

# Functional Surfaces Modified with Gelatin and TiO<sub>2</sub> Nanoparticles

CRISTIAN MUNTENIT<sup>1</sup>, ADRIAN CIRCIUMARU<sup>1,2\*</sup>, VASILE BRI<sup>1</sup>, CEZAR IONUT BICHESCU<sup>1</sup>, IULIA GRAUR<sup>1,2</sup>

<sup>1</sup>Dunarea de Jos University of Galati, Research and Development Centre for Thermoset Matrix Composites, 47 Domneasca Str., 800008, Galati, Romania

<sup>2</sup>Diagnose and Measurement Group, 41 Rosiori, 800055, Galati, Romania

*The paper presents the obtaining of zinc and zinc composite coatings using electrochemical TiO<sub>2</sub> nanoparticles as well as the determination of the influence of gelatin used as an additive on electrically co-deposited layers. The obtained coatings were studied at the electronic scanning microscope (SEM) for microstructure observation. A distinction was made between the pure zinc electro-deposited layer and the influence of nano-TiO<sub>2</sub> on the morphology of zinc nanocomposite layers Zn/nano-TiO<sub>2</sub>, as well as the determination of the degree of inclusion of nano particles of TiO<sub>2</sub> into the zinc matrix. It was confirmed that with the introduction of nano-TiO<sub>2</sub>, both the roughness of the electro-deposited layer and the micro hardness of the electro-deposited layer significantly increased compared to the micro hardness of the pure zinc electro-deposited layers confirming the existence and beneficial effects of nano-TiO<sub>2</sub> in electro-co-deposited nanocomposite layers.*

**Keywords:** electrodeposition, zinc composite layers, titanium dioxide, gelatin

Zinc coatings and composite coatings have been used and are widely used since ancient times as the most advantageous methods of corrosion protection for ferrous and non-ferrous materials. Especially electrodeposition is one of the most conventional methods in the industry as electrochemical coating method [1-5]. This method presents some advantages: requires simple appliances, does not require expensive reagents, and it presents great efficiency in the sense that it can produce generous quantity, excellent quality and with a large variety of applicability of the resulting products [6, 7]. One of the studied additives and, the most commonly used in the electrodeposition process is gelatin [8-10]. It reduces the adsorption of hydrogen ions used as an additive along with the basic chloride and, of course, increases efficiency [11-14]. A significant current and future interest is that of using the electrodeposition process in order to obtain composite materials and ceramic materials embedded in a metal matrix. These types of ceramic particles can be: Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, all of them having a better corrosion resistance than zinc [15-17]. In this case, when the electrolyte solution contains particles that are in suspension, it is highly probable a process of these particles agglomeration due to their positive electric charge [18-22]. This problem of particle agglomeration and sedimentation having effects on deposited layer structure can be solved by introducing gelatin into the electrolyte solution [23-25]. The purpose of the research was to improve the quality of the deposited layer aiming to decrease the roughness of the co-deposited layer and to increase the mechanical properties, especially the hardness [26-30].

## Experimental part

Experiments to obtain pure zinc coatings were performed at room temperature. The composites required an elevated temperature of about 50°C, precisely to dissolve the gelatin used as additive. The test specimens were made of carbon steel, 30mmx50mmx0.5mm, used as cathode, and the anode consisted of 99.95% zinc pieces with dimensions 30mmx50mmx5mm. Before being subject to the electrodeposition process, the specimens

were prepared by a special program starting with removal of oxides by means of polishing with abrasive paper, continuing with chemical attack with HCl for 2 min at room temperature, rinsing with distilled water and drying in a hot air stream. The electrodeposition conditions were as follows: electrodeposition time of 10 min; the stirring rate at which the magnetic stirrer was moving in the solution agitation direction: 100 rpm to ensure a uniform dispersion of the dispersed phases into the electrolyte; a current density of 33.3 mA/cm<sup>2</sup> (denoted as 1, to facilitate the following information), 66.6 mA/cm<sup>2</sup> (denoted as 2), 100 mA/cm<sup>2</sup> (denoted as 3) and 120 mA/cm<sup>2</sup> (denoted as 4). Four types of layers were deposited, each using the same basic electrolyte, but with some modifications: Zn deposited layer - I; Zn deposited layer but with gelatin into the basic electrolyte - II; Zn/TiO<sub>2</sub> co-deposited layer with TiO<sub>2</sub> into the basic electrolyte - III; Zn/TiO<sub>2</sub> co-deposited layer with TiO<sub>2</sub> and gelatin into the basic electrolyte - IV.

All the depositions were performed in an electrochemical cell which was placed on a magnetic stirrer with heating, inside of which was inserted a magnet in order to keep the TiO<sub>2</sub> powder suspended, to ensure the gelatin uniform distribution and to maintain the concentration of the initial solution throughout the electro-deposition. Zinc matrix composites are typically obtained from sulfate solutions, but sometimes alkaline electrolytes with cyanide and non-cyanide alkaline electrolytes can be used. Particles that can be co-deposited in the zinc matrix are: silicon carbide, silicon oxide, aluminum oxide, titanium dioxide, cerium oxide, vanadium oxide, graphite. The dispersed particles are introduced into the electrolyte solution at a concentration of 10-200g/L. The particles are kept in suspension by mechanical, chemical or ultrasonic stirring. The particle size introduced into the electrolyte solution varies between 0.01-100µm. By introducing the different particles into the electrolyte, together with the deposition of the zinc some of these particles will be also deposited, they will be inserted into the Zn matrix (leading to a composite) and there will appear some modifications regarding the structure of deposited layers with consequences regarding their mechanical and physical properties. Co-deposition of the dispersed phase cannot

\* email: adrian.circiumaru@ugal.ro

be treated as a phenomenon separate from the electrodeposition process of the parent metal, which constitutes the metal matrix. In practice, solutions containing 150-300g/L  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , about 1-2 gram-equivalents, are usually used. High zinc sulfate solutions at medium current density give macro-crystalline deposits. Other salts, as an addition to the zinc sulfate electrolyte, usually sulfates, alkali metal chlorides, alkaline earth metals or soluble salts are used. For example:  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Al}_2\text{SO}_4$ . Sulfates and alkali metal chlorides are introduced into the electrolyte in particular to increase electrical conductivity, since solutions of zinc sulfate and sulfates of bivalent metals (cadmium, nickel, copper, etc.) do not have good electrical conductivity. Addition of sodium sulfate between 10g/L and 100g/L in  $\text{ZnSO}_4$  solution has almost no influence on cathodic polarization; alternatively, the electrical conductivity of the solution considerably increases, which affects favorably the dispersion capacity of the electrolyte. In the electrolysis of acid-zinc solutions, the value of anodic and cathodic polarization also depends on the nature of the anion to which the zinc or other cations introduced into the solution. The electrolyte composition used to obtain pure zinc and composite coatings is shown in table 1.

**Table 1.**  
ELECTROLYTE COMPOSITION IN THE ELECTRODEPOSITION PROCESS

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	200 g/l
$\text{Na}_2\text{SO}_4$	15 g/l
$\text{ZnCl}_2$	35 g/l
Gelatin	5 g/l
Particles	10 g/l
pH	4.85
Temperature	20-50°C
Current density	33.3 – 120 $\text{mA}/\text{cm}^2$
Deposition time	10 min
Stirring rate	100 rpm

## Results and discussions

After the electro-(co)-deposition of Zn and composite layers the samples were analyzed to determine the layers thickness considering that the entire deposited mass of substance is uniform distributed on the surface and that the deposited material density is the same. The last assumption is not correct and the results were far from the ones determined by direct measurement. For a more significant determination of the layer thickness, the samples were subjected to a metallographic microscope (Reichert-Jung MeF3) investigation. The texture determination of the surface was possible with the microtopograph (STIL Micromesure station). For characterization of pure zinc deposits and zinc composites, structural and morphological characterization, but also to note the degree of inclusion of  $\text{TiO}_2$  particles, in the case of composite coatings, the specimens were analyzed using the SEM scanning microscope (SEM) the JEOL JSM-T220A Scanning Microscope, both on the surface and transversally

to determine the inclusion degree of the particles in the layer. Depending on the results obtained, comparisons had been made between the morphology of the pure zinc surfaces and the morphology of composite layers obtained at the same electrolysis parameters (time, current density, stirring rate, etc.). The Vickers microsurface tests of pure zinc and zinc composite deposits were possible using a LECA M-400-H1 hardness microtest tester with a 10KgF load, a pyramidal diamond indenter, with a square base line, the top having an angle of  $136^\circ$ .

## Layer thickness

With the increase in the current density, the ion migration rate also increases, resulting in the formation of fine-grained coatings. This explains why an increase in the current density determine an increase on growth rate of the previously formed crystals until the cathode reaches a value at which new crystals begin to appear. This density cannot be increased indefinitely because it favors the formation of a compact loose layer on the surface of the cathode and the appearance of dendrites on the edges where the current density is always higher compared to the rest of the surface. If the current density is very high, there appears the risk of hydrogen releasing, which causes a noticeable reduction in the current efficiency. The thickness of the coated layers was determined by cross-section, the introduction of the samples into epoxy resin, to the MECAPRESS C hot pressing machine and transversal observation of the layer using optical microscopy figure 1 and figure 2.

The graph in figure 1 shows that the deposited or co-deposited layer thickness depends on current density and on the composition of the electrolyte. For lower current density the thinnest layers are the ones deposited in gelatin presence while at higher current density the thinnest layers are the ones deposited with basic electrolyte. An explanation could reside in the fact that raising the current density there appears an increase on charge carriers mobility and, as consequence, the increase of the deposited amount of substance. The same graph shows that the highest thickness is reached for co-deposited Zn with the electrolyte containing  $\text{TiO}_2$  and gelatin.

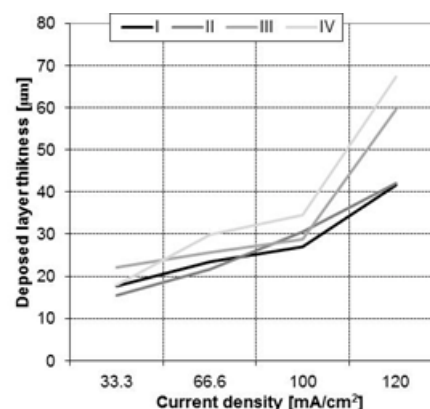


Fig. 1. Layer thickness of electro-deposited layers (analysis regarding the current density)

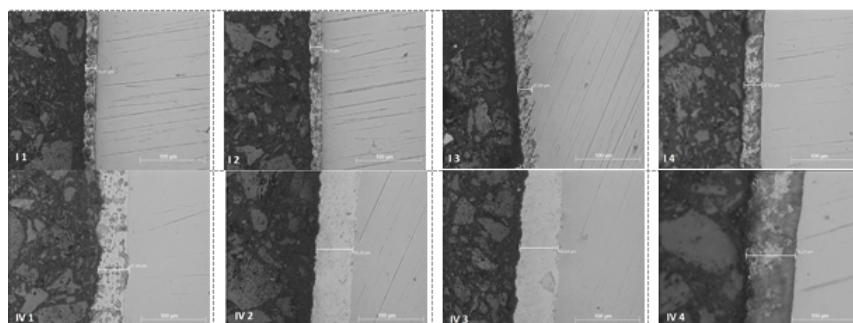


Fig. 2. Layer thickness of electro-deposited layers Zn deposited layers (up) and Zn/ $\text{TiO}_2$  co-deposited layers (down)

In figure 2 the images captured from microscope are presented. Because of the results already presented in figure 1 we choose to present only Zn deposited layer thickness at the four values of current density (the layer with the lowest values of thickness) and the Zn co-deposited layer with basic electrolyte containing  $\text{TiO}_2$  and gelatin (the layer with the higher values of thickness) and just to observe some differences between the aspect of material of type I (Zn deposited layer with basic electrolyte) and material of type IV ( $\text{Zn/TiO}_2$  co-deposited layer with  $\text{TiO}_2$  and gelatin electrolyte).

#### *The effect of electrolyte modification on electro-deposited layer roughness*

The roughness is a measure of surface texture of deposited zinc layers and for studied materials the experimental results are shown in figure 3 and figure 4. The higher the roughness, the more irregular the surface is, and the faster it gets wear. The ruggedness of the deposited layer varies with the current density leading to co-deposited layers with particular mechanical properties.

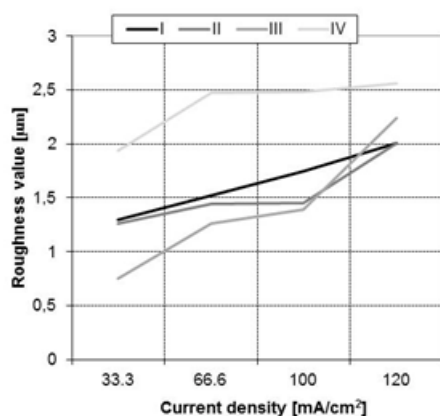


fig. 3. Roughness of deposited surfaces (analysis regarding current density)

The addition of gelatin to the electrolyte solution had no significant influence on the deposition of zinc (excepting the regime denoted as 2), but it formed a film over the deposited zinc clusters, which made the deposited layer uniform in the form of grains. Thus, the addition of gelatin to the electrolyte solution did not influence the thickness of the deposited layer, nor its roughness. Gelatin addition has led to significant changes in the mechanical properties of the deposit. Previous results showed that the use of gelatin in zinc coatings does not influence the mechanical properties of the deposited coating. Thus, the use of gelatin as an additive in obtaining the co-deposited composite layers might be neutral regarding the mechanical properties of co-deposited composite layers. Analysing figure 3 one may notice that the highest values of roughness are reached

for the IV denoted type of co-deposited layer meaning that both  $\text{TiO}_2$  and gelatin presence are determining a decrease of Zn deposited layer uniformity. The III type co-deposited layer, on another hand, shows the lowest values of roughness (except the highest value of current density) meaning that the  $\text{TiO}_2$  presence leads to a lower roughness.

#### *Morphology*

The surface characterization, as well as, the analysis of  $\text{TiO}_2$  dispersed phase, were possible by SEM (scanning electronic microscopy) and by EDAX (X-ray analysis) of the surface of deposited or co-deposited layers.

Figure 5 shows SEM images of randomly chosen areas of the analyzed surface and reveal different morphological aspects of surfaces especially in the case of the gelatin presence into the electrolyte that is leading to a granular aspect of surfaces. That could mean that using gelatin into the electrolyte some larger structures acting as charge carriers are formed contributing to  $\text{TiO}_2$  and Zn transport to cathode.

The  $\text{TiO}_2$  ceramic particles have been preferentially deposited placed together with the zinc deposits in layers with thickness greater than pure zinc or zinc deposited with gelatin into the electrolyte. Zinc grains grow, and when two grains of zinc are bonded they capture ceramic particles of  $\text{TiO}_2$ , and those that have not been included are pushed to the grain boundary, randomly distributed, as a result of zinc matrix formation. This phenomenon leads (as it was presented above) to better mechanical properties of co-deposited layers. Particle dispersion was possible with the addition of gelatin. This is used and further promoted as an additive in the electrodeposition of ceramic particles, in order to disperse them and keep them suspended in the electrolyte solution with magnetic stirrer.

It is easily to notice that gelatin presence into the electrolyte leads to a granular aspect of layers surfaces and these granules are growing together with the increase in current density. Also it might be noticed the fact that Zn/ $\text{TiO}_2$  co-deposition leads to morphological changes from randomly distributed symmetrical structures in the Zn deposition to acicular structures in the case of Zn/ $\text{TiO}_2$  co-deposition.

Regarding the atomic species distributions, zinc was investigated in the case of I-type and II-type materials (fig. 6) and Zn, Ti and O were studied for the other two materials - III and IV- (fig. 7). Regarding the Zn distribution it is noticeable that this seems to not be influenced (at the lowest value of current density) by the gelatin presence but, increasing the current density its contribution becomes significant (especially for the third value of the current density-the 3 regime). Anyway the gelatin presence does not influence on the distribution of Zn on the deposited layer

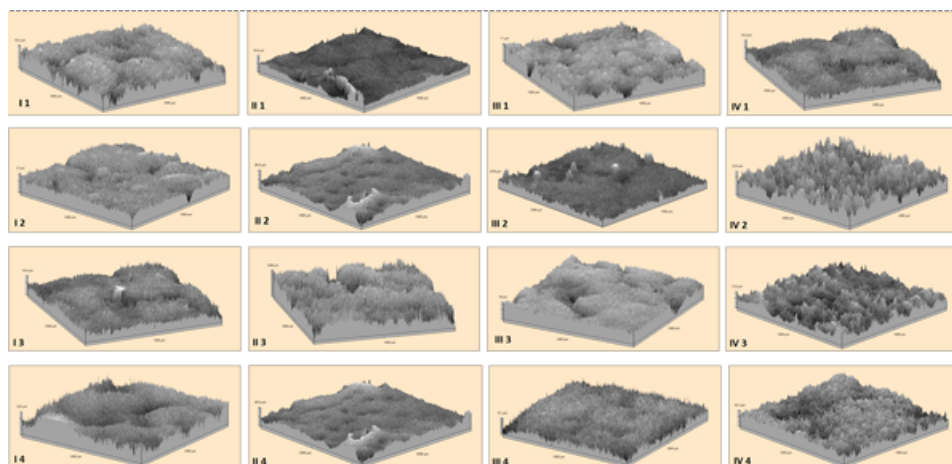


Fig. 4. Deposited and co-deposited layers surfaces analysis (roughness)



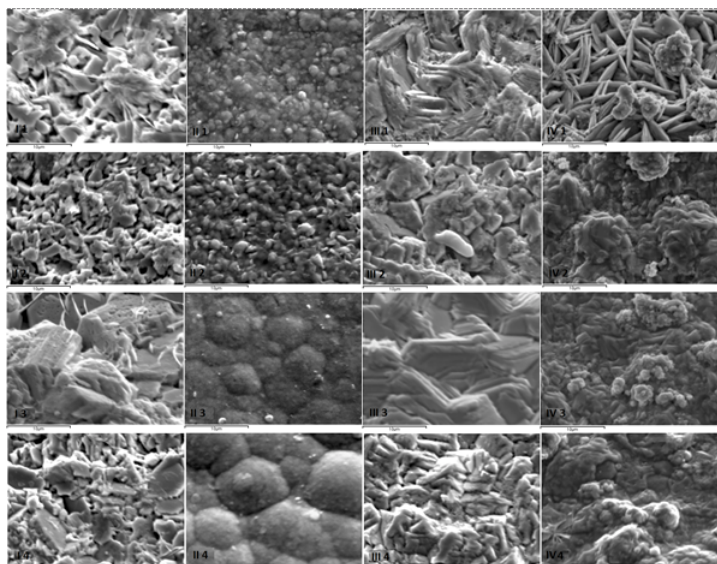


Fig. 5. Surface morphology by means of SEM

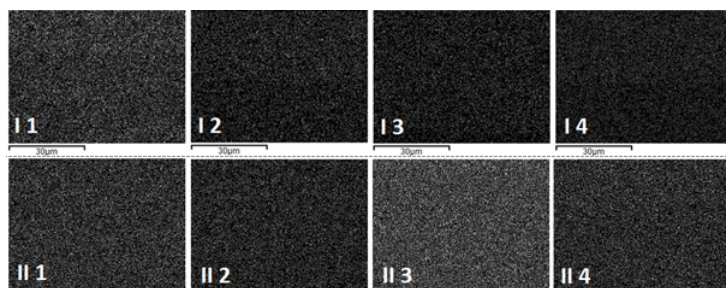


Fig. 6. Zn distribution by EDAX means

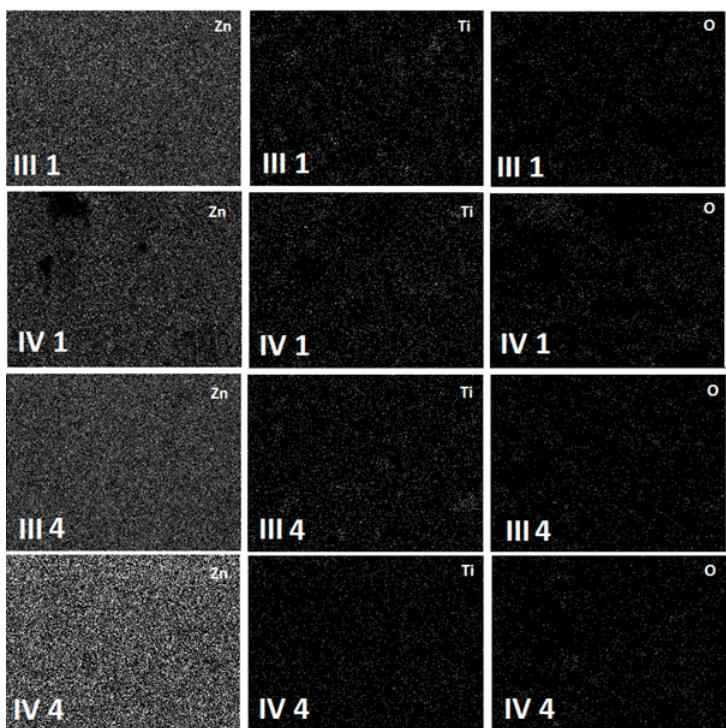


Fig. 7. Zn, Ti and O distributions on the electro-co-deposited layers by EDAX

(it is not noticeable the appearance of aggregates). From figure 7 it is observable the fact that the presence of both  $\text{TiO}_2$  and gelatin (at the highest current density value) leads to the best concentration and uniform distribution of Zn. The highest concentration of  $\text{TiO}_2$  is reached in the case of III-type material at the highest current density value meaning that the gelatin presence is blocking, in some way, the co-deposition of  $\text{TiO}_2$  together with the zinc.

#### Micro hardness

As stated, added gelatin has contributed to the improvement of mechanical properties, especially

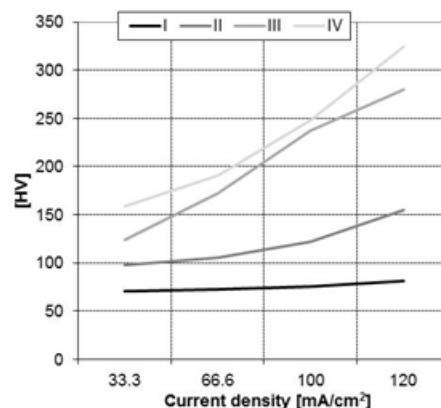


Fig. 8. Micro hardness

hardness. Micro hardness of the biphasic composite layer deposited improves with the introduction of  $\text{TiO}_2$  particles, as it may be noticed in fig. 8. In fact the micro-hardness of layers increases with the current density and by adding some components on the electrolyte. The presence of gelatin leads to a more compact layer of Zn while the micro-hardness of co-deposited layers is explainable by the presence of  $\text{TiO}_2$  particles into the composite layer.

#### Conclusions

The study aimed to obtain by electrochemical method coatings of composite materials with Zn matrix and  $\text{TiO}_2$

dispersed particles in order to obtain better coatings from mechanical point of view. To prove the assumption that the presence of  $\text{TiO}_2$  improves the mechanical properties some relevant parameters had been analyzed - layer thickness, roughness, micro-hardness and, also structural analysis had been developed.

The electrolysis regime used was the following: 33.3mA/cm<sup>2</sup>, 66.6mA/cm<sup>2</sup>, 100mA/cm<sup>2</sup>, 120mA/cm<sup>2</sup>, temperature: ~50°C for Zn / gelatin coatings and 20°C-25°C for the others, the agitation rate of the electrolyte 100rpm, concentration of  $\text{TiO}_2$  particles in solution of 10g/L and 5g/L, respectively, for gelatin.

The critical factors that influence the quality of composite coatings are: electrolyte composition, electrolysis conditions (current density, deposition time, temperature, agitation mode). Using (EDAX), we were capable to determine both the qualitative and quantitative presence of  $\text{TiO}_2$  and gelatin particles both on the surface and the obtained composite layer.

The presence of gelatin into the electrolyte leads to a manifest modification of morphology but is not affecting the Zn concentration and uniform distribution on the deposited layer. The presence of  $\text{TiO}_2$  particles into the co-deposited layer leads to an improvement of micro-hardness and favourize an increase on Zn concentration into the co-deposited layer at higher values of current density.

## References

1. MESSLER, R. W., J. Thermoplast. Compos, 27, nr. 1, 2004, p. 51.
2. MESSLER, R. W., Joining of Materials and Structures: From Pragmatic Process to Enabling Technology, 45, NR. 3, 2004, p. 661.
3. HULUBA, R., PIRVU, C., NICOLESCU, C., MARIN G., MINDROIU, M., Mat. Plast., **53**, no. 1, 2016, p. 130.
4. WANG, C. B., WANG, D. L., CHEN, W. X., WANG, Y. Y., Wear, 253, nr. 5-6, 2002, p. 563.
5. XINXIN, L., TAKAHITO, O., RONGMING, L., MASAYOSHI, E., Micro. Engn., 65, nr. 1-2, 2003, p. 1.
6. VACAREANU, L., GRIGORAS, M., Mat. Plast., **50**, no. 3, 2013, p. 153.
7. ZIMMERMAN, A.F., PALUMBO, G., AUST, K.T., ERB, U., Mater. Sci. Eng., 328, nr. 1-2, 2002, p.137.
8. RAPOPORT, L., LVOVSKY, M., LAPSKER, I., LESHCHINSKY, V., VOLOVIK, Y., FELDMAN, Y., MARGOLIN, A., ROSENSTVEIG, R., TENNE, R., Nano Lett., 1, nr. 3, 2001, p. 137.
9. TEODORESCU, M., SCHACHER, L., ADOLPHE, D., GRADINARU, I., ZETU, I., STRATULAT, S., Mat. Plast., **50**, no. 3, 2013, p. 225.
10. MUSIANI, M., Electrochim. Acta., 45, nr. 20, 2000, p. 3397.
11. PRAVEEN, B. M., VENKATESHA, V. T., Appl. Surf.Sci., 254, nr. 8, 2008, p. 2418.
12. PIRVU, C., MINDROIU, M., CRACIUNESCU, O., CONSTANTIN, D., Mat. Plast., **53**, no. 4, 2016, p.722.
13. PRAVEEN, B. M., VENKATESHA, V. T., ARTHOBA NAIKA, Y., PRASHANTHAB, K., Surf. Coat. Technol., 201, nr. 12, 2007, p. 5836.
14. EARAR, K., CERGHIZAN, D., SANDU, A.V., MATEI, M.N., LEATA, R., SANDU, I.G., BEJINARIU, C., COMAN, M., Mat. Plast., **52**, no. 4, 2015, p. 487.
15. JEGANNATHAN, S., SANKARA NARAYANAN, T. S. N., RAVICHANDRAN, K., RAJESWARI, S., Surf. Coat. Technol., 200, nr. 12-13, 2006, p. 4117.
16. MINDROIU, M., PIRVU, C., POPESCU, S., DEMETRESCU, I., Mat. Plast., **46**, no. 4, 2009, p. 324.
17. ASTHANA, R., KUMAR, A., DAHOTRE, N. B., Materials Processing and Manufacturing Science, **12**, nr. 3, 2006, p. 436.
18. POPESCU, A.M.J., CONSTANTIN, V., OLTEANU, M., DEMIDENKO, O., YANUSHKEVICH, K., Rev. Chim.(Bucharest), **62**, nr. 6, 2011, p.626.
19. YIFENG WANG, XUECHENG GUO, RUIHAO PAN, DIHAN, TAO CHEN, ZENGHUA GENG, YANFEI XIONG, YANJUN CHEN, Mater. Sci. and Eng., **53**, 2015, p. 223.
20. NABIL SOROUR, WEI ZHANG, EDWARD GHALI, GEORGE HOULACHI, Hydrometallurgy, 171, 2016, p. 321.
21. XULI XIA, IGOR ZHITOMIRSKY, JOSEPH R. McDERMID, Jmatprotec, **209**, 2009, p. 2633.
22. SEKAR, R., JAYAKRISHNAN, S., J. Appl. Electrochem., 36, 2006, p. 594.
23. YOUSSEF, K.M.S., KOCH, C.C., FEDKIW, J. Electrochem. Soc., 151, 2004, p. 104.
24. YIM, Y.B., HWANG, W.S., HWANG, J. Electrochem. Soc., 142, 1995, p. 2605.
25. LI, M.C., JIANG, L.L., ZHANG, W.Q., QIAN, Y.H., LUO, S.Z., SHEN, J.N., J. Solid State Electrochem, 11, 2007, p.550.
26. GUGLIELMI, N., J. Electrochem. Soc., 119, 1972, p.1010.
27. BIEST, O.V.D., VANDEPERRE, L.J., Rev. Mater. Sci., 29, 1999, p. 1143.
28. BAIK, D.S., FRAY, D.J., J. Appl. Electrochem., 31, 2001, p. 1142.
29. STAROSTA, R., ZIELINSKI, A., J. Mater. Process. Technol., 157, 2004, p.435.
30. YOUSSEF, K.M.S., KOCH, C.C., FEDKIW, P.S., J. Electrochem. Soc., 151, 2004b, p.105.

Manuscript received: 15.06.2018