air Force Institute of Technology (Instytut Techniczny Wojsk Lotniczych)

Zn-Cr ALLOY COATINGS: ELECTRODEPOSITION AND PROPERTIES

Powłoki stopowe Zn-Cr: elektroosadzanie i właściwości

Abstract: The electrodeposition process of Zn-Cr alloy coatings under the conditions of direct and pulsed current is discussed. The Cr content in the obtained alloy coatings, the current efficiency of the process, surface morphology, structure and wettability as a function of deposition parameters, such as current density, were determined. The Zn-Cr alloy coatings of good quality contained up to 20 wt.% Cr (for direct current) and up to 9 wt.% Cr (for pulse current). All the obtained coatings had a structure typical of zinc coatings (h.c.p.) and had a hydrophobic character. The morphology of the coatings changed significantly under the influence of changes in deposition conditions.

Keywords: electrodeposition, Zn-Cr alloy coatings, hydrophobic

Streszczenie: W niniejszej pracy omówiono proces elektroosadzania powłok stopowych Zn-Cr w warunkach prądu stałego i pulsacyjnego. Określono zawartość Cr w otrzymanych powłokach stopowych, wydajność prądową procesu, morfologię powierzchni, strukturę i zwilżalność w funkcji parametrów osadzania, takich jak gęstość prądu. Powłoki stopowe Zn-Cr o dobrej jakości zawierały do 20% wag. Cr (dla prądu stałego) i do 9% wag. Cr (dla prądu pulsacyjnego), Wszystkie otrzymane powłoki miały strukturę typową dla powłok cynkowych (h.c.p.) oraz wykazywały charakter hydrofobowy. Morfologia tych powłok ulegała istotnej zmianie pod wpływem zmian warunków osadzania.

Słowa kluczowe: elektroosadzanie, powłoki stopowe Zn-Cr, hydrofobowość

1. Introduction

Electrodeposition processes of metals and alloys are the basis of numerous technologies of new materials, which are difficult to obtain on the basis of metallurgical methods. An example of such materials are zinc alloy coatings, especially with iron group metals. They play an important role in many branches of industry, such as the automotive, military and the electrotechnical equipment industry. The electrodeposition method allows not only for depositing zinc alloys with iron group metals of any composition, but also for shaping the structure of deposited coatings and precisely determining their thickness. This is very important due to the increasing use of these alloys for corrosion protection.

Economic reasons and growing public awareness about the harmfulness of the chromating process due to the presence of highly toxic and carcinogenic chromium (VI) caused attempts to find non-toxic alternatives to this process. One such alternative is Zn-Cr alloy coatings prepared from chromium (III) salt solutions. Interest in these alloys is due to the fact that the conventional conversion coating contains mainly chromium (III) oxides with varying degrees of hydration. Therefore, it can be assumed that the oxidation product of chromium alloys may be passive films also containing chromium (III), so the zinc-chrome alloy should have better corrosion resistance.

Publications on researches on this subject are limited, fragmentary and incoherent, although literature references to the use of chromium-containing zinc alloys in industry can be found [1, 2, 4–18, 20–22].

Literature review and the investigations carried out so far justify the need for further detailed research on the electrodeposition process of zinc-chromium alloy coatings. The purpose of the present work was to determine the possibility of depositing zinc-chromium alloy coatings from acidic solutions, the current efficiency of the deposition process and analysis of composition, thickness distribution, morphology, structure and additionally wettability of the obtained coatings.

2. Experimental methods

The process of coating deposition was carried out under direct and pulse current conditions. The cathode was made of DC04 steel plates with an area of 0.18 dm². Zinc anode were used.

The cleaning of steel electrodes was carried out by electrolytic degreasing and etching in 1 : 1 hydrochloric acid, and occasionally by abrading the surface with abrasive material.

For the studies, a chloride bath with the following composition was used:

- zinc chloride - 68-75 g/dm³
- chromium(III) chloride – 67 g/dm³
- boric acid - 28-32 g/dm³
- potassium chloride - 180-190 g/dm³
- additive „R” produced by GALW-IMP company - 30 ml/dm³

The coatings were deposited from a bath with a pH of 2-2.5 at room temperature, under direct current (DC) conditions at different current densities $j = 1-2-2,5-3-4-5-6$ A/dm² (fig. 1a) and under rectangular pulse current conditions (AC) at different average current densities j_{avg} with its density in peak j_{peak} and time of pulse t_{on} (tab. 1; fig. 1b).

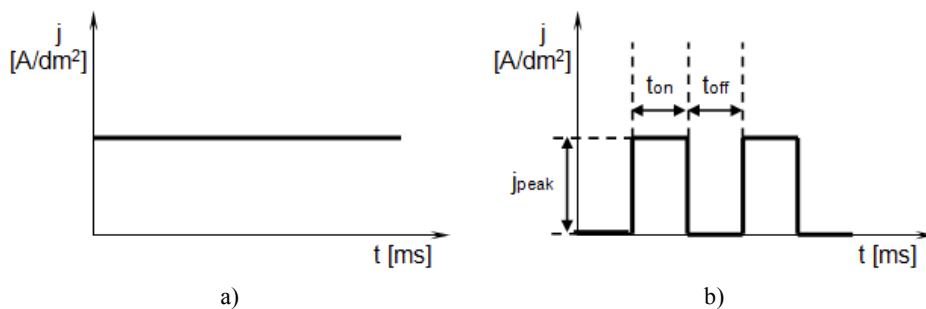


Fig. 1. Typical direct current waveform (a); typical rectangular pulse-current waveform (b)

Table 1

Rectangular pulse conditions of electrodeposition

j_{avg} [A/dm ²]	j_{peak} [A/dm ²]	t_{on} [ms]
2	20	2
3	30	2
4	40	2
5	50	2

After deposition, the Zn-Cr alloy coatings were characterized for its surface topography and chemical composition using scanning electron microscopy (HITACHI) and XRF spectrometer (Fischerscope X-RAY XDV-SDD), respectively. In addition, the X-ray diffractometer was employed to characterize the crystalline structure of the Zn-Cr alloy coatings (Cu-K α radiation, $\lambda = 1,541837$ Å).

The surface hydrophobicity features were identified by measurements of contact angle on the dedicated laboratory rig. The test stand was composed of electronic microscope camera with resolution 10 million pixels, X-Y-Z table, Minilab 201 syringe dispenser and 12 V illuminating lamp. For measurements, the droplet of 5 μ l volume was deposited with dispenser onto sample surface from the height of 5 mm. Contact angle was computed with dedicated image analysis software.

3. Results and discussion

In order to increase the chromium content in the deposited coatings, it was decided to investigate the co-deposition process of zinc and chrome using a rectangular pulse current. It is one of the solutions of difficult alloy deposition, in the case when chemical and electrochemical parameters of the components differ significantly [13, 14, 18]. Influence of current conditions on chromium content in Zn-Cr alloys was investigated:

- cathodic current density (under conditions of direct current);
- average density current and the peak current density (under conditions of pulse current).

3.1. Electrodeposition process of Zn-Cr alloy coatings

The introduction of chromium (III) ions into zinc solutions significantly influences the process of electrodeposition of zinc. Strong inhibition of metallic zinc release in favor of gaseous hydrogen evolution is observed. Hydrogen separation, on the other hand, favors the alkalization of the cathodic space, which results in faster hydrolysis of chromium (III) ions and adsorption of chromium (III) hydroxide on the cathode. These products can inhibit the discharge of zinc (II) ions and, consequently, decrease the current efficiency of the process by up to approx. 50% compared to the process of deposition of zinc from an acidic solution. The current efficiency of the Zn-Cr coating process was 30-66% under direct current conditions (compared to 88-92% for zinc coating process under similar conditions) and 18-86% under pulse current conditions (for the zinc coating process in similar conditions 86-90%). The results are presented in the following fig. 2.

The obtained coatings, depending on the deposition conditions (cathodic current density) and the chromium content in the coating, changed their appearance from light gray, through gray to black. The black color had coatings with the highest chromium content.

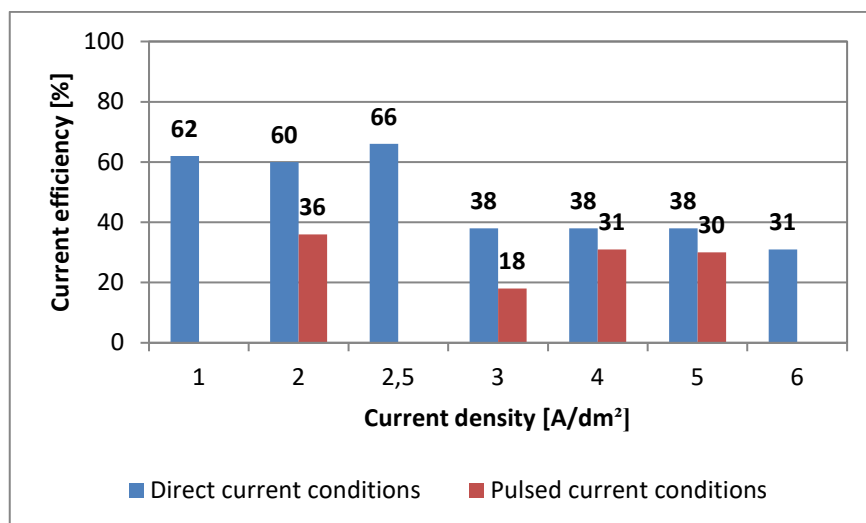


Fig. 2. Current efficiency of electrodeposition process Zn-Cr coatings under direct current and pulsed current conditions

3.2. Composition of Zn-Cr alloy coatings

Zn-Cr coatings are difficult to obtain by electrochemical method, although the standard electrode potentials of both metals are very similar. In this case, the speed of co-deposition of zinc and chromium in Zn-Cr coatings is limited mainly by kinetic constraints, that is the low overpotential of zinc deposition (for Zn 10^{-2} V) and high for chromium deposition (for Cr 10^{-1} V, resulting from the high electrode inertia of the chromium (III) complexes in the solution), and significantly different exchange current (for Zn 10^{-4} – 10^{-5} A/cm², for Cr 10^{-8} – 10^{-9} A/cm²) [3]. The obtained coatings contain significantly lower contents of the second component (chromium) despite the fact that it is a more noble metal than zinc. The share of chromium from approx. 0.01 wt.% to approx. 19 wt.% in the obtained Zn-Cr alloy coatings (fig. 3). Additionally the difficulties of chromium deposition from the chromium (III) salt solution are caused by the inert nature of the vast majority of chromium (III) complex ions. This causes that the state of balance between the formed complexes and their components is very slow.

The interesting result was the obtaining of Zn-Cr alloy coatings with high and even the highest chromium content under direct current conditions, which until now were considered difficult or even unattainable. For current densities of 3 A/dm² and 4 A/dm², coatings with the highest chromium content of approx. 15-19 wt.% were obtained. These result needs further investigations and explanation,

Up to now, higher chromium content has been achieved using electrolysis with pulse current, because it allows for a significant increase of the electrode polarization, which increases the speed of the partial process of electrodeposition of chromium. The interruption

of the cathode polarization during the break after the current pulse additionally causes that the electrode layer is enriched with labile complexes of chromium, the pH of the electrode layer is reduced, and the zinc can be additionally subjected to secondary, chemically selective digestion. The performed tests confirmed the possibility of increasing the chromium content in the Zn-Cr coatings obtained by applying pulse current in the deposition process. However, for the used solution this effect was visible only in a certain area of research. In the pulse conditions coatings with a chromium content of approx. 4.5 wt.% to approx. 8.5 wt.% were obtained (fig. 3).

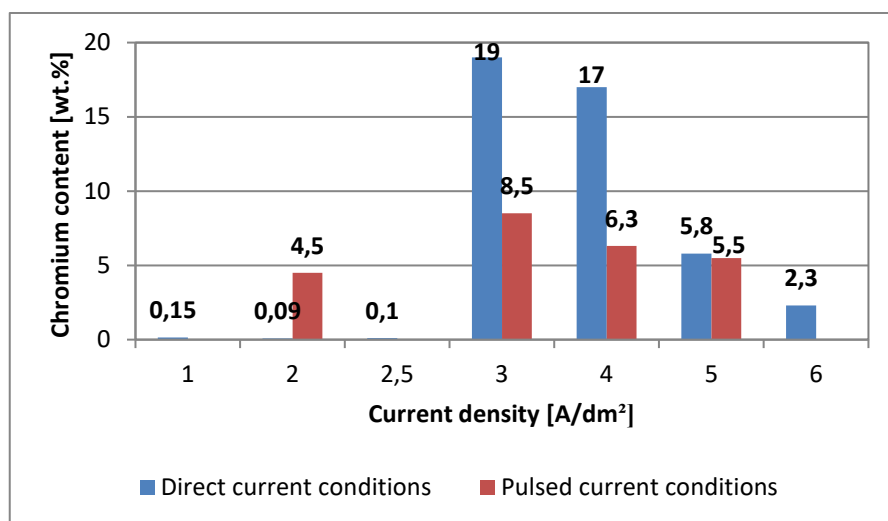


Fig. 3. Chromium content in Zn-Cr coatings obtained under direct current and pulsed current conditions

3.3. Structure of Zn-Cr alloy coatings

The properties of the coatings are determined not only by the composition. Thus, the surface morphology and structure of Zn-Cr coatings were investigated, and the examples of results are presented in figs. 4-5 and in tab. 2.

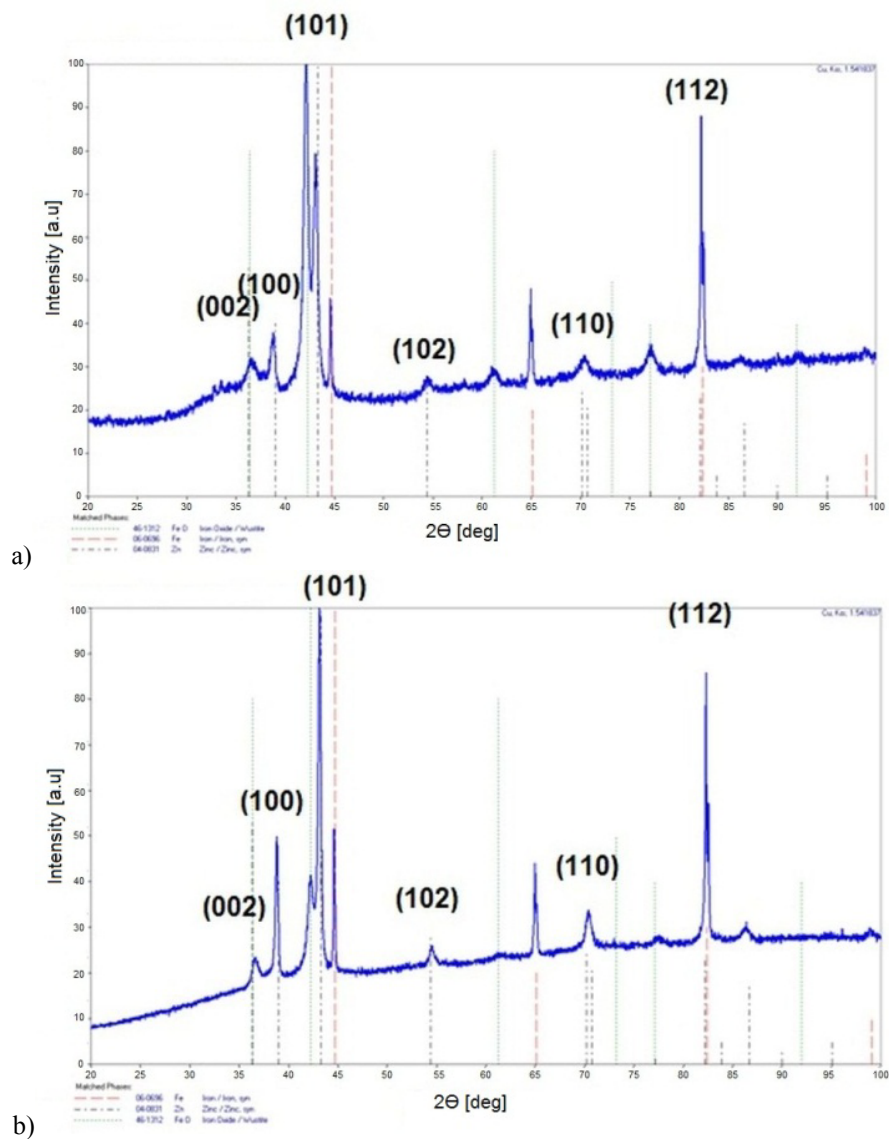


Fig. 4. XRD spectrum of a Zn-Cr coatings obtained under direct current conditions (a) $j=3\text{A/dm}^2$ and under pulse current conditions (b) $j_{\text{avg}}=3\text{ A/dm}^2$, $j_{\text{peak}}=30\text{ A/dm}^2$

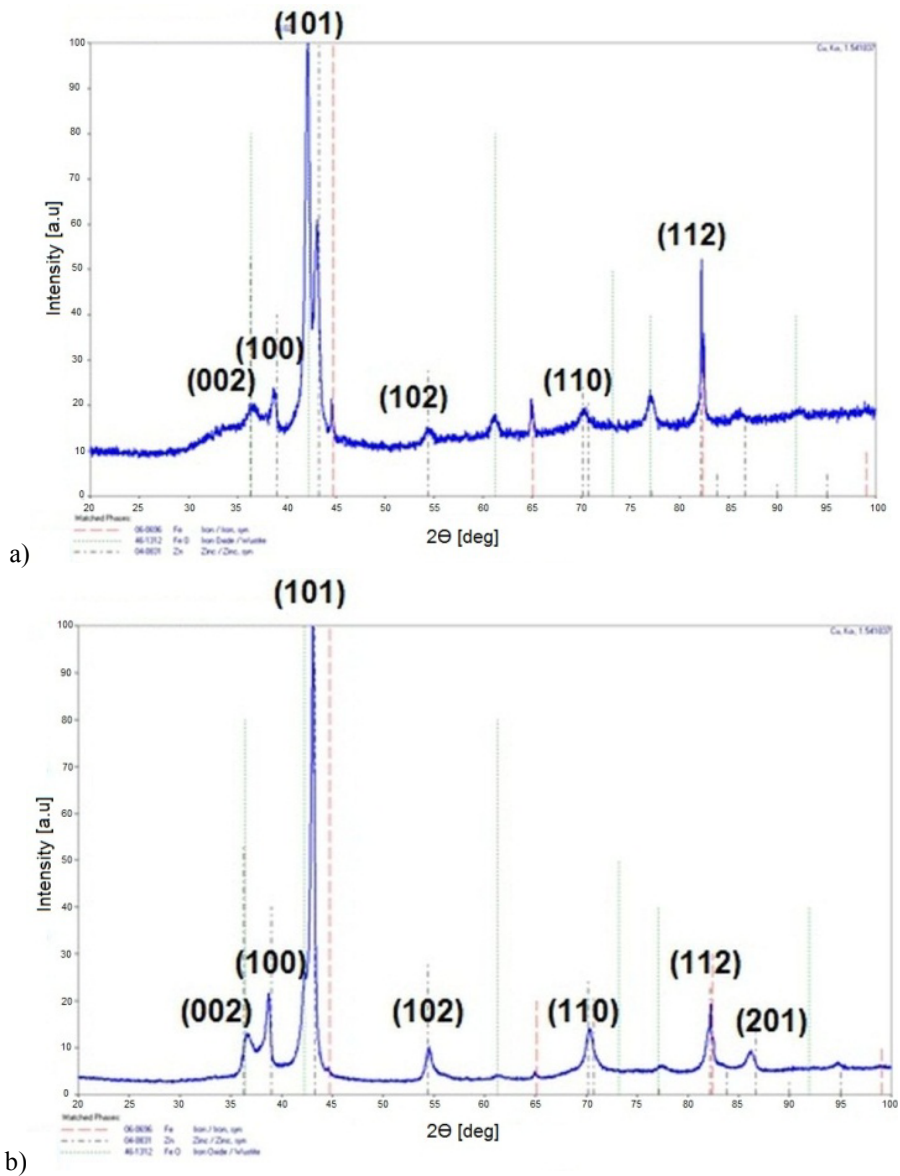


Fig. 5. XRD spectrum of a Zn-Cr coatings obtained under direct current conditions (a) $j = 4 \text{ A/dm}^2$ and under pulse current conditions (b) $j_{\text{avg}} = 4 \text{ A/dm}^2$, $j_{\text{peak}} = 40 \text{ A/dm}^2$

Table 2

Lattice parameters of Zn and Zn-Cr coatings

	Zn	Zn-Cr-DC j=2 A/dm ²	Zn-Cr-DC j=3 A/dm ²	Zn-Cr-AC j _{avg} =3 A/dm ²	Zn-Cr-DC j=4 A/dm ²	Zn-Cr-AC j _{avg} =4 A/dm ²
a [Å]	2.662	2.665	2.680	2.675	2.683	2.681
c [Å]	2.662	2.665	2.680	2.675	2.683	2.681
c [Å]	4.933	4.945	4.882	4.895	4.874	4.870
V [Å ³]	30.28	30.42	30.36	30.33	30.39	30.31

The presence of chromium in the Zn-Cr coatings in the obtained range did not have a significant influence on their structure. All obtained coatings had the typical h.c.p. structure of zinc. There were no reflections from the pure chromium and zinc-chromium intermetallic compounds as well as chromium oxides. Unfortunately, we obtained not enough chromium in the Zn-Cr coating to get peaks that can be identified as Zn-Cr, because as is known from the literature data the structure of Zn-Cr coatings is gradually changed from the h.c.p. structure to the b.c.c. structure only with the corresponding increase in chromium [2, 5, 16, 20]. Zn-Cr coatings with a chromium content below 20 wt.% have the h.c.p. structure, and above 35 wt.% of chromium (such a high chromium content has been achieved so far only in special, isolated cases) the b.c.c. structure that all of the Zn stays in solid solution in the chromium lattice. However, coatings with a chromium content of approx. 20 wt.% to approx. 35 wt.% have a complex phase composition, both the h.c.p. structure and a b.c.c. structure.

Surface morphology of Zn-Cr alloy coatings undergoes significant changes under the influence of changes in deposition conditions (figs. 6-7) and has a significant impact on their wettability, which in turn may affect its corrosion properties. All obtained Zn-Cr alloy coatings have a hydrophobic character with a different contact angle from 115° to 150° (fig. 8). Surface irregularities in the form of properly formed cause hydrophobic or hydrophilic effects, and in the case of the creation of the surface with nanostructure may give the effect of superhydrophobicity, the extensive discussion of which is in the work [19, 23]. The obtained results indicate the possibility of further research towards the production of self-cleaning surfaces and moisture resistant, which can significantly increase their anti-corrosion properties.

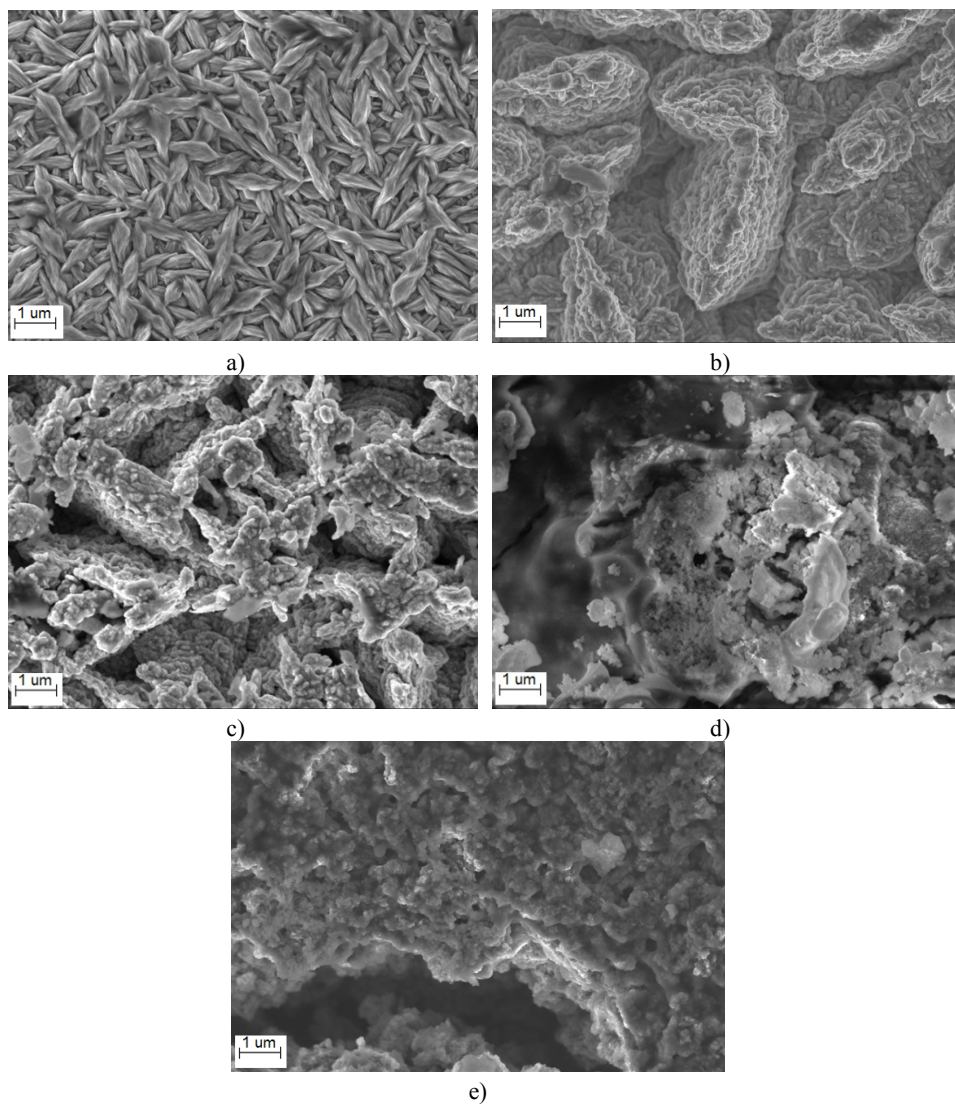


Fig. 6. SEM image of the surface of Zn-Cr coatings obtained under direct current conditions: a) $j = 1 \text{ A/dm}^2$, b) $j = 2 \text{ A/dm}^2$, c) $j = 2.5 \text{ A/dm}^2$, d) $j = 3 \text{ A/dm}^2$, e) $j = 4 \text{ A/dm}^2$

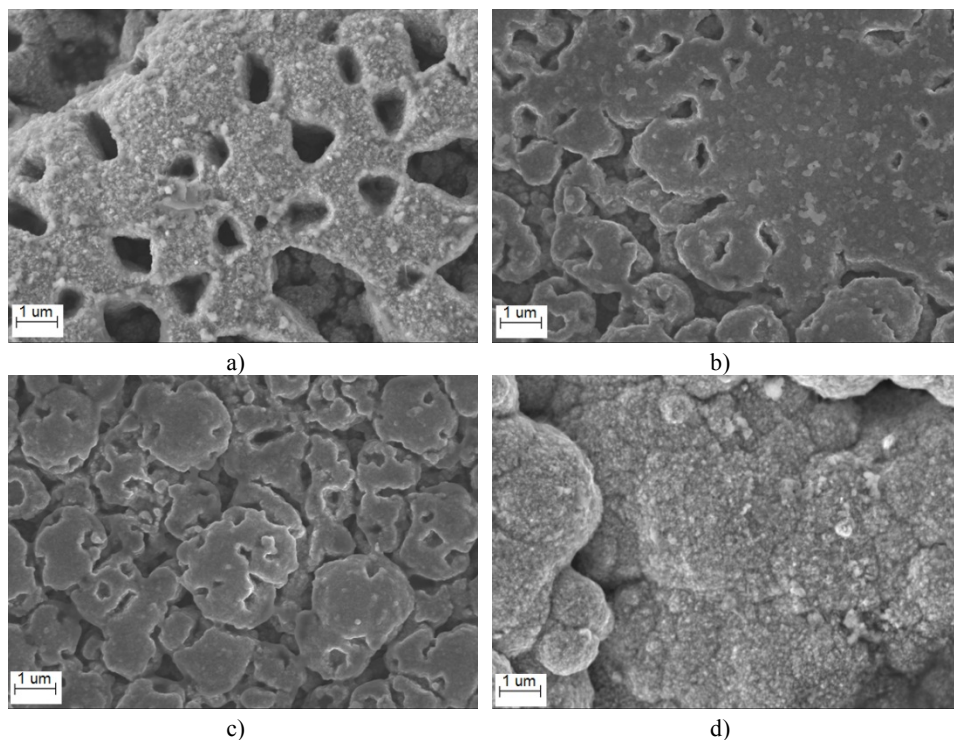


Fig. 7. SEM image of the surface of Zn-Cr coatings obtained under pulse current conditions: a) $j_{avg} = 2 \text{ A/dm}^2$, b) $j_{avg} = 3 \text{ A/dm}^2$, c) $j_{avg} = 4 \text{ A/dm}^2$, d) $j_{avg} = 5 \text{ A/dm}^2$

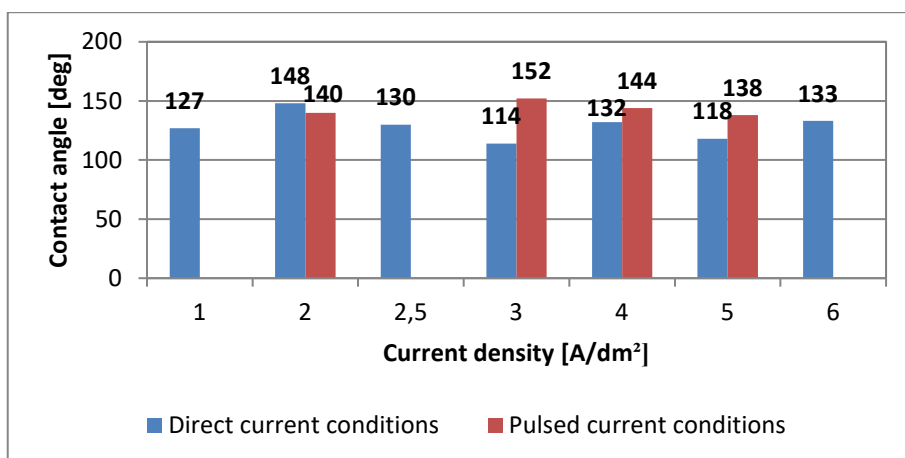


Fig. 8. Value of the contact angle for Zn-Cr coatings obtained under direct current and pulsed current conditions

4. Conclusion

The results of the preliminary studies carried out for the Zn-Cr alloy coatings obtained from the acid bath showed, above all, that coatings of different composition can be obtained. This is the most important and at the same time the most difficult element in the production of these coatings. Depending on the choice of the current characteristic, the chromium content in the coating can be significantly influenced (coatings with a chromium content of up to approx. 20%) and, consequently, their properties such as surface morphology, structure and wettability. XRD measurements did not show a change in the structure of deposited Zn-Cr alloy coatings. All obtained Zn-Cr alloy coatings have the h.c.p. structure of Zn. The promising results obtained - regarding the possibility of obtaining a different composition of Zn-Cr alloy coatings - make it possible to look more and more positively on their use in electroplating in the future. In addition, they are considered as coatings that can undergo an autopassivation process, because the introduction of a passivation promoter such as chromium into the zinc coating can lead to the formation of an oxide protective film. So they could inhibit the dissolution of the sacrificial Zn coatings. Therefore, may be these coatings could completely eliminate the use of conversion coatings on zinc coatings, for example due to possible better anticorrosion properties.

5. References

1. Akiyama T., Kobayashi S., Ki J., Oghai T., Fukushima H.: Role of polyethylene glycol in electrodeposition of zinc-chromium alloys. *Journal of Applied Electrochemistry*. Vol. 30, No. 7, 2000.
2. Alonso F., Madina V., Viviente J.L., Mursell T., Onate J.I.: Zn-Cr alloy coatings produced by ion beam assisted deposition. *Surface and Coatings Technology*. No. 103-104, 1998.
3. Antropov L.I.: *Theoretical Electrochemistry*, Mir Publishers, Moscow, 1977.
4. Berezin N.B., Gudín N.N., Čevela V.V., Filippova A.G.: Effect of complexation on electroplating of zinc-chromium alloys from acidic glycine baths *Zastita Metallov*. Vol. 28, No. 6, 1992.
5. Berezin N.B., Gudín N.N., Filippova A.G., Matulenis E.A., Borisov Ju.V.: Electroosazhadenie splawa cink-chrom impulsnym tokom. *Zastita Metallov*. Vol. 29, No. 1, 99-10, 1993.
6. Boiadjieva Tz., Kovacheva D., Lyutov L., Monev M.: Deposition of Zn-Cr alloy coatings from sulfate electrolyte: effect of polypropylene glycol 620 and glycine and combinations thereof. *Journal of Applied electrochemistry*. Vol. 38, No. 10, 2008.

7. Boiadjieva Tz., Kovacheva D., Petrov K., Hardcastle S., Monev M.: Effect of anodic treatment on the composition and structure of electrodeposited Zn-Cr alloy coatings. *Corrosion Science*. Vol. 46, No. 3, 2004.
8. Boiadjieva Tz., Kovacheva D., Petrov K., Hardcastle S., Sklyarov A., Monev M.: Electrodeposition, composition and structure of Zn-Cr alloys. *Journal of Applied electrochemistry*. Vol. 34, No. 3, 2004.
9. Boiadjieva Tz., Monev M., Kronberger H., Tomandl A., Petrov K., Angerer P.: Effect of PEG 400 on Zn-Cr alloy electrodeposition. *Journal of the Electrochemical Society*. Vol 157, No. 3, 2010.
10. Boiadjieva Tz., Petrov K., Kronberger H., Tomandl A., Avdeev G., Artner W., Lavric T., Monev M.: Composition of electrodeposited Zn-Cr alloy coatings and phase transformations induced by thermal treatment. *Journal of Alloys and Compound*. Vol. 480, No. 2, 2009.
11. Boiadjieva-Scherzer Tz.: Effect of PPG-PEG-PPG Co-Polymer on Zn-Cr Alloy Electrodeposition. *Journal of Materials Science and Engineering A*. Vol. 6, No. 5-6, 2016.
12. Boiadjieva-Scherzer Tz., Kronberger H., Fafilek G., Monev M.: Hydrogen evolution reaction on electrodeposited Zn-Cr alloy coatings. *Journal of Electroanalytical Chemistry*. Vol. 783, 2016.
13. Bradley P.B., Landolt D.: A surface coverage model for pulse-plating of binary alloys exhibiting a displacement reaction. Vol. 42, No. 6, 1997.
14. Bradley P.B., Landolt D.: Pulse-plating of copper-cobalt alloys. *Electrochimica Acta*. Vol. 45, No. 7, 1999.
15. el-Sharif M.R., Su Y.J., Chisholm C.U., Watson A.: Corrosion of electrodeposited zinc-chromium alloy coatings. *Corrosion Science*. Vol. 35, No. 5-8, 1993.
16. Guzman L., Adami M., Gissle W., Klose S., De Rossi S.: Vapour deposited Zn-cr alloy coatings for enhanced manufacturing and corrosion resistance of steel sheets. *Surface and Coating Technology*. Vol 125, No. 1-3, 2000.
17. Itani H., Duchoslav J., Arndt M., Steck T., Gerdenitsch J., Faderl J., Preis K., Winkler W., Stifter D.: X-ray photoelectron and scanning Auger electron spectroscopy study of electrodeposited ZnCr coatings on steel. *Analytical and Bioanalytical Chemistry*. Vol 403, No. 1, 2012.
18. Kostin N.A., Kublanovskij V.S.: *Impulsnij elektroliz splavov*, Naukova Dumka, Kiev, 1996.
19. Osuchowska E., Buczko Z., Olkowicz K.: Wpływ ukształtowania powierzchni na zwilżalność powłok Zn-Cr. *Przemysł Chemiczny* Vol 98, No. 4, 2019.
20. Scott C., Olier C., Lamandé A., Choquet P., Chaleix D.: Structural evolution of co-deposited Zn-Cr coating produced by vacuum evaporation. *Thin Solid Films* Vol. 436, No. 2, 2003.
21. Steck T., Gerdenitsch J., Tomandl A., Achleitner W., Faderl J., Lavric T., Boiadjieva-Scherzer Tz., Kronberger H.: Zinc-chromium coated steel sheet:

- properties and production. GALVATECH 8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet, IAM 1133, 2011.
22. Watson A., Su Y.J., el-Sharif M.R, Chisholm C.U.: The electrodeposition of zinc chromium alloys and formation of conversion coatings without use of chromate solutions. Transaction of The Institute of metal Finishing. Vol. 71, No. 1, 15-2, 1993.
 23. Yan Y.Y., Gao N., Barthlott W.: Mimicking natural superhydrophobic surfaces and grasping the wetting process: A review on recent progress in preparing superhydrophobic surfaces. Advances in Colloid and Interface Science. Vol 169, No. 2, 2011.