

## Electrochemical behaviour of ternary Ni-Zn-P thin films deposition on steel substrate

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Ternary Ni-Zn-P alloy thin films with a thickness of 15-20 μm are considered as a replacement for cadmium sacrificial coatings for anticorrosive protection of steel parts working in highly corrosive media. Anticorrosive Ni-Zn-P thin films has been electrochemically deposited from aqueous sulphate solutions on carbon steel substrate. The influence of bath composition (variable ZnSO<sub>4</sub>·7H<sub>2</sub>O contents) and electrodeposition type (potentiostatic or galvanostatic) on physical-chemical and corrosion characteristics of obtained films have been studied. Films are characterized by energy dispersive analysis (EDAX) and scanning electron microscopy (SEM). The corrosion tests are performed in 3% NaCl solution with optimal resulting values of -916.2 mV vs. saturated calomel electrode (SCE) for the corrosion potential and 13.4 μA·cm<sup>-2</sup> for the corrosion current density. The calculated value for the corrosive attack protection efficiency is 67.7%.

**Keywords:** Corrosion, Thin films, Ni-Zn-P, Electrodeposition, Sulphate, Corrosion test

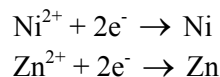
Ni-Zn-P is applied in the chemical and electronics industries not only for anti-corrosion coatings, but also for its magnetic and electrical properties. There is also an option to apply Ni-Zn-P films of varying thickness and composition as screens and filters for electromagnetic radiations. Zinc exhibits a low electrode standard potential ( $E_0 = -0.7$  V, measured vs. standard hydrogen electrode-SHE), thus being capable of acting as a sacrificial coating for plated steel parts. The difference between the standard potentials of zinc and the substrate (iron) represents the corrosion force of the protection coating in corrosion conditions, and the high value of this

difference leads to a rapid dissolution of zinc. The dissolution rate of the protective coating was considerably reduced by alloying zinc with other elements (Ni, Co, Fe, etc.) that shifted the standard electrode potential of the alloy to values closer to the substrate<sup>1-3</sup>. Among these alloys, the best anticorrosive properties, similar to those of cadmium, are presented by the Zn-Ni alloy<sup>4-6</sup>. However, electrochemical deposition of Zn-Ni alloys is an anomalous process. Although Ni is nobler than Zn, co-depositing these metals results in obtaining large quantities of Zn in the deposited alloy. As an effect of high Zn concentration, the alloy dissolution rate is also high in corrosive medium conditions<sup>7-9</sup>.

Electrochemical deposition of Zn-Ni alloys is an anomalous codeposition process by nature; various studies and research work were performed for improve the characteristic of the Zn-Ni codeposition, thus increasing the Ni content in the alloy, which determines a decrease in the dissolution rate of the anticorrosive alloy coating. These researches were mainly based on the following conditions:

1. Using inert species in the deposition bath, to inhibit zinc codeposition, and,
2. Developing ternary anticorrosive alloys: Zn-Ni-X (X = Cd, Co, P, Si, etc.).

Among these, ternary Ni-Zn-P alloys were of special interest because of the corrosion resistance enhanced capability brought by an addition of 1-5% P in Zn-Ni alloys. Anticorrosive Ni-Zn-P thin films depositions can be performed both electrochemically as well as chemical plating (deposition without power support-electroless)<sup>10-12</sup>. The mechanism of incorporating phosphorus in the alloy is complex and it is based both on direct electrochemical reactions<sup>13-19</sup>:



as well as indirect electrochemical reactions, H<sub>2</sub>PO<sub>2</sub><sup>-</sup> disproportionation reaction respectively:



resulting in phosphorus incorporation in the cathodic deposited alloy. The present study describes the experimental works performed for electrochemical obtaining of Ni-Zn-P thin films on steel substrate

from acid sulphate solutions. The effect of bath composition and deposition type (potentiostatic or galvanostatic) on physical-chemical and corrosion characteristics of obtained films are studied.

## Experimental Section

### Ni-Zn-P - thin films electrodeposition

Ni-Zn-P thin films were electrochemically deposited on carbon steel samples (C=0.3% wt.) 50×25 mm in size, 0.6 mm in thickness. The electrolysis cell utilised is presented in Fig 1. The steel sample (cathode) was fastened between 2 platinum anodes, (sizes: 50×30×0.2 mm), at an interelectrode gap of 20 mm.

SCE was used as reference electrode. The electrolyte was stirred at a 30-40 rpm rate using an AG 3 electric plate with magnetic stirrer. Before depositing, the surface of the steel samples was prepared. This is necessary because the adherence between the substrate and the coating, with favorable consequences on anticorrosive protection efficiency, can be provided only by adequate preparation of the sample surface. Preparing the substrate for film deposition comprised the following operations:

1. Polishing on abrasive paper increasing in granulation;
2. Acetone degreasing and rinsing in double distilled water;
3. Sample etching, for removing traces of surface adherent oxide, with 50% H<sub>2</sub>SO<sub>4</sub> solution at a temperature of 50-60°C, for 1-2 minutes, followed by washing with double distilled water.

The chemical composition of electrodeposition baths is presented in Table 1. Solutions were prepared using p.a. purity chemical solutions and double distilled water. Solutions pH was set and maintained at 4.5 with concentrated (50%) H<sub>2</sub>SO<sub>4</sub> solution.

Films were deposited in both potentiostatic and galvanostatic working regime. Working temperature was 60±2°C. The deposition time was 30 minutes for each selected bath type. The deposition bath was stirred using a Teflon embedded magnetic stirrer, at a 30-40 rpm rate.

### Corrosion characteristics of deposited Ni-Zn-P films

Corrosion resistance was determined for thin films (with a thickness of 15-20 μm), coated samples and

the substrate, using the potentiodynamic curves technique). This technique consists in plotting potentiodynamic curves with a 2049 Amel Potentiostat/Galvanostat. A saturated calomel electrode (SCE) was used as reference electrode and a platinum electrode as the trace electrode. Samples to be investigated formed the working electrode (uncoated steel and coated with anticorrosive films). The surface subjected to corrosion was approximately 1 cm<sup>2</sup>. The corrosion tests were done in 3% NaCl solution, at room temperature (25±1°C). Potentiodynamic curves were plotted from -100 mV to 1500 mV (vs. SCE).

## Results and Discussion

### Deposited films analysis

Obtained thin films were characterized using energy dispersive X ray microanalysis (EDAX) for determining concentration and elemental distribution and scanning electron microscopy (SEM) for determining morphology and microstructure. In order to increase the elemental distribution accuracy, EDAX analysis was performed in various points

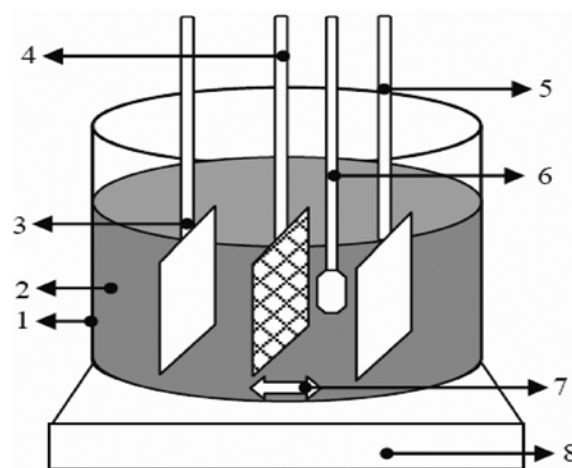


Fig. 1 — Thin films electrodeposition installation

- 1-Electrolysis vessel (600 cm<sup>3</sup> capacity);
- 2-Electrolyte;
- 3-Anode;
- 4-Cathode (steel sample);
- 5-Anode;
- 6-Reference electrode (RE is placed between the anode and the cathode);
- 7-Magnetic agitator;
- 8-Magnetic heater-agitator.

Table 1 — Composition of electrochemical deposition baths

Electrolyte	Chemical composition / g·L <sup>-1</sup>				
	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	NiSO <sub>4</sub> ·6 H <sub>2</sub> O	NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> Na <sub>3</sub> O <sub>7</sub> ·2H <sub>2</sub> O	NH <sub>4</sub> Cl
A	40	40	10	10	25
B	80	40	10	10	25
C	160	40	10	10	25

situated along a diagonal of the steel parts. The analyses were performed using a XL-30-ESEM TMP type electronic microscope, fitted with an EDAX detection device.

Table 2 contains the elemental chemical composition of electrolessly deposited thin films, determined by EDAX, and electrodeposition conditions. Figure 2 presents the EDAX spectra recorded for samples F1(a), F3(b) and F6(c) respectively.

SEM micrographs for samples F1, F3 and F6 are presented in Fig. 3. Sample (a) shows predominantly compact zones, and some areas presenting voids, crevices, gaps in deposited film structure. In (b) the film exhibits a compact structure, with dendritic grains of regular size. In (c) an uneven crystal growth is observed, with acicular structure, particular for metals deposited at high current densities.

In Fig. 4 are presented SEM micrographs which reveal elemental and relative elemental distributions along a straight line for samples F2, F4 and F5, respectively. An even distribution of alloy component elements in the structure of the deposited film is noticed.

#### Thin films corrosion characteristics

- Potentiodynamic curves for the studied samples are presented in Fig. 5.
- The potentiodynamic curve for an unplated steel sample (witness) is also presented, for comparison.
- The following parameters characterizing corrosion resistance of the samples were determined using these curves:
  - corrosion potential ( $E_i=0$ );
  - corrosion current critical density ( $i_{corr}$ );
  - corrosion attack protection efficiency ( $P_e$ ).

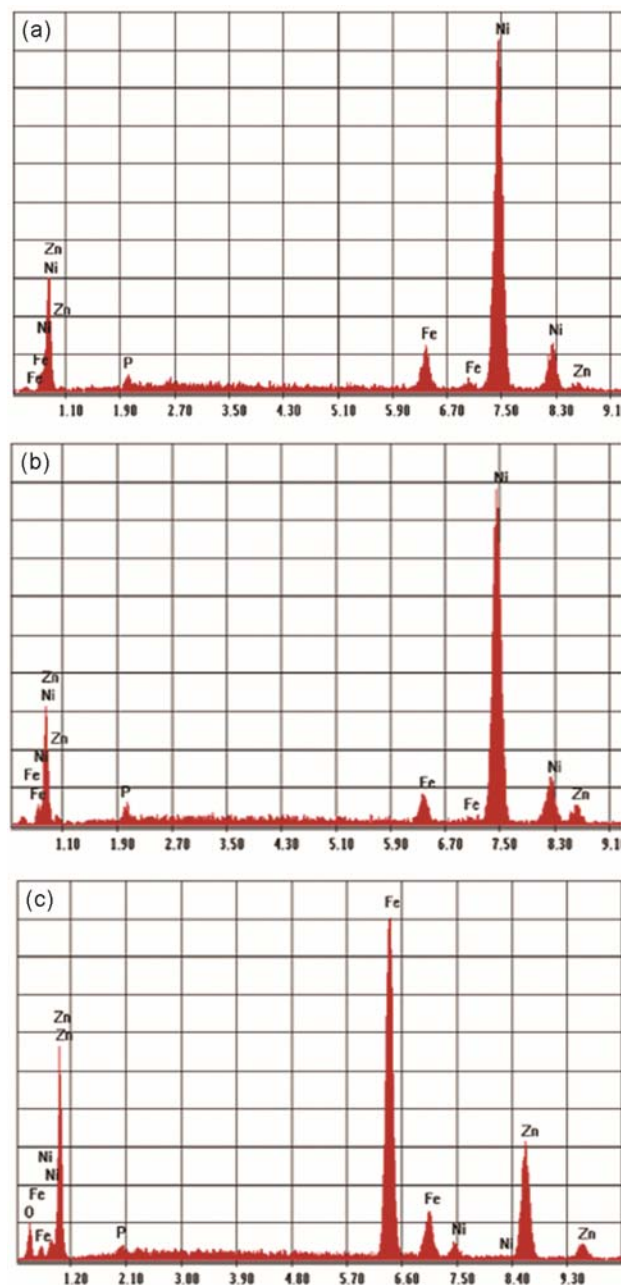


Fig. 2 — EDAX spectra for samples F1 (a), F3(b) and F6 (c)

Table 2 — EDAX elemental chemical composition

Sample	Chemical composition % wt.			Electrodeposition conditions		
	Zn	Ni	P	Electrolyte	Work regime/mode	
					Potentiostatic V	Galvanostatic mA
F 1	15.1	67.2	16.8	A	1.6	2
F 2	25.7	57.4	16.8	B	1.6	2.5
F 3	40.7	53	6.3	C	1.6	3
F 4	8.7	65.7	25.6	A	3.5-4	200
F 5	18.8	77.8	3.5	B	3.5-4	200.0
F 6	89	8.2	2.8	A	3.5-4	200.0

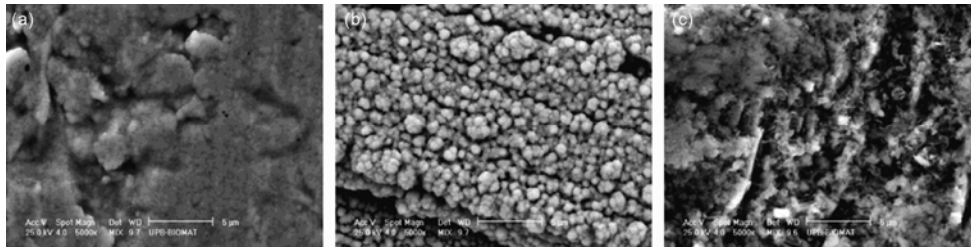


Fig. 3 — SEM micrographs for samples F1 (a), F3(b) and F6 (c) (magnification  $\times 5000$ )

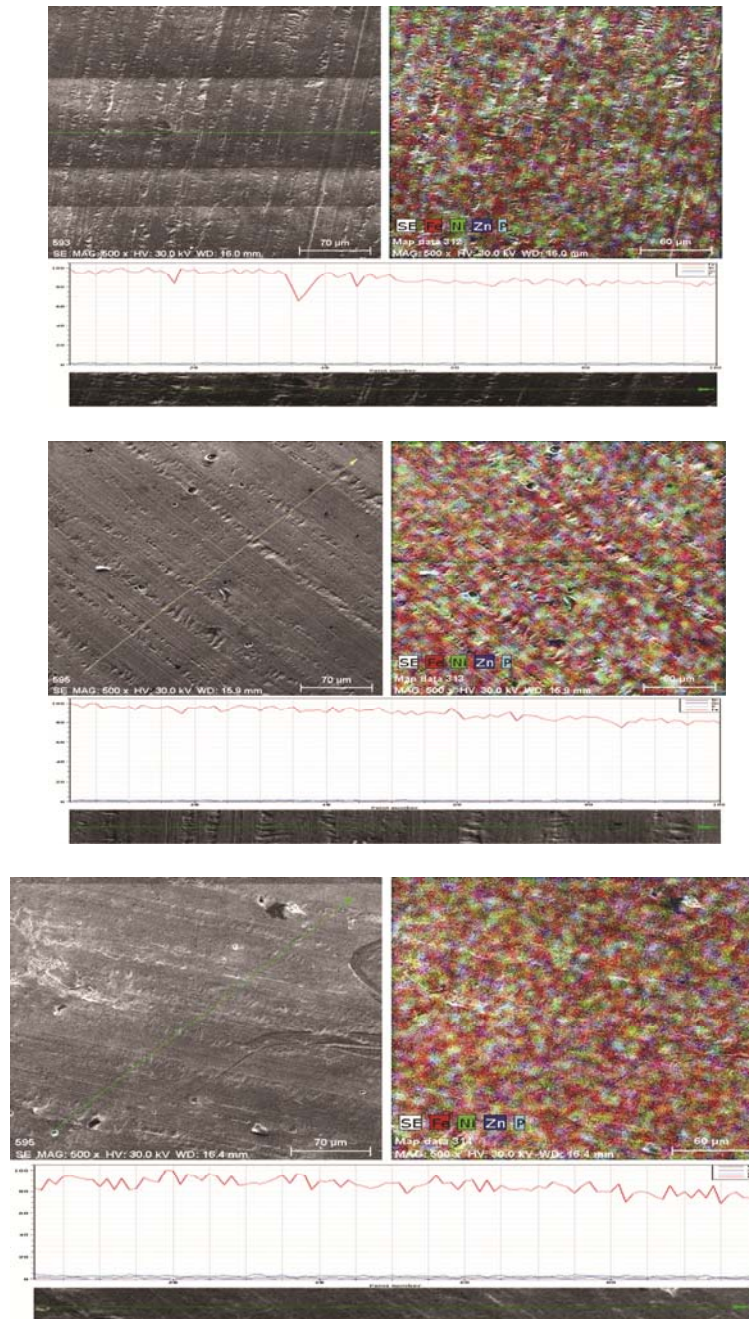


Fig. 4 — SEM micrographs revealed elemental and relative elemental distributions along an analysis line for samples F2 (a), F4 (b) and F5 (c), respectively (magnification  $\times 500$ )



Also, the film protection efficiency to corrosive attack ( $P_e$ ) was determined with the equation:

$$P_e = \left( 1 - \frac{i_{\text{corr, coating}}}{i_{\text{corr, substrate}}} \right) \cdot 100 \quad \dots (1)$$

where:  $i_{\text{corr, coating}}$  - are the film and strate corrosion current densities,  $i_{\text{corr, substrate}}$  - are the film and substrate corrosion current densities.

In Table 3 the main parameters of electrochemical corrosion process are presented for the analyzed samples: corrosion potential ( $E_i=0$ ); corrosion current critical density ( $i_{\text{corr}}$ ); corrosion attack protection efficiency ( $P_e$ ).

Corrosion resistance of the films was analyzed based on multiple evaluation criteria. From Comparing th corrosion current densities values ( $i_{\text{corr}}$ ) presented in Table 1 it can be determined that the witness sample has a corrosion current density value much greater than most coated samples, which indicates weak corrosion resistance. According to this criterion, most deposits have better corrosion behavior than the reference substrate. Regarding the corrosion potential ( $E_i=0$ ) value, it is considered that films with

more electropositive  $E_i=0$  potential exhibit better corrosion behavior. According to this criterion the obtained films have superior corrosion resistance comparative to the reference substrate. Comparing corrosion and EDX data once can conclude that better corrosion resistance have the samples with higher nickel concentration (samples F1 and F3). In addition from the Tafel curves once can see than sample F3 present an anode passivation and even transpassivation.

Finally, according to Nozawa et all<sup>20,21</sup>, a surface with high corrosive attack protection ( $P_e$ ) has a  $P_e$  parameter value close to 100%. For investigated films, it is worthy of note that  $P_e$  parameter values are greater than for the substrate, indicating a good corrosive attack protection capacity. Closest values to 100% were determined for samples F1 and F3. According to evaluation criteria presented above, we can conclude that the obtained thin films improve steel substrate corrosion resistance. Also, both in the anodic and cathodic section of the potentiodynamic curve (Fig. 5), sudden current density fluctuations are observed for the substrate, indicating that the substrate material is susceptible to local pitting corrosion<sup>22-28</sup>.

## Conclusion

The experimental results highlighted a series of influences of electrochemical obtaining conditions on the composition, structure and corrosion resistance of Ni-Zn-P thin films deposited on carbon steel substrate from acid sulphate baths.

Chemical composition of the films determined by EDAX analysis, dependent on  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  concentration in the deposition bath, and work regime had wide ranges: 15.1-40.7 % wt. Zn in potentiostatic regime and 8.7-89 % wt. Zn in galvanostatic regime.

Films deposited in potentiostatic regime show a compact structure, with even dendritic grains, and zones with gaps, crevices. Films deposited in galvanostatic regime, present acicular structure, in particular for metals deposited at high current densities.

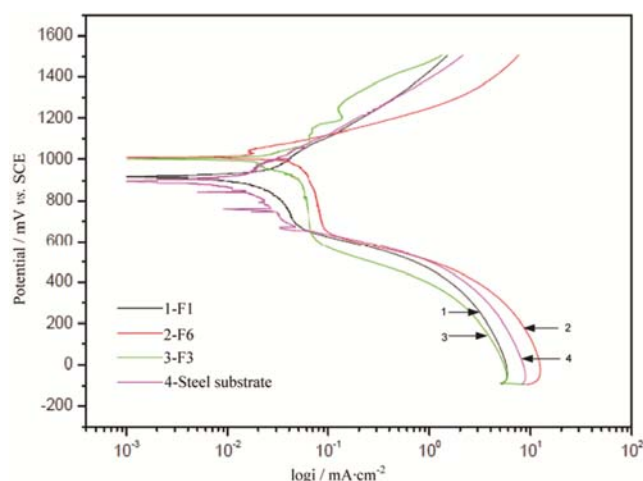


Fig. 5 — Potentiodynamic curves for samples F1, F3, F6 and steel substrate

Table 3 — Main parameters of corrosion process for analyzed samples

Sample	$i_{\text{corr}}$ $\mu\text{A} \cdot \text{cm}^{-2}$	$E(i=0)$ mV	$P_e$ %
Steel substrate	41.6	895	-
F 1	13.4	916.3	67.8
F 3	18.8	1007.2	54.8
F 6	26.2	1017.9	37

Steel samples coated with Ni-Zn-P films present corrosion resistance superior to uncoated steel sample (witness sample). From the recorded potentiodynamic curves the critical  $i_{\text{cor}}$  corrosion current densities were determined to be 13.4-26.2  $\mu\text{A}\cdot\text{cm}^{-2}$ , compared to 41.6  $\mu\text{A}\cdot\text{cm}^{-2}$  for the uncoated sample.

Also, calculated values of 37%, 54.8%, and 67.7% respectively for corrosion protection capacity are superior to those of the uncoated steel sample.

## References

- 1 Abou-Krishna M M, Assaf F H & Toghan A A, *J Solid State Electr*, 11 (2007) 244.
- 2 Li Y, Kumar P, Shi X, Nguyen T A, Xiao Z & Wu J, *Int J Electrochem*, 7 (2012) 8151.
- 3 Hammami O, Dhoubi L, Bercot P & Rezrazi E M, *Surf Coat Tech*, 219 (2013) 119.
- 4 Grimshaw P, Calo J M, Shirvanian P A & Hradil G, *Ind Eng Chem Res*, 50 (2011) 9525.
- 5 Li Y, Kumar P, Shi X, Nguyen T A, Xiao Z & Wu J, *Int J Electrochem Sci*, 7 (2012) 8151.
- 6 Bachvarov V D, Peshova M T, Vitkova S D, & Boshkov N S, *Cent Eur J Chem*, 12 (2014) 1183.
- 7 Ganesan P, Kumaraguru S P, & Popov B N, *Surf Coat Tech*, 201 (2007) 7896.
- 8 Ganesan P, Kumaraguru S P, & Popov B N, *Surf Coat Tech*, 201 (2006) 3658.
- 9 Fratesi R, & Roventi G, *Surf Coat Tech*, 82 (1996) 158.
- 10 Abd El Ehim S S, Fouad E E & Abd El Wahab S M, *Electrochem Acta*, 41 (1996) 1413.
- 11 Durairajan A, Haran B S, White R E, & Popov B N, *J Electrochem Soc*, 147 (2000) 1781.
- 12 Bouanani M, Cherkaoui F & Fratesi R, *J Appl Electrochem*, 29 (1999) 637.
- 13 Gafin H A & Orchard S W, *J Electrochem Soc*, 140 (1993) 3458.
- 14 Pourbaix M, *Atlas of electrochemical equilibria in aqueous solution*, Pergamon Press, Oxford, (1966).
- 15 Pasăre M M & Bonino J P, *Rev Chim*, 12 (2007) 1190.
- 16 Kamimoto Y, Yamamoto K, Yamashita S, Sakai T & Ichino R, *Sci Adv Mater*, 6 (2014) 2269.
- 17 Constantin I, *J. Metallurgy*, (2014), <http://dx.doi.org/10.1155/2014/827393>.
- 18 Fall M, Diagne A A, Guene M, Della Volpe C, Bonora, P L, Deflorian F, & Rossi S, *B Chem Soc Ethiopia* 20 (2006) 279.
- 19 Lori A J, Omoniyi K I, Ekanem J E & Ekwumemgbo A P, *B Chem Soc Ethiopia*, 23 (2009) 1.
- 20 Nozawa K, Nishihara H & Aramaki K, *Corros Sci*, 39 (1997) 1625.
- 21 Nozawa K & Aramaki K, *Corros Sci*, 41 (1999) 57.
- 22 Zamfir S, Vidu R & Brânzoi V, *Coroziunea materialelor metalice*, (EDP, București), (1994).
- 23 Brânzoi V, Brânzoi F & Pilan L, *Caracteristici generale privind coroziunea și protecția anticorozivă a metalelor în diverse medii*, (Printech, București), (2006).
- 24 Scharfstein L R, *Handbook on corrosion testing and evolution*, (New York), (1971).
- 25 West J M, *Basic Corrosion and Oxidation*, (New York), (1980).
- 26 Shreir L L, *Corrosion*, Vol 1, 2<sup>nd</sup> Edition, (Newnes-Butterwords), London, (1976).
- 27 Dutra C A M, Silva J W J, & Nakazato R Z, *Mater Sci Appl*, 4 (2013) 644.
- 28 V Thangaraj & A Chitharanjan H, *Indian J Chem Technol*, 14 (2007) 253.