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ELECTROCHEMICAL OBTAINING OF ALLOY COATINGS Zn-Fe-P FROM SULFATE ELECTROLYTES

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Abstract

The present work investigates the galvanostatic obtaining of alloy coatings Zn-Fe-P from sulfate electrolytes. Cyclic voltaamogramms show that the co-deposition of zinc with phosphorus is possible only in the presence of iron ions in the electrolytic bath. The including of P in the coating occurs at iron amounts higher than 9 wt% - higher iron concentration leads to higher phosphorus amounts. Fine crystal surface structure with spherical agglomerates characteristic for the amorphous layers is obtained even of 0,5 - 2 wt% phosphorus. Entirely amorphous and uniform coatings can be practically obtained only at very thin films. Potentiodynamic curves in 1N Na_2SO_4 show that Zn-Fe-P alloy containing up to 2 wt% P and 20 wt% Fe demonstrate better corrosion characteristics compared to Zn-Fe coatings.

Key words: *electrodeposition, Zn-Fe-P alloys, cyclic voltammetry*

1. INTRODUCTION

The interest for obtaining of galvanic alloys Zn-Fe-P has been increased in the last years. These coatings are promising materials in many areas aimed to protect different metallic constructions, industrial devices, cars etc from corrosion damages (Gu and Marder, 1991, Kawasaki Steel Corporation, 1985).

The alloys presented above characterize with excellent corrosion resistance and very good weldability as a result of their high hardness and melting point compared to the pure zinc (Kawasaki Steel Corporation, 1985, Mingyuan et all., 1991).

Zhang et all. have investigated the mutual behavior and influence of Fe and P in electrochemically obtained Zn-Fe-P alloys. The coating is deposited from a slightly acidic chloride electrolyte with different amounts of added H_3PO_3. It has been established that accordingly to the experimental conditions P and Fe contribute for their mutual reduction and their content in the coating changes simultaneously what is explained from the viewpoint of the quantum chemistry.

Ordine and co-authors have investigated the incorporation of P in the electrodeposited alloys Zn-Fe from sulfate electrolytes as well as their anticorrosion properties. Nevertheless, they do not report about the electrochemical conditions for obtaining of the alloys and about their chemical composition but restrict the investigations only with the deposition of crystalline and amorphous Zn-Fe-P coatings.

The obtaining of Zn-Fe-P alloys and studying of their corrosion resistance is object of some patents (Irie et all., 1987, Oshima et all., 1997). The electrolytes used are slightly acidic chloride or alkaline. Formation process of the layers is realized on iron plates at stream deposition and current density of 100 A/dm^2. The authors have established that even minimum amounts P (under 1%) in the alloys would be very effective to increase the corrosion characteristics and the adhesion of the coatings.

These patents also claimed that Zn-Fe-P coatings demonstrate better weldability and paintability as well as allow painting, application of conversion coatings and deposition of other galvanic layers compared to the Zn-Fe alloys.

The lower P content up to 1% in the deposited coating has favorable effect by changing the microstructure, decreasing the residual stresses (Bouanani et all., 1999) and ensuring better adhesion of the coating (Swathirajan and Mikhail, 1988).

Till now the literature date available concerning the deposition conditions, composition and structure of Zn-Fe-P alloys from sulfate electrolytes is rarely scarce and contradictory.

The aim of the present investigation is to study the possibility for electrochemical co-deposition of P in the Zn-Fe systems from sulfate electrolytes, determination of their chemical composition, structure and some of the corrosion characteristics.

2. EXPERIMENTAL

The compositions of the main electrolytes used in the present investigation are shown in Table 1.

Table 1. Composition of the electrolytes for alloy deposition:

Bath composition	I Zn(70)-Fe	II Zn(70)-Fe-P	III Zn(22)-Fe-P	IV Zn(22)-Fe
$FeSO_4.7H_2O$, g/l	200	200	200	200
$ZnSO_4.7H_2O$, g/l	70	70	22	22
$Na_3C_6H_5O_7.5,5H_2O$, g/l	50	50	50	50
$NaH_2PO_2.H_2O$, g/l	-	13	13	-
H_3PO_2 (50 %), ml/l	-	26	26	-
Fe^{2+}/Zn^{2+}	2,6	2,6	8,4	8,4

The samples are galvanostatic deposited in thermostatically electrolytic cell with a volume of 400 ml, circulating of the electrolyte and at cathodic current densities D_k = 5 to 20 A/dm^2. Deposition time varies from 5 to 15 minutes; working temperature was 40 ºC, pH values of the solutions – from 1,5 to 3. Non-soluble Ti-Pt meshes were used as anodes. The alloy coatings were deposited onto copper substrates with dimensions 1x10x20 mm (working area of 4 cm^2). The electrolyte composition was analytically controlled by using chemical analysis of the Fe^{2+}-ions and zinc ions.

The chemical composition and the surface morphology of the samples are investigated by scanning electron microscope with EDS analysis, model JEOL JSM 6390.

Phase composition was determined with Philips PW 150 unit for X-ray diffraction analysis with $Cu_{K\alpha}$ radiation.

The influence of the different components of the electrolyte on the cathodic and anodic processes was investigated using cyclic potentiodynamic curves. The latter were realized using computerized Gamry Instruments system in wide potential area: -1,38 V up to +1,3 V with scan rate of 5 mV/s in three-electrode thermostatically isolated electrochemical cell with a volume of 150 ml. The working electrode was Pt plate with working area of 1 cm^2; reference electrode was saturated calomel electrode (SCE). Aiming the comparison of the curves obtained from different background electrolytes the missing substances were replaced with relevant amounts $MgSO_4$ while the ionic force must remain unaltered.

The calculation of the ionic force of the missing components ($FeSO_4.7H_2O$ and $ZnSO_4.7H_2O$) in the electrolyte is done by using the equation:

$$J = 1/2\sum m_i .z^2_i ; \qquad \text{where}$$

m_i – concentration of the ions of the type i;

z_i – their valence;

Corrosion studies were realized by using potentiodynamic polarization curves in a standard three-electrode cell at room temperature in a model medium of 1N Na_2SO_4 with pH ~ 6. The galvanostatic obtained alloy samples were firstly immersed in the electrolyte for 10 minutes aiming stabilizing the open-circuit potential. Thereafter the PD curves were carried out beginning from 100 mV in cathodic direction toward the corrosion potential. Scan rate was 1 mV/s.

3. RESULTS AND DISCUSSION

Figure 1 presents the CVA curves of pure zinc deposition (curve 1) and of zinc in the presence of citrate and phosphorus-containing additives at pH 3 (Electrolyte II, Table 1). In the absence of additives (curve 1) a limited current can be registered in the cathodic area between the potential values of about -1200 up to -1380 mV after the deposition zinc peak at -1140 mV. In the presence of sodium citrate and P-containing additives – sodium hypophosphate and hypophosphorus acid – the area of the limited current disappeared (curve 2). Most probably, this is a result of the influence of the additives on the hydrogen reaction what means they facilitate the hydrogen reduction without influence on the reaction $Zn^{2+} + 2e^- = Zn$. This follows from the overlapping of the anodic branches of CVA curves 1 and 2. Similar is also the influence of the additives at lower pH value - 2. It is important to note that the potentials of the anodic peaks do not shift what means that the co-deposition of Zn and P is less probable.

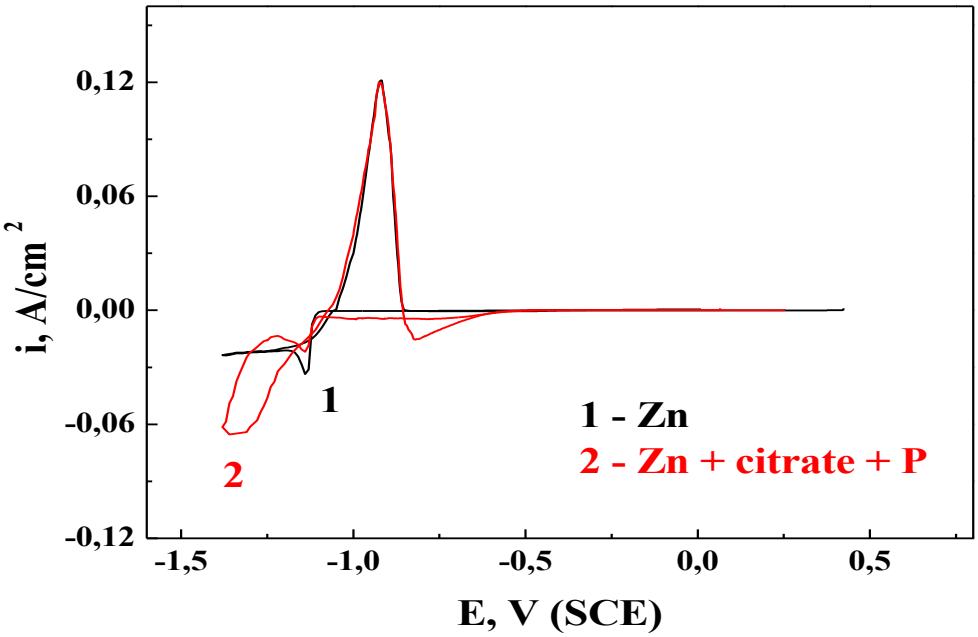


Fig 1. CVA curves obtained at pH 3 from:

1 – Electrolyte I without $FeSO_4.7H_2O$ and $Na_3C_6H_5O_7.2H_2O$;

2 – Electrolyte II without $FeSO_4.7H_2O$;

The CVA curves of the individual iron deposition from electrolytes containing citrate or citrate and hypophosphite ions at pH 2 (Fig. 2, curves 1 and 2) demonstrate that the P-containing additives depolarize the beginning of the cathodic reaction with about 400 mV. A shift of the maximum of curve 2 is registered in the anodic area with 280 mV in positive direction. Such strong displacement can follows only as a result of the incorporated P in the coating.

Similar shift of the anodic maxima is observed also at pH 3 although in lower degree. All these facts lead to the conclusion that the co-deposition of Fe and P at lower pH value is more facilitated i.e. the decrease in pH values leads to increase of the P content in the iron-based coatings.

Figure 3 represents the CVA curves obtained at pH 2 from Electrolytes II and III. The cathodic branches of Zn-Fe-P alloy curves are placed between the curves of the electrolyte containing only Zn and P and the electrolyte containing only Fe and P. This is indication for anomalous alloy deposition compared to the deposition of the pure metals i.e. the metal with more negative potential (zinc) will be predominantly deposited with depolarization in the alloy. Similar dependence is finding out by Brenner during deposition of Zn-Fe alloy. The adding of P-containing compounds does not change the anomalous character of the alloy deposition. The anodic peak of curve 2 received from electrolyte containing 70 g/l $ZnSO_4.7H_2O$ consists of two different overlapping peaks at potentials of - 640 mV and of about - 450 mV. They are shifted in negative direction compared to the peaks from curve 3 (- 410 mV and - 300 mV) obtained from the electrolyte with lower $ZnSO_4.7H_2O$ (Electrolyte III) content. This indicates that different alloys with various

chemical compositions can appear throughout the length of the curve. The peaks on curve 3 are displaced to these obtained from electrolyte containing only iron and phosphorus (-84 mV) – curve 4. Nevertheless, the data presented do not give the possibility to decide if the alloys obtained from Electrolyte III are more reach on Fe or P compared to these obtained from Electrolyte II. The results for the same electrolytes at pH 3 do not qualitative differ from these presented in Fig. 8 at pH 2.

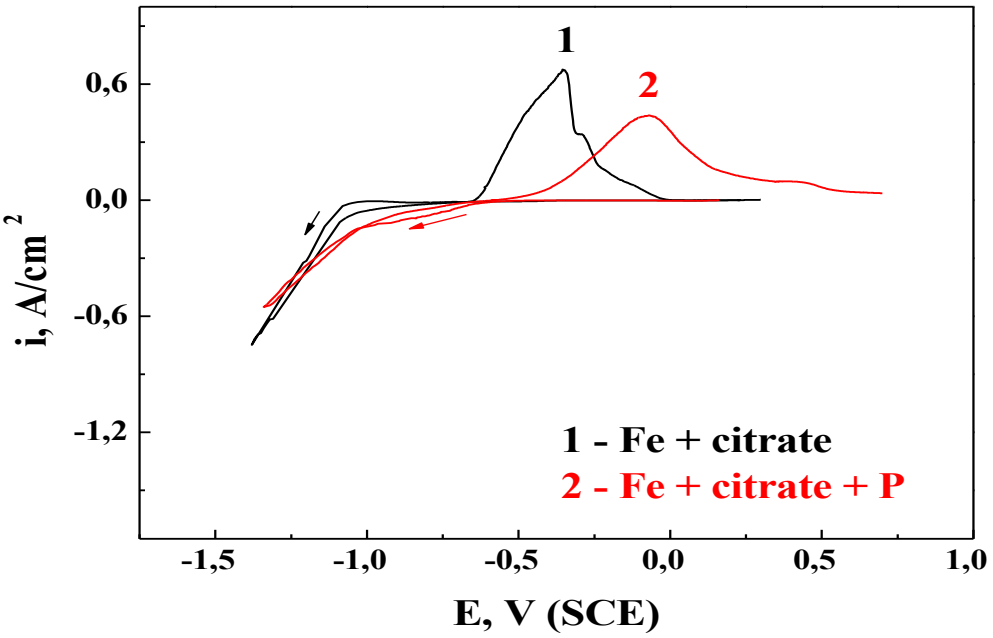


Fig. 2. CVA curves obtained from electrolytes at pH 2:

1 - electrolyte I without $ZnSO_4.7H_2O$;

2 – electrolyte II without $ZnSO_4.7H_2O$

Figure 4 compares the CVA curves from Electrolytes II and III (curves 1 and 3) with the curves obtained from Electrolytes I and IV without phosphorus (curve 2 and 4) at pH 3 and final potential value of -1200 mV. A special moment here is that the presented curves have been stopped and hold in the cathodic branches at potential value of -1200 mV. On the individual curves this potential corresponds to different current density values: curve 1 – hold 5 min at i – 15A/dm^2; curve 2 – hold 3 min at i – 5A/dm^2; curve 3 – hold 5 min at i ~ 9 A/dm^2; curve 4 – hold 3 min at i ~ 5 A/dm^2.

Contrary to curves 2 and 4 the anodic parts of curves 1 and 3 obtained from electrolytes containing hypophosphite ions demonstrate a step-wise delay of the dissolution (or a new peak) at potential area of about – 310 mV. This can be also a result from the higher iron content incorporated in the layers (as consequence of the higher current densities) and also of the included phosphorus in the alloys. One reason for this delay can be the different phase content of the coatings deposited from electrolytes in the presence of P-containing additives.

In order to precise the influence of the composition of the electrolytes and to investigate the possibility to incorporate P in the Zn-Fe alloy coatings additional coatings deposition at galvanostatic regime is performed.

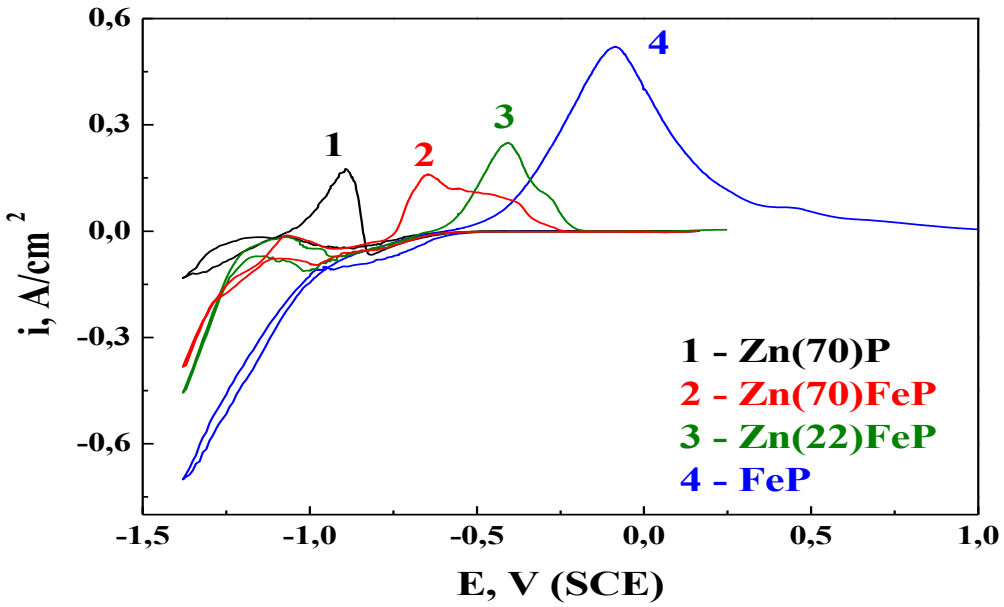


Fig. 3. CVA curves obtained from electrolytes as follows:

1 – Electrolyte II without $FeSO_4$.$7H_2O$ pH 2; 2 – Electrolyte II pH 2; 3 - Electrolyte III pH 2;

4 – Electrolyte II without $ZnSO_4$.$7H_2O$ pH 2

The Zn-Fe-P alloys deposited from Electrolyte II (Fig.5a) show the opposite tendency – at lower pH value the Fe percentage is higher achieving about 60% at pH 1,5. In these cases the amount of the incorporated P is very high (Fig.5b). Therefore, a definite interdependence exists between the iron and phosphorus in the alloy. Zhang et all., concluded and explained this fact from quantum-mechanical point of view.

It is known from the literature that in the case of alloy deposition of metals from the Fe group with phosphorus the quantity of the latter in the coatings increases at lower pH values (Armyanov et all., 1997). Similar dependence was registered by us when recording the CVA curves. This means that also during the electrodeposition of Zn-Fe-P at lower pH more P will be incorporated in the alloy what will determine higher Fe percentage.

From other side when the electrodeposition of the alloys is carried out from the Electrolyte III (Fig.5a,b) containing lower zinc sulfate amounts the increasing of Fe content in the alloy at pH 3 (at which value Fe is about 40% and P is not higher than 2%) can be expected. This indicates that the quantity of the incorporated P depend more on the pH value than on the composition of the electrolyte.

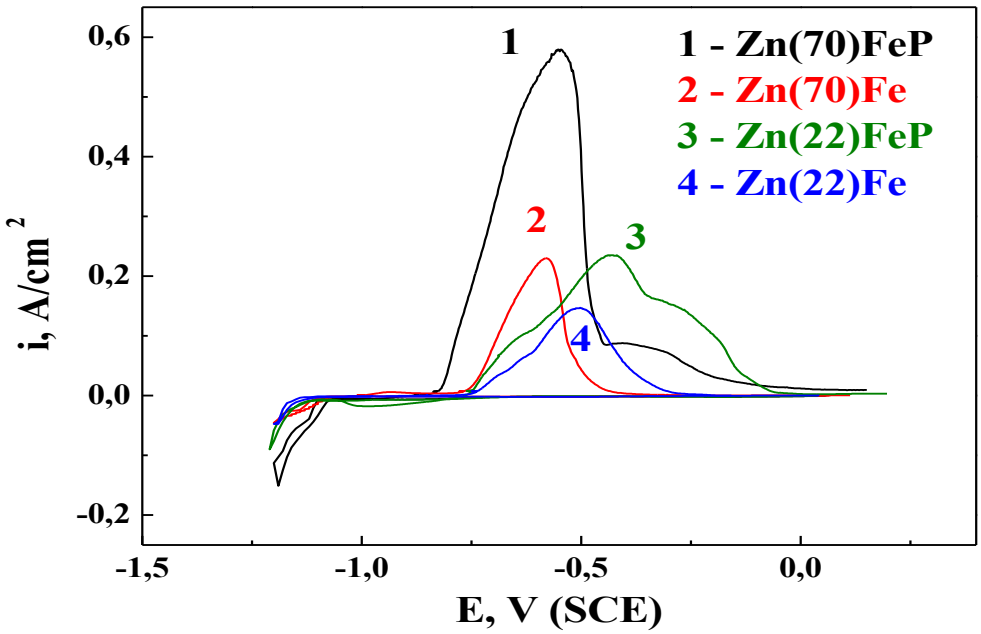


Fig. 4. CVA curves obtained from electrolytes as follows:

1 – Electrolyte II; 2 – Electrolyte I; 3 – Electrolyte III; 4 – Electrolyte IV

3.1. Influence of pH of the electrolyte on the chemical content of the obtained alloys

The samples obtained at equal current density – 10 A/dm^2 (Fig. 5a) – from Electrolyte I without hypophosphite ions demonstrate decreased Fe content in the alloy at low pH values.

Fig. 5 leads to the conclusion that both electrolytes containing phosphorus (II and III) at low pH values (1,5 up to 2) can provoke in some cases the obtaining of coatings with different P content at equal pH values. The probable reason for this phenomenon could be the simultaneous self-dissolution process of the coating - for example in the middle of the samples. The microprobe analysis in these areas shows that the zinc content there is very low while these of Fe and P - relative high. That is the reason to presume that a self-dissolution process for the zinc is realized at low pH values.

Outside the self-dissolution area that in the most cases is dark-colored the microprobe analysis shows completely different composition.

This phenomenon needs additional investigation.

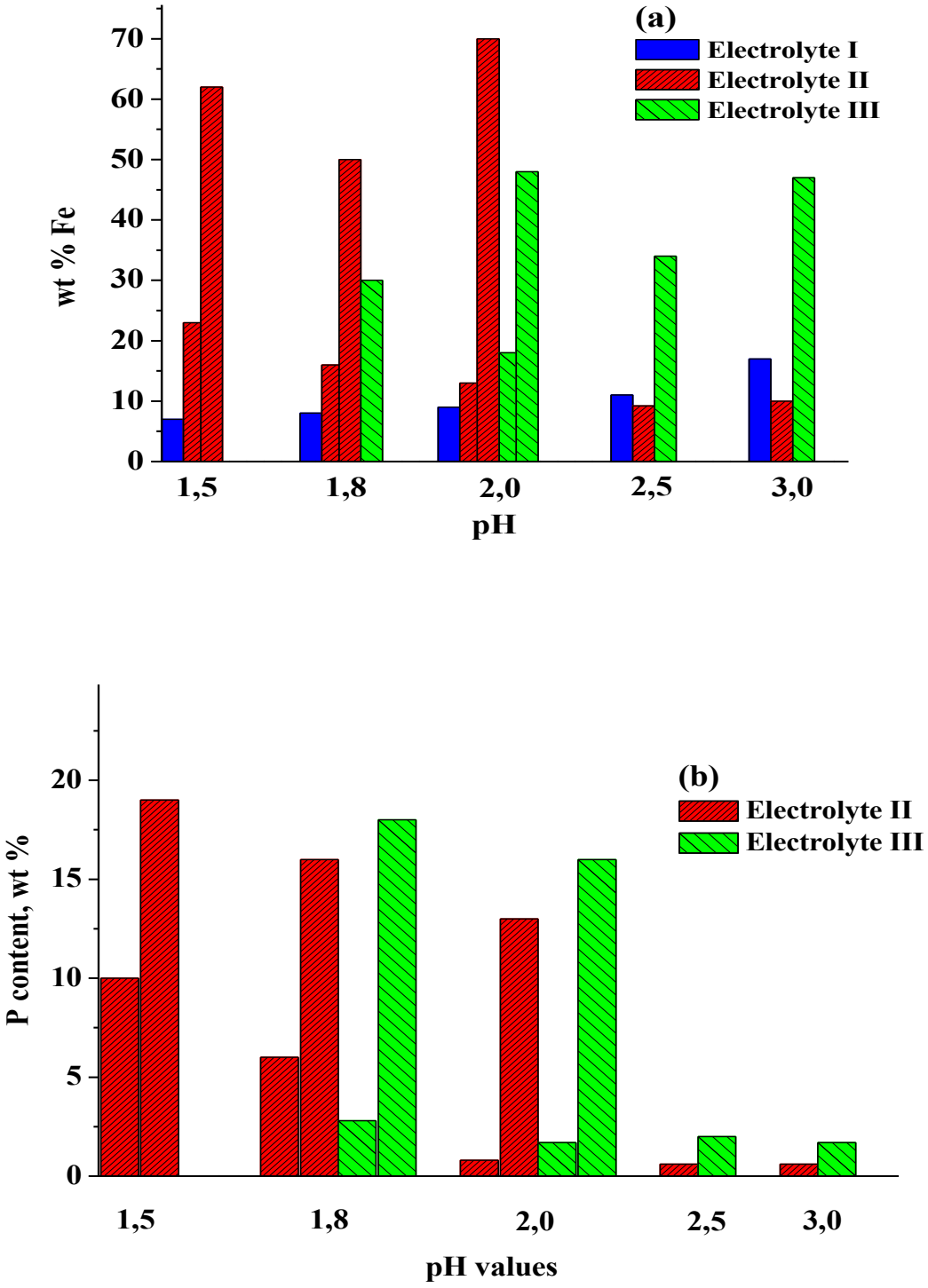


Fig. 5. Influence of the pH value of the electrolyte on the Fe- (a) and P (b)-content in Zn-Fe-P alloys obtained from Electrolytes I, II, III at current density $D_k = 10A/dm^2$

3.2. Influence of the cathodic current density D_k on the chemical composition of the alloys

The data presented in Fig. 6 show that the increase of the cathodic current density leads to higher Fe content in the alloy at pH 3. Simultaneously, small P amounts up to about 1% are also incorporated although at higher D_k values i.e. at higher Fe percentage in the coatings. Phosphorus does not present in the coatings at current densities lower than 10 A/dm^2 which corresponds to about 9 % Fe in the alloy.

At low pH values during the deposition the tendency for increasing the iron content in the alloy with increasing current density is retained.

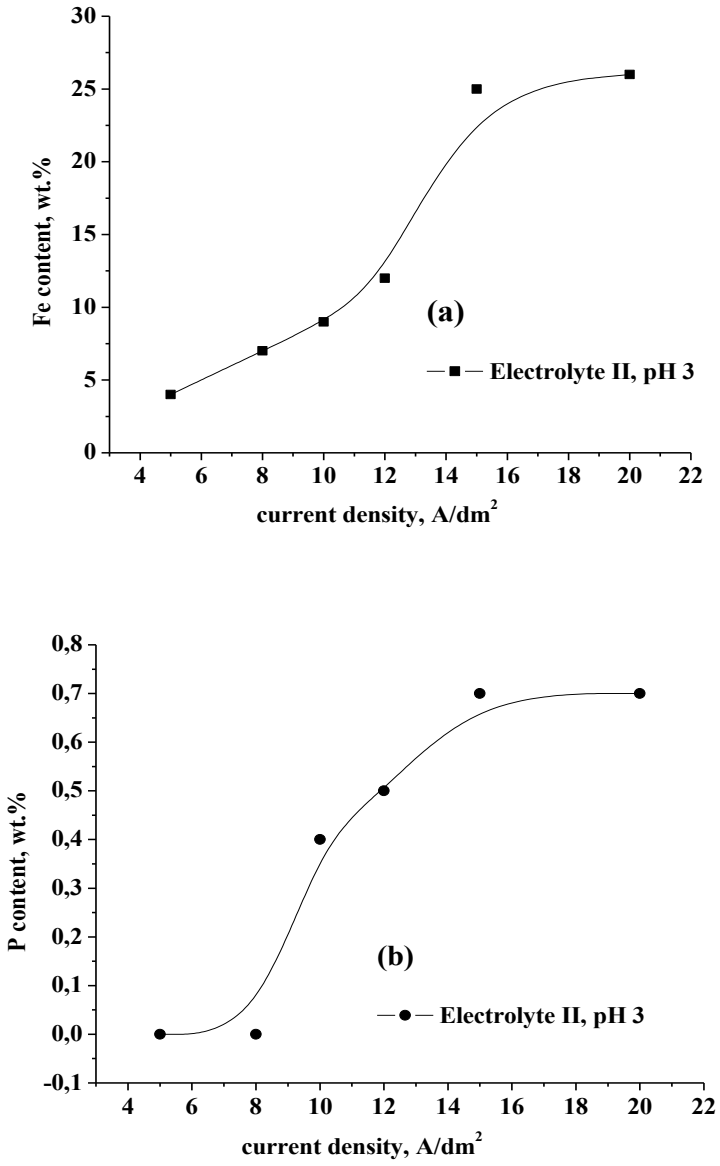


Fig. 6. Influence of the cathodic current density on the Fe (a) and P (b) content in the

Zn-Fe-P alloys during electrodeposition from Electrolyte II at pH 3

3.3. Phase composition and surface morphology of the alloy coatings

The alloy coatings Zn-Fe obtained from electrolyte without phosphorus demonstrate the simultaneously appearance of several different phases (Fig.7). For example, the intermetallic compounds $FeZn_{13}$, $FeZn_{11}$, Fe_3Zn_{10} as well as Zn are identified in the deposited layers using the data reported in (JCPDF-ICDD). They all have hexagonal close packed structure. Similar is the conclusion about the phase composition of the galvanic alloys Zn-Fe in (Panagopoulos et all., 2009). The type of the diffraction patterns shows that these coatings consist of large-scaled crystals. SEM images of the surface demonstrate large grains with well presented edges and walls – Fig.8 a, b). The layers deposited at lower pH values have fine grained structure.

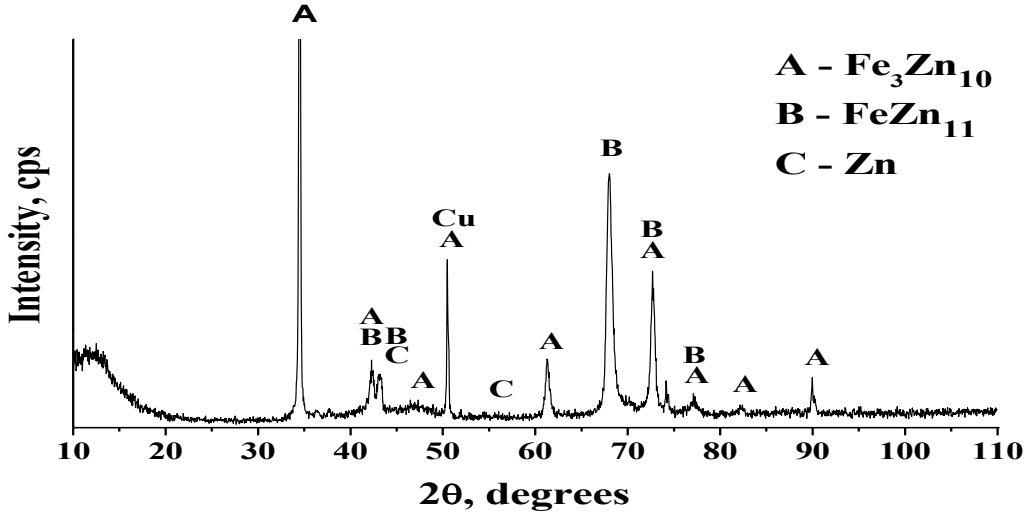
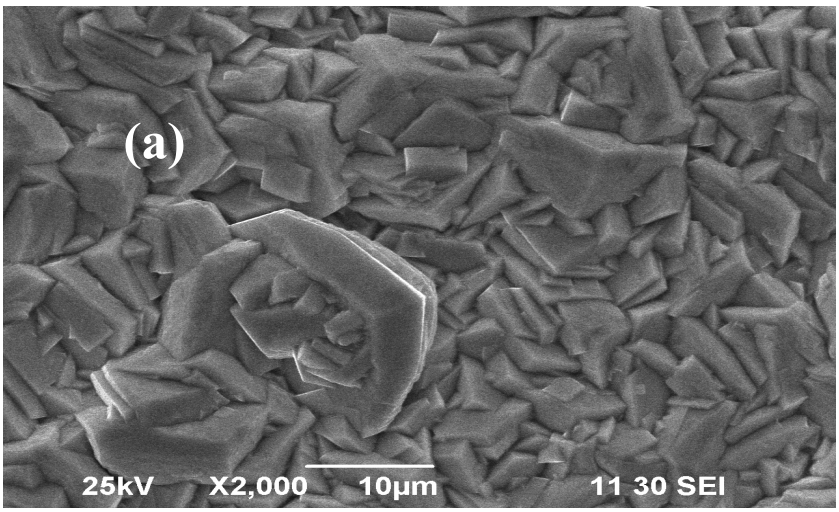


Fig. 7. XRD pattern of alloy with composition Zn 93% and Fe 7% obtained at pH 1,5 and D_k - 10 A/dm^2 from Electrolyte I



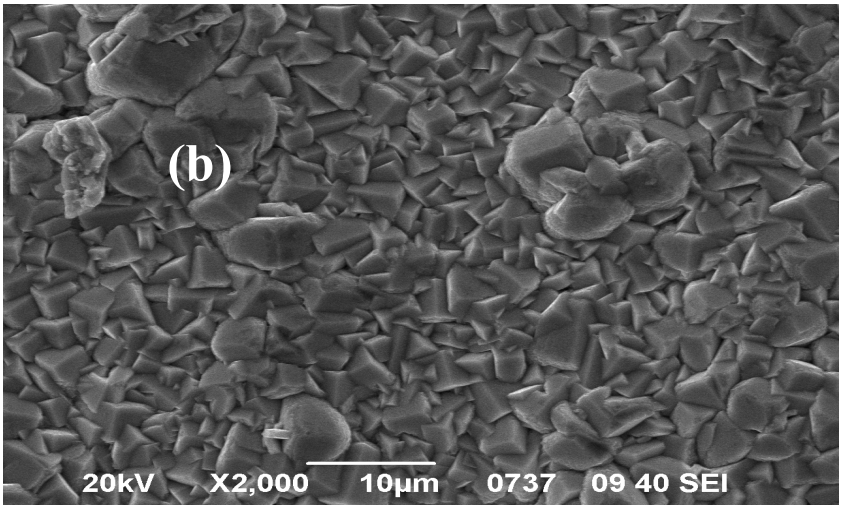


Fig. 8. SEM images of Zn-Fe coatings obtained from Electrolyte I: (a) – pH 3; (b) – pH 2

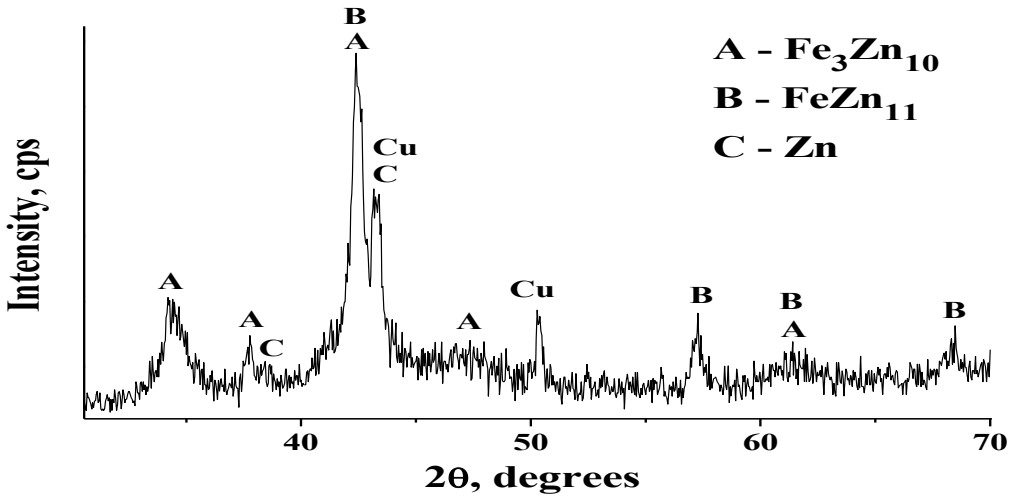


Fig. 9. XRD pattern of alloy with composition Zn 79%, Fe 19% and P 2% obtained at pH 2 and $D_к$ - 15A/dm^2 from Electrolyte II

The presence of P in the electrolyte and its incorporation in the coating in small amounts (0,5 - 2 wt.%) leads to obtaining of more fine crystal alloys (the diffraction lines are partially broaden - Fig. 9). The surface morphology seems to be more even and without well presented edges. Additionally, several spherical structures characteristic for the amorphous coatings also appear - Fig. 10 and 12.

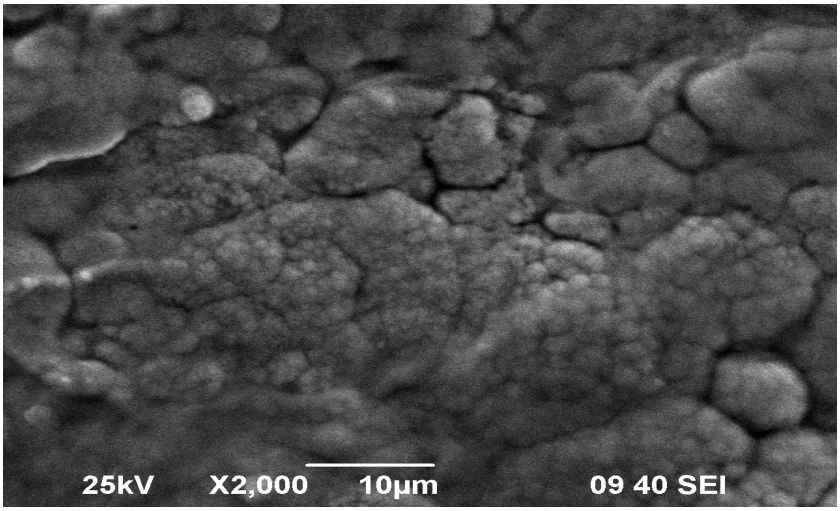


Fig. 10. SEM image of the surface of the coating from Fig. 9.

Substantial influence on the structure of the deposited Zn-Fe-P coatings has the iron content in them. As much higher it is so fine crystalline are the deposited layers. At Fe content of about 50 % and more the main registered phase is α–Fe (body centered cubic lattice) – probably solid solution of the zinc in iron with small amounts of some of the intermetallic compounds presented above (Fig.11).

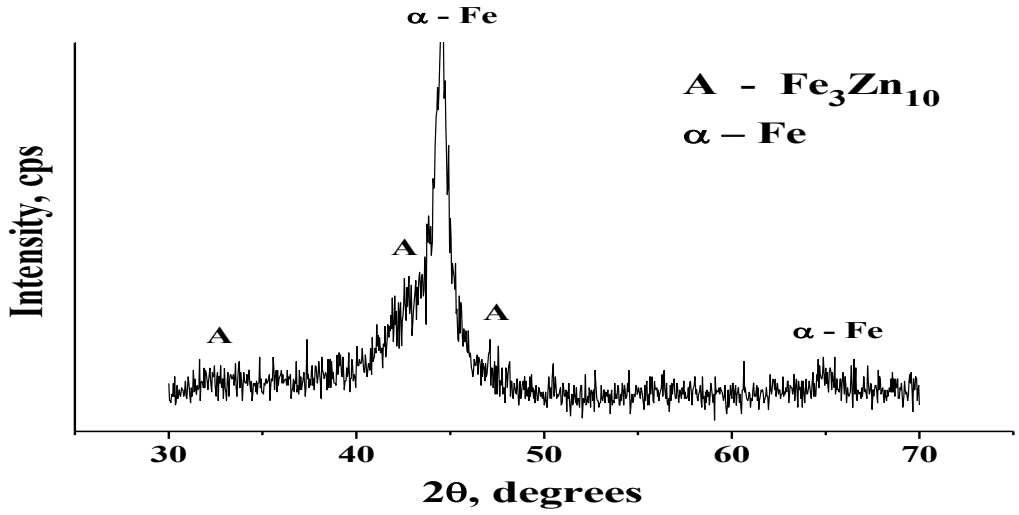


Fig.11. XRD pattern of alloy with composition Zn 45,6%, Fe 52,7% and P 1,7%

obtained at pH 3 and $D_к$ - 10A/dm^2 from Electrolyte III

As discussed above the higher Fe content (more than 35 %) in the alloy leads to higher percent of the incorporated P. This reflects also the surface morphology - Fig.13 a) and Fig.15 a).

Fig.13 shows the diffraction pattern of amorphous Fe-P alloy sample with 17 wt.% P. It is known that the amorphous galvanic alloys can be obtained in the presence of P as amorphous agent if the latter is more than 12 at.%. (9 wt.%) (Sridharan and Sheppard, 1997). An amorphous halo can be observed at $2\theta = 45^{o}$. The morphology of these coatings is very typical and consists of rounded spherical elements - Fig.14.

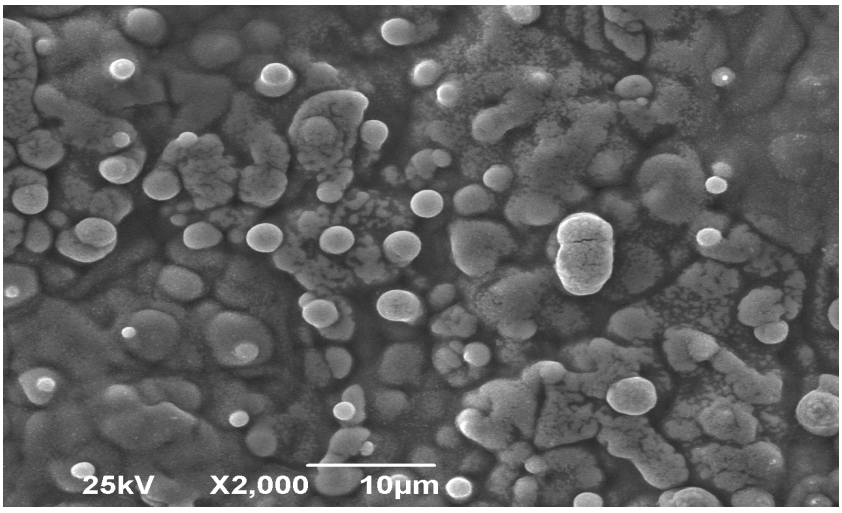


Fig.12. SEM image of the surface of the coating from Fig. 11

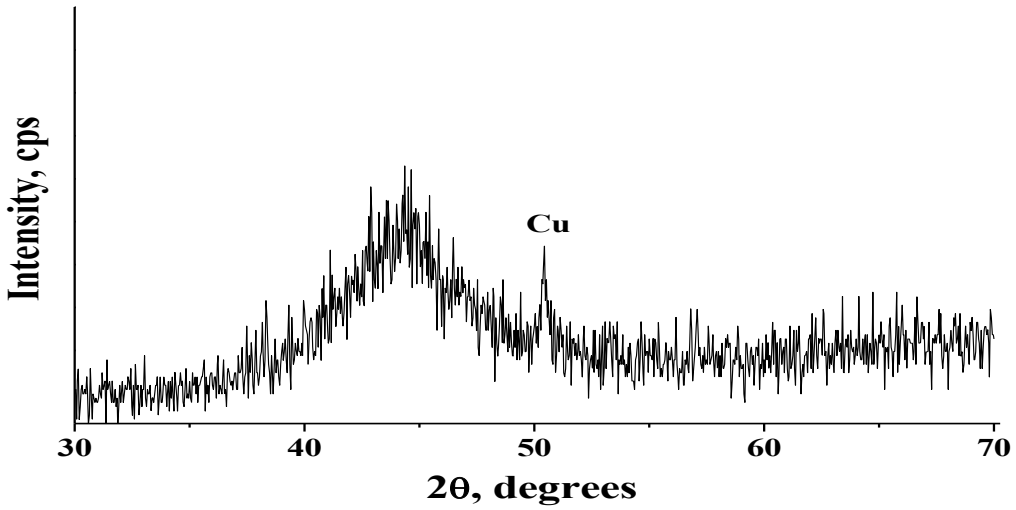


Fig. 13. XRD pattern of alloy with composition Fe 83% and P 17%

obtained at pH 2 and Dκ - 10A/dm^2 from Electrolyte II

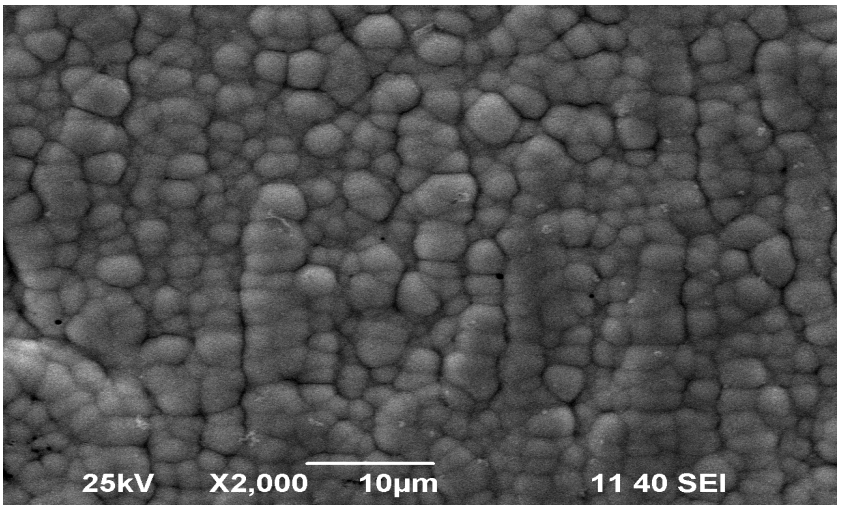


Fig. 14. SEM image of the surface of the coating from Fig. 13.

Practically, entirely amorphous and uniform deposited Zn-Fe-P coatings can be very difficult obtained. In several cases these layers can be realized only as very thin layers (Fig.15).

Thicker amorphous coatings obtained at lower pH values (about 1,5) characterize with very high P content - 10-20 wt.%. These coatings are very uneven and the composition differs in the different parts of the surface. The color and morphology also differ.

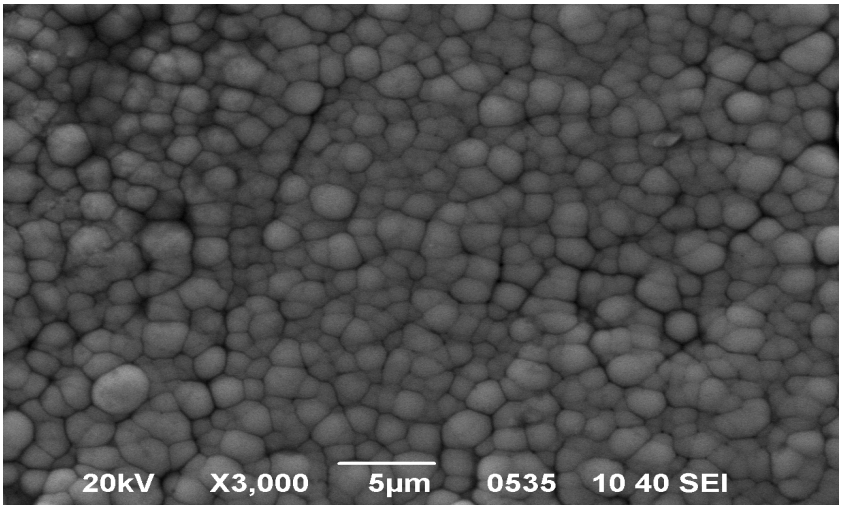


Fig. 15. SEM image of the surface of amorphous coating containing Zn-36%, Fe-48%, P-16% obtained at pH 2; $D_к$ - 10A/dm^2 from Electrolyte III

3.4. Electrochemical corrosion investigations

Potentiodynamic polarization curves of Zn-Fe alloy (curve 2) and of the Zn-Fe-P coatings with different iron content (curves 3 and 4) compared to galvanically obtained bright Zn (curve 1) and to the substrate (low-carbon steel) – curve 5 – are demonstrated in Fig. 16.

At iron content of about 20 % in the Zn-Fe-P coatings the incorporation of phosphorus in small quantities leads to potential shift in positive direction with about 80 mV (Fig. 16, curve 3) compared to the curve of the sample without P (curve 2).

At phosphorus amount of up to 2 wt.% the considerable increase of iron percentage over 40% in the layers do not change the place of the corrosion potential (E_{corr}) - curves 3 and 4. A pseudo-passive zone with current density values in the range of 1.10^{-2} A/cm^2 can be registered at high anodic polarizations of about -600 mV on curve 3. Curve 4 presents similar area but with higher current density values. This alloy characterizes also with a delay in the anodic dissolution process even at potential value of about -850 mV. It is evident that the incorporation of P in the coatings improves the corrosion characteristics of the alloys. This influence can be due to the fact that Zn-Fe-P coatings (curves 3 and 4) are substantially different in their structure and morphology compared to the Zn-Fe layer (curve 2). The structure of the coatings Zn-Fe consists of large crystals and is composed of 3 phases like the sample presented in Fig. 7 and Fig. 8a). The sample $Zn_{79,3}Fe_{19,7}P_1$ (curve 3) has a similar phase composition but with much more fine crystals and his surface is strongly smoothed out. The alloy with high Fe amount (curve 4) contains mainly α–Fe characterized with body centered cubic lattice (BCC). Its surface morphology is similar to this presented in Fig. 12. From other side, the incorporation of P in the corrosion products (curves 3 and 4) probably makes them more insoluble which leads to appearance of pseudo-passive zones at high polarizations. Corrosion currents of Zn-Fe-P samples are obviously lower than these of the pure electrolytically deposited Zn (curve 1). Regarding the iron substrate (curve 5) these alloys have more negative potential i.e. similar to the pure Zn they will carry out the role of protective anodic (sacrifice) layer.

It must be noted that the completely characterization of the corrosion behavior of the electrochemically obtained Zn-Fe-P alloys needs additional investigations also in other corrosion media and with other appropriate methods.

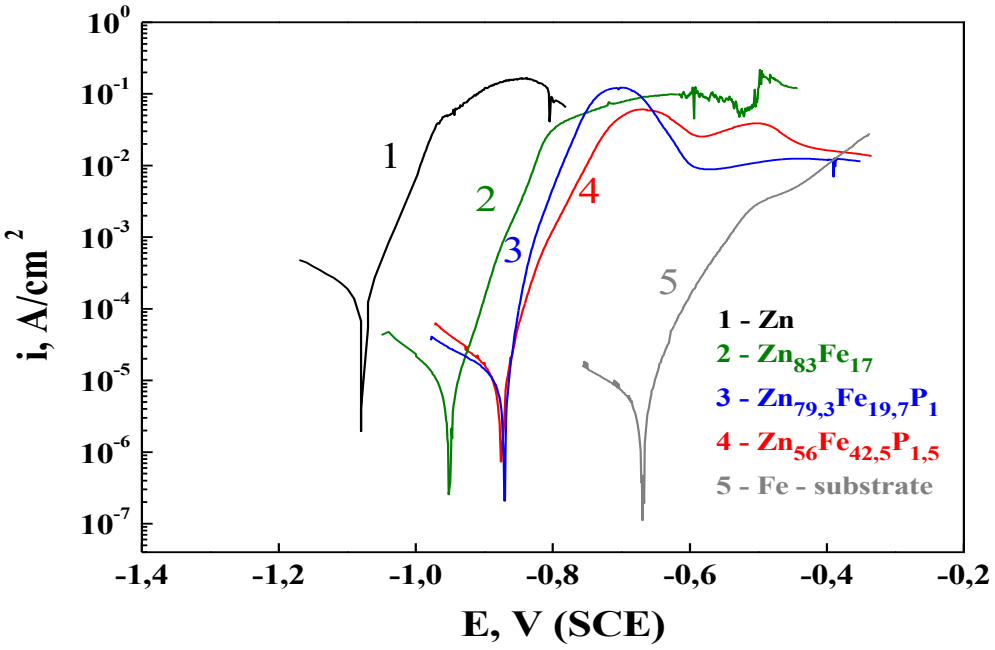


Fig. 16. Potentiodynamic polarization curves of alloy coatings in 1 N Na_2SO_4 solution

4. CONCLUSIONS

It is determined that the incorporation of phosphorus in the alloy coating does not occur at Fe content under 9 wt.%. From other side, the higher iron amount in the alloy leads to higher percent included P.

Phosphorus content is higher in the coatings obtained at lower pH values (1,5 - 2). Nevertheless, in such a case the deposition process is accompanied with simultaneously running self-dissolution process of the zinc in a definite zone which leads to non-uniform in their composition and decorative appearance layers. Entirely amorphous (phosphorus content over 10 wt.%) and uniform deposited on the surface Zn-Fe-P coatings can be practically obtained only in very thin layers (1 – 2 μm).

The presence of phosphorus in the coating although in small quantities (0,5 - 2 wt..%) has as a result the obtaining of alloys with fine crystals and also the reducing the phase composition The same can be concluded about their surface morphology the latter being more smooth and without well presented edges. Some spherical formations characteristic for the amorphous layers can be registered.

In a model corrosion medium of 1N Na_2SO_4 the Zn-Fe-P coatings with up to 2 % P and 20 to 40 % Fe demonstrate better corrosion characteristics compared to the Zn-Fe coatings and in the same time remain as a sacrifice layer in the system iron substrate / Zn-Fe-P coating.

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