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MICROSTRUCTURE AND CORROSION RESISTANCE OF ELECTRODEPOSITED Zn-Ni-P THIN FILMS

Ionuț CONSTANTIN[1], Petru MOLDOVAN[2]

Ternary Zn-Ni-P alloy thin films were electrochemically deposited from aqueous sulfate electrolytes on mild steel foils. The films were characterized by dispersive X-ray microanalysis (EDAX) and scanning electron microscopy (SEM) to determine their chemical composition and microstructure. The corrosion tests were carried out in a 3.5% NaCl solution. The value of the lowest corrosion rate was of 0.095% and the highest value for the corrosion protection efficiency was of 73.11%.

The results have shown the influence of the deposition bath and of the process parameters on the microstructure and properties of the electrodeposited coatings.

Keywords: thin films, electrodeposition, ternary alloy, corrosion

1. Introduction

Zinc and some alloys of zinc are used extensively for the corrosion protection of steel components, with numerous applications in various industrial sectors, such as the automotive industry [1,2]. Due to its low electrode standard potential of – 0.76 V (measured vs. hydrogen normal electrode), zinc can act as a sacrificial coating for coated steel parts. The value difference between the standard potential of zinc and the potentials of the steel substrates represents the corrosion force of the protective coating in corrosive media, and the high value of this difference leads to a rapid dissolution of zinc. Therefore, the dissolution rate of the anticorrosive coating was significantly reduced by alloying Zn with metals such as Ni, Co and Fe, which resulted in shifting the standard electrode potential of the alloy to values closer to the values of the substrate [3-6].

Among these alloys, Zn-Ni exhibits the best anticorrosive properties. The electrochemical deposition of Zn-Ni alloys is an anomalous process because although Ni is a nobler element than Zn, the co-deposition of these metals results in the obtaining of large quantities of Zn in the obtained alloy. A major effect of this high Zn concentration is the dissolution rate of the alloy is also high in corrosive conditions [1,2,5]. Numerous studies were carried out for reducing the

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[1] National R&D Institute for Nonferrous and Rare Metals – IMNR, Bucharest, Romania, e-mail: iconstantin@imnr.ro

[2] Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: petru.moldovan@upb.ro

anomalous effect of the co-deposition process and for enhancing the Ni content in the alloy, which results in the decreasing of the dissolution rate of the corrosion protection coating. The research focused mainly on the use of inert species in the deposition bath to inhibit the co-deposition of zinc and on developing ternary Zn-Ni-X (X= Cd, Co, P, Si, etc.) alloys [1-12]. Among these, ternary Zn-Ni-P alloys received special consideration, since it was found that an addition of 1-5 wt.% P considerably enhances the corrosion resistance of Zn-Ni alloys and presents a beneficial effect on the microstructure and the surface morphology of the electrodeposited films and on the adhesion between the coating and the substrate [10].

The aim of the present paper is to study the electrochemical deposition of Zn-Ni-P thin films on steel substrates from sulfate electrolytes and the microstructural and electrochemical characterization of the obtained coatings. The effects of the chemical composition of the plating bath and of the electrodeposition mode (potentiostatic/galvanostatic) on the physical-chemical characteristics and on the corrosion behavior of the obtained coatings are studied.

2. Experimental

The electrodeposition of the Zn-Ni-P alloy thin films was carried out at 25ºC using a Princeton Applied Research 263A potentiostat/galvanostat (which includes the Virtual Potentiostat 32 software). The ZNP coatings were deposited on mild steel substrates (foils, 50x25 mm, thickness of 0.6 mm) by potentiostatic and galvanostatic electrodeposition. The composition of the electrolyte is given in Table 1.

Table 1

Chemical composition of the deposition bath

Electrolyte	Chemical composition				
	$ZnSO_4*7H_2O$	$NiSO_4*6H_2O$	$NaH_2PO_2*H_2O$	$C_6H_5Na_3O_7*2H_2O$	NH_4Cl
1	40	40	10	10	25
2	80	40	10	10	25
3	160	40	10	10	25

The electrochemical cell consisted of a three-electrode setup. A platinum foil (3 cm^2) was used as a counter electrode and the reference electrode was a standard commercial saturated calomel electrode (SCE, 0.241V versus RHE). All the potentials in this paper are given versus SCE. The electrodeposition was performed between –1.5 V and –3 V for 30, 60 and 90 minutes. Prior to the plating process, the samples were etched using a 50% H_2SO_4 solution at 50-60^0, for 1-2 minutes and afterwards washed with double distilled water.

The electrodeposited thin films were analyzed using dispersive X-ray microanalysis (EDAX) to determine the concentration of the consisting elements and their distribution. The microstructure and morphology of the coatings were assessed by scanning electron microscopy (SEM) using a XL-30-ESEM TMP microscope fitted with an EDAX detector.

The corrosion studies were performed on the electrodeposited samples (50 x 25 mm area) using a PARSTAT 2273 potentiostat and the professional „PowerCorr”software. The electrochemical tests were carried out in a 3.5% NaCl solution at a temperature of 25°C, using a three electrode electrochemical cell. The steel samples coated with the deposited thin films had the role of the working electrode, and a platinum sheet was the cell counter electrode. A SCE electrode was used as reference electrode. The working electrode potential sweep rate was of 0.166 mV/s and the open circuit potential (E_{OPC}) was measured for 30 minutes for each sample. During the open circuit experiments, the currents which were generated when exposing the sample to the corrosive medium were measured in a time-depending manner. The polarization resistance was determined by linear polarization. The analyzed sample was scanned at ± 20 mV vs. open circuit potential E_{OPC}. The measurement time was of 30 minutes. For the determination of the Tafel plots, the potential was varied in steps of 0.166 mV, in an interval of ± 250 mV vs. E_{OCP}, for 1 to 2 hours.

The obtained results allowed the determination of the corrosion process kinetic parameters for the investigated thin films.

3. Results and discussion

The determined chemical composition of the thin films is presented in Table 2.

Table 2

Chemical composition of the Zn-Ni-P thin films

Sample	Chemical composition [wt.%]			Synthesis conditions		
					Deposition mode	
	Zn	Ni	P	Electrolyte	Potentiostat [V]	Galvanostat [mA]
1	2.58	32.81	12.26	1	1.6	2
2	5.41	68.86	25.73	2	1.6	2.5
3	44.15	49.53	6.32	3	1.6	3
4	6,36	74,37	19,27	1	3.5-4	200
5	19,86	58,49	21,65	2	3.5-4	200
6	38.59	42.42	18.99	3	3.5-4	200

The EDAX analysis revealed that the composition is similar in different areas of the samples. The percentages of the elements present in the thin film vary depending on the content of zinc in the deposition bath. Fig. 1 presents the results of the EDAX analysis for the obtained coatings. The purity of the deposit is demonstrated by the fact that only Zn, Ni, P, and Fe are present in its composition. The peak corresponding to Fe appears due to the interference between the film and the steel substrate [7].

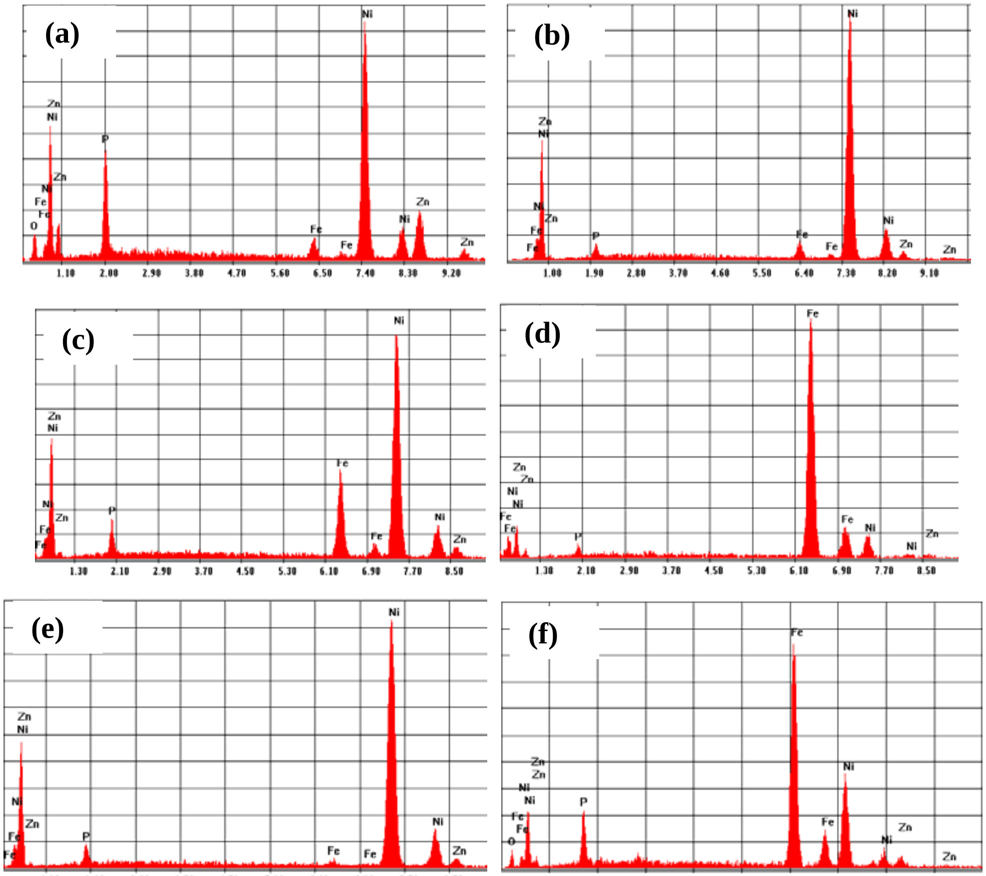

Fig. 1. EDAX spectra for the thin film samples: (a) 1; (b) 2; (c) 3; (d) 4; (e) 5 and (f) 6

From the SEM images presented in Fig. 2 it can be observed that the electrodeposited thin films exhibit a homogenous morphology with an uniform distribution of spherical particle conglomerates (Figs. 2a, 2b and 2c). The Zn-Ni-P thin films are very fine at low current densities (Figs. 2a, 2b and 2c), while as the current density increases a dendrite growth can be observed on the surface of the grain deposit (Fig. 2d). This film presents local growth structures as spheres with “cauliflower” features of various sizes. The particle shape changes and the microstructure becomes more irregular (Fig. 2e), appearing almost destroyed at higher current densities (Fig.

2f), when an uneven crystal growth with an acicular structure is observed, which is particular to coatings deposited at high current densities. All the electrodeposited thin films are compact and do not present any cracks.

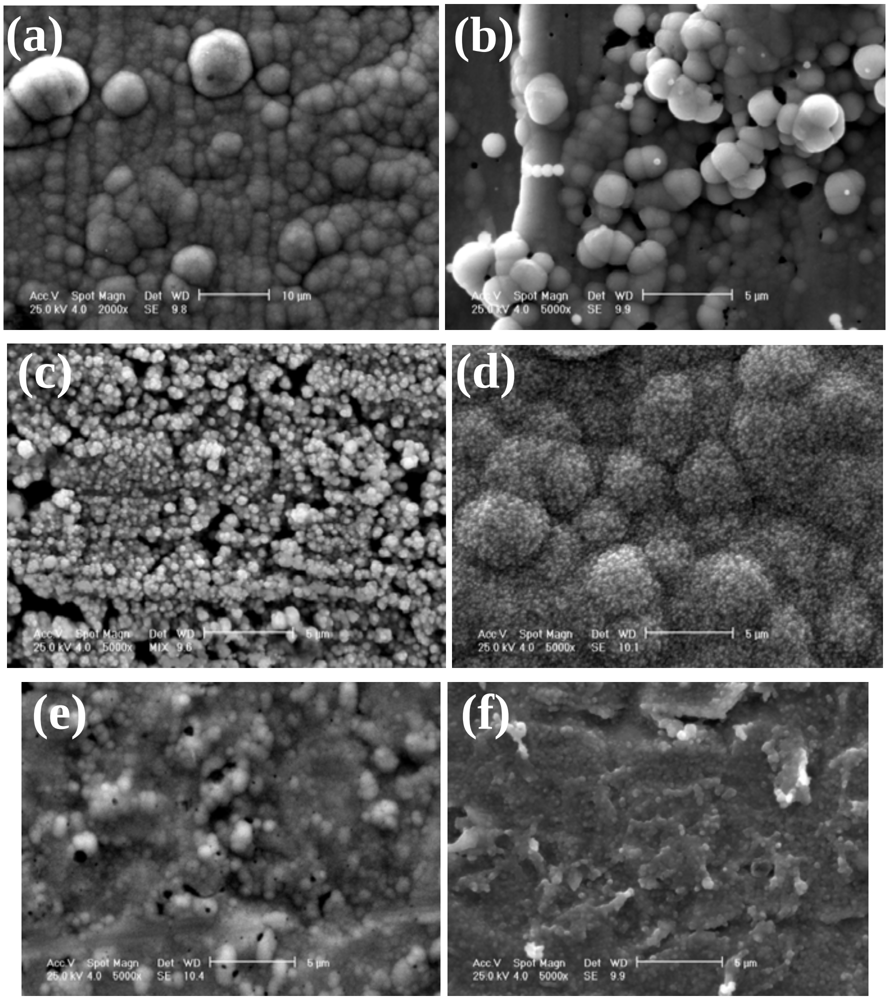

Fig. 2. SEM micrographs for the deposited thin films: (a) 1; (b) 2; (c) 3; (d) 4; (e) 5 and (f) 6

In Table 3 are presented the values of the open circuit potential for the unplated substrate and for the electroplated samples and the corrosion parameters are presented in Table 4. The Tafel curves plotted for some of the Zn-Ni-P thin films are given in Fig. 3. The corrosion resistance of the coatings was assessed based on multiple criteria. When taking in account values for the corrosion current (I_{cor}) it can be concluded that the substrate presents a much higher value than the plated samples, indicating a low corrosion resistance. In the case of the corrosion potential (E_{corr}), it is considered that films with a more positive potential exhibit a better corrosion behavior. This criterion also demonstrates that the Zn-Ni-P thin films have a superior corrosion resistance compared to the steel substrate. Also, according to Nozawa et al. [13,14], a surface is protected against corrosion when the corrosion protection efficiency (E) has a value close to 100%. For the studied thin films, it can be observed that the protection efficiency is higher than for the unplated sample. The highest values are obtained for samples 1 (73.11%) and 2 (62.98%).

Table 3

E_{OCP} potentials measured in open circuit

Sample	Steel substrate	1	2	3	4	5	6
E_{OCP} [mV]	- 614	-531	-557	-517	-482	-403	-381

Table 4

Kinetic corrosion parameters for the steel substrate and the electroplated samples

Sample	I_{corr} [µA]	E_{corr} [V vs SCE]	β_c [mV]	β_a [mV]	R_p [Ω]	RC [mm/an]	E [%]
Substrate	15.162	-0.556	368.45	44.98	3.762	0.361	0
1	4.092	-0.527	11.52	21.39	74.648	0.095	+ 73.11
2	5.604	-0.537	32.09	27.01	27.896	0.133	+ 62.98
3	8.088	-0.390	48.28	40.04	13.032	0.198	+47.15
4	8.193	-0.496	47.61	38.58	13.182	0.191	+ 46.35
5	10.512	-0.421	76.06	41.22	12.348	0.233	+ 31.27
6	12.125	-0.419	84.06	42.13	14.302	0.285	+ 25.39

where: I_{corr} = corrosion current
E_{corr} = corrosion potential
β_c and β_a = Tafel slopes (cathodic and anodic)
R_p = polarization resistance
RC = corrosion rate
E = corrosion protection efficiency

The determined values of the corrosion rate for the deposited coatings are lower than for the uncoated steel substrate. It can be observed that samples 1 and 2 present the lowest corrosion rates (0.095 and 0.133%, respectively).

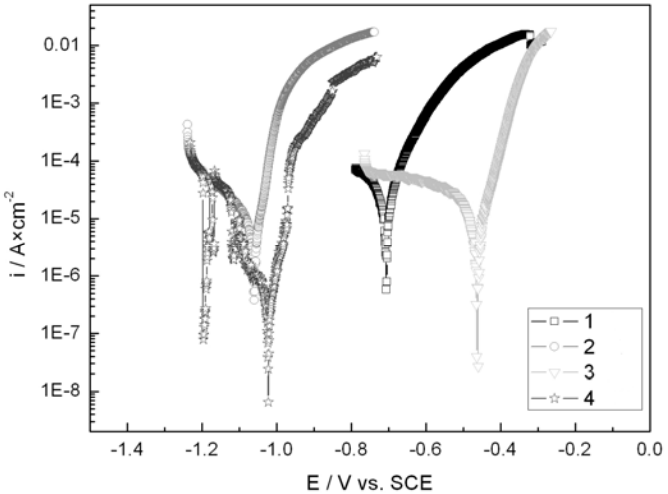

Fig.3. Tafel curves for samples 1, 2, 3 and 4

4. Conclusions

The obtained results have shown a series of influences of the experimental conditions on the chemical composition, microstructure and corrosion resistance of the Zn-Ni-P thin films electrodeposited on mild steel substrates from sulfate aqueous electrolytes.

The dispersive X-ray microanalysis (EDAX) revealed that the contents of the elements which are present in the thin films vary depending on the content of zinc in the deposition bath.

From the SEM images it could be observed that the electrodeposited thin films exhibited a homogenous morphology with a uniform distribution of spherical particle conglomerates. The Zn-Ni-P thin deposited at low current densities films exhibited a very fine morphology. As the current density increased a dendrite growth could be observed on the surface of the grain deposit. The morphology changed, appearing almost destroyed at higher current densities, when an uneven crystal growth with an acicular structure could be observed. All the electrodeposited thin films were compact and did not present any cracks.

The corrosion studies revealed that the corrosion protection efficiency is higher for the steel samples coated with Zn-Ni-P films than for the unplated sample. The highest value obtained was of 73.11%. The corrosion rates for the electrodeposited coatings were lower than for the uncoated steel substrate. The lowest corrosion rate obtained was 0.095%.

It can be concluded that the electrodeposited Zn-Ni-P ternary alloy thin films represent a promising alternative for the replacement of cadmium coatings for steel parts working in highly corrosive media.

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