

CORROSION BEHAVIOR OF ELECTROLESS Ni-P/NANOZnO COATINGS

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Abstract: Electroless Nickel-phosphorus (EN) coatings provide high performance in various industrial fields due to their unique properties such as excellent corrosion and wear resistance. This paper aims to study the effect of ZnO nano-particles addition on corrosion behavior of EN coatings. Various amounts of ZnO nano-particles with average diameter of 50 nm were added to hypophosphite reduced EN bath to deposit composite coatings. Microstructural investigations were carried out via scanning electron microscopy (SEM). Chemical composition of the coatings was investigated via energy dispersive spectroscopy (EDS). Electrochemical impedance spectroscopy (EIS) and polarization tests were used to study the corrosion properties of the coatings in a 3.5 wt.% NaCl solution. SEM investigations showed that the coating deposited from the bath containing 2 g/L of ZnO nano-particles had the most amount of nano-particles incorporated in the coating. EDS results revealed that incorporation of ZnO nano-particles in the composite coating resulted in a decrease in phosphorous content of the coating. Corrosion tests showed that corrosion resistance of the electroless Ni-P/nanoZnO composite coatings in 3.5 wt.% NaCl solution had an improvement in comparison to electroless Ni-P base coating.

Keywords: Electroless, Nickel-phosphorus, ZnO nano-particle, Corrosion

1. INTRODUCTION

Electroless nickel plating (EN) was used by A. Brenner and G. Riddell for the first time in 1946. These coatings are diverse with their impressive characteristics such as good corrosion and suitable wear resistivity behaviors [1 and 2]. Incorporation of different fine hard particles in these coatings has been a subject of many works in recent years. It has been shown that modification of physical and mechanical properties, including increased resistance to wear and abrasion, increased corrosion and oxidation resistance, and increased hardness could be yielded by incorporation of hard fine particles in EN coatings [3-7]. Besides hard fine particles, incorporation of carbon nano-tubes in these coatings has been reported to result in better tribological as well as corrosion properties [8-10]. It has been shown that the composite EN coatings have a better corrosion resistance in comparison to the pure EN coatings [11-15].

This work aims to evaluate the effect of nano-ZnO ceramic particles incorporation on corrosion

behavior of electroless Ni-P coatings.

2. EXPERIMENTAL

2. 1. Deposition Procedure and Condition

Plates used as substrate to obtain Ni-P and Ni-P/ZnO coatings were st37 steel in the size of 25×25×6 mm. After polishing with SiC paper – from grade #100 to #400 - all the specimens were pretreated and then plated through the following procedure:

1. Ultrasonic cleaning in acetone for 6 minutes;
2. Cleaning in an alkaline solution for 10 minutes, at 80°C;
3. Cleaning in 10 Vol.% followed by 5 Vol.% H₂SO₄ solutions, for 30 s in each case, at room temperature;
4. Electrocleaning in an alkaline solution for 20-25 minutes according to ASTM G 1-90 (the current density was 10 mA/cm²) [16];

After each step specimens were rinsed with deionized water.

Table 1. The condition of bath used for Ni-P and Ni-P/ZnO plating

bath (Sample) #	1	2	3	4
Nano-ZnO concentration (g/L)	0	1	2	3

An available industrial bath was used to obtain EN coatings. Plating temperature was set within 88–93 °C using a thermal sensor and the pH was set within 4.5–4.7 range. The bath was agitated using magnetic stirrer at a speed of 300 rpm.

The diameter of ZnO nano-particles used was about 50 nm. The amount of ZnO nano-particles used in different baths is given in table 1.

The plating bath was prepared in a 200 mL cell. To avoid agglomeration of ZnO nano-particles, they were dispersed in the bath using a high frequency ultrasound wave producer setup prior to deposition.

A thin layer of pure EN coating was initially deposited on the steel plates to reach a better adhesion. The deposition time for this layer was 15 min. Samples were then moved to the composite plating solution immediately and plating was continued for 3 hr.

2. 2. Morphology of the Coatings

Scanning electron microscopy (CAMSCAN MV2300) was used to study the morphology of the coatings. Coatings were subjected to ultrasonic cleaning in acetone to remove any probable squalor beforehand.

2. 3. Phase and Elemental Composition Analysis

X-ray diffraction (Philip's Xpert pro type X-ray diffractometer with a cobalt target and an incident beam mono-chromator with the wavelength of $k = 1.7889 \text{ \AA}$) patterns were used to recognize the phases present in the coatings. The elemental analysis of the coatings was obtained via energy dispersive spectroscopy.

2. 4. Electrochemical Measurements

Corrosion behavior of the coatings was studied through electrochemical impedance spectroscopy and potentiodynamic polarization tests, both of which were carried out in a standard three electrode cell. Ag/AgCl and platinum electrodes were employed as reference and counter electrodes, respectively; while a specific area (100 mm²) of the samples was used as the working electrode. The electrochemical measurements were carried out in 3.5 wt. % NaCl solution. The polarization tests were conducted using an EG&G potentiostat/galvanostat (model 273A). The EIS tests were carried out using a Solartron Model SI 1255 HF Frequency Response Analyzer (FRA) coupled to a Princeton Applied Research (PAR) Model 273A Potentiostat/Galvanostat. The samples were immersed in the electrolyte before the tests started so that an established Open Circuit Potential (OCP) is achieved. The polarization curves were obtained by sweeping the electrode potential in the range of -200 to 400 mV vs. OCP starting from cathodic area. The EIS measurements were also carried out around OCP. The amplitude of the sinusoidal AC signal applied in the EIS measurements, was 5 mV and the frequency range was from 0.01 Hz to 100 kHz.

3. RESULTS AND DISCUSSION

3. 1. Deposition of Composite Coatings

During deposition of the composite coatings from the baths containing different amounts of nano-particles, it was noticed that the plating baths would decompose for the baths containing 2 g/L ZnO nano-particles or more. This phenomenon was happening some times after deposition started and for higher concentration of ZnO nano-particles happened after a little while. This could be as a result of the increased surface area and hence increased internal energy of the bath composition, which occurred above a tolerable amount nano-ZnO [17].

A cross-sectional view (taken by OM) of the coatings deposited from the baths # 1, 2, 3, and 4

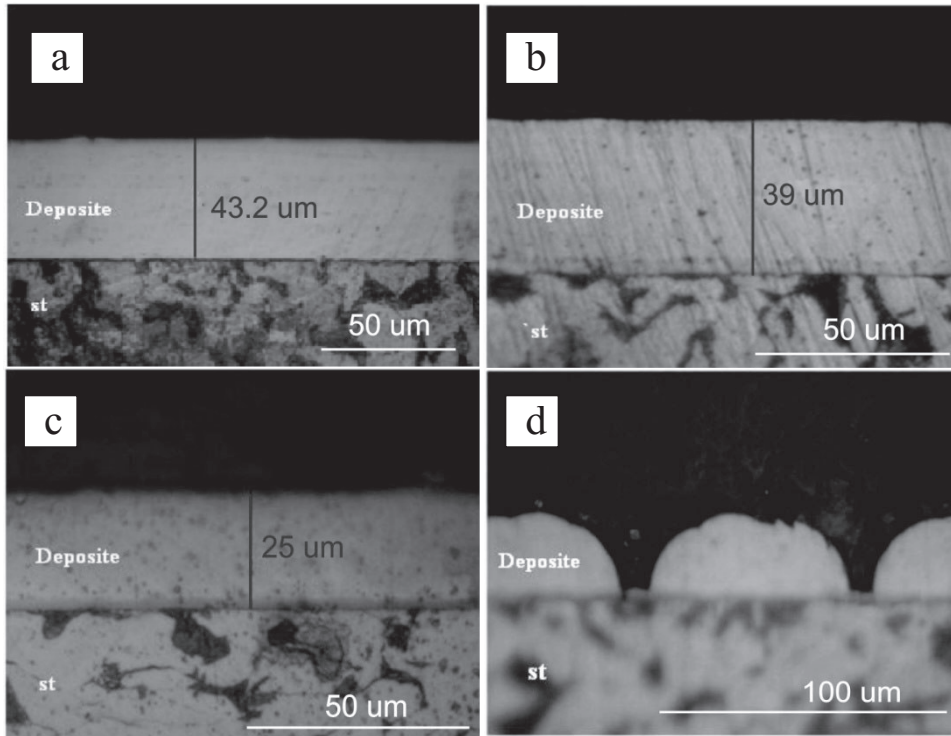


Fig. 1. The cross-sectional views of coatings # 1(a), 2(b), 3(c), and 4(d), taken by optical microscope (OM).

is shown in Fig. 1 (a, b, c, and d). As it can be seen the addition and further increase of the nano-particles contents in the plating bath has lowered the thickness of the coatings and for the coating deposited from the bath # 4 the deposit is non continuous and the thickness is lowest.

3. 2. Elemental Analysis of Coating Composition

Zn-X-ray map results for the Ni-P composite coatings (obtained from baths #2 and 3) are shown in Fig. 2. The lighter spots in these figures are representatives of Zn-X-rays. As it can be seen from the Fig. 2, nano-particles are well-dispersed all around the surface in both of the composite coatings. Comparing the X-ray maps of the two composite coatings, it is clear that the incorporation of ZnO nano-particles in the coating obtained from the bath # 3 is rather more in comparison to the coating deposited from the bath # 2.

Table 2 presents the relative amounts of nickel and phosphorous elements in pure Ni-P and composite coatings. It is seen that incorporation

of ZnO nano-particles in the coating has decreased the amount of phosphorous in the composite coating in comparison to nickel. This effect has also been reported by Novakovic [18]. The reason for this phenomenon is unidentified. The phosphorus content does not show a distinct difference for the composite coatings obtained from 1 g/L and 2 g/L ZnO nano-particles containing baths.

3. 3. Morphology of the Coatings

The morphology of the pure and composite coatings - yielded by SEM - is shown in Fig. 3a,

Table 2. Elemental analysis of the coatings compositions obtained from EDAX analysis.

Coating	Nickel (wt.%)	Phosphorous (wt.%)
Ni-P	90/6	9/4
Ni-P/ZnO	91/1	8/9

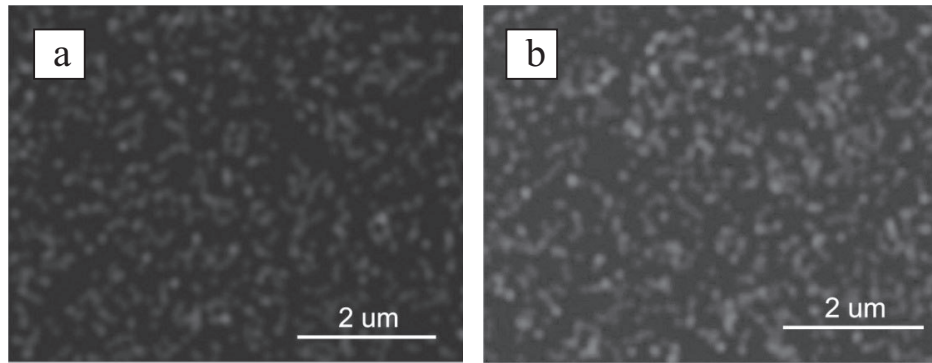


Fig. 2. Zn-X-ray maps taken from the surface of the composite coating # 2 (a) and 3 (b).

b, and c. As it can be concluded from Fig. 3a, b, and c the incorporation of ZnO nano-particles in the coating has resulted in a rougher surface for composite coatings in comparison to the pure one. It is also seen that the increase in the amount of the ZnO nano-particles incorporation in the Ni-P matrix has caused to obtain a more uneven surface (Fig. 3b and c). Since the rougher morphology could be a proof for the presence of

the nano-particles at the surface, it can be concluded that the increase in the nano-particles amount in the bath has caused in an increased amount of nano-particles incorporation in the coating (as it also was shown by Fig 2a and b).

3. 4. X-Ray diffraction Analysis

The XRD patterns of the composite (coating

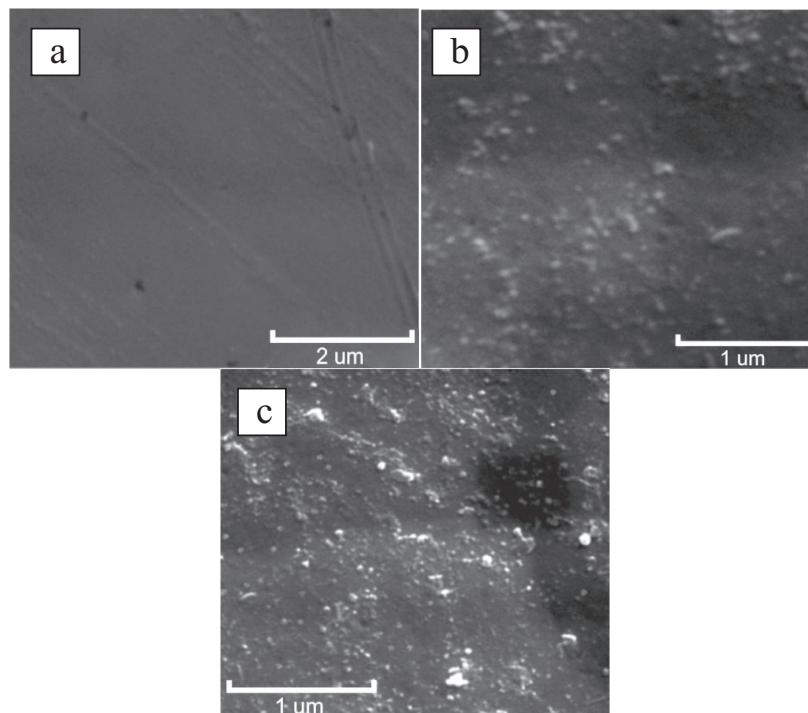


Fig. 3. The surface morphology of the Ni-P ,a., Ni-P/ZnO (1 g/L nano-particle in the bath), b., and Ni-P/ZnO (2 g/L nano-particle in the bath),c.

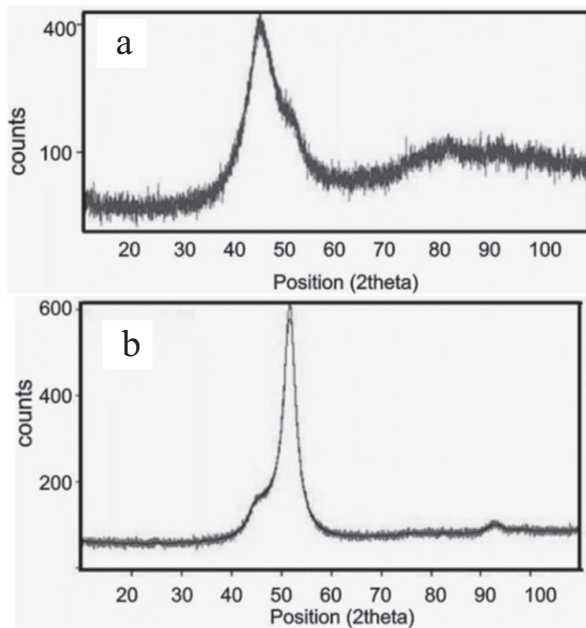


Fig. 4. The XRD pattern of the Ni-P (a) and Ni-P/ZnO (b) coatings.

deposited from bath # 3) and pure Ni-P coatings are shown in Fig. 4. It is shown that nano-particles incorporation in the Ni-P matrix has not been effective on the structure of the composite coating and the XRD patterns of the both composite and pure Ni-P coatings show an amorphous phase.

3. 5. Electrochemical Corrosion Behavior of the Ni-P and Ni-P/ZnO Coatings

Taffel polarization curves for both Ni-P and

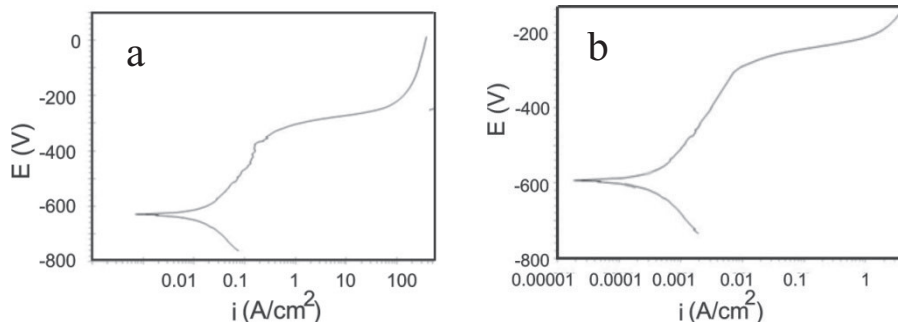


Fig. 5. Taffel polarization curves for Ni-P, a, and Ni-P/ZnO, b.

Ni-P/ZnO coatings are shown in Fig. 5. Corrosion current and corrosion potential quantities extracted from these curves are shown in table 3.

It is seen that ZnO nano-particles addition to the Ni-P matrix has enhanced the corrosion resistance of the coatings. Fig. 6 shows the nyquist diagrams of the coatings obtained from EIS test. To evaluate the electrochemical corrosion parameters, the equivalent circuit seen in Fig. 7 is used [11 and 19]. R_s , R_{ct} , and CPE parameters demonstrate solution resistance, charge transfer resistance, and constant phase element respectively. CPE is a measure of double layer capacitance which is aberrant from ideal capacitance [20 and 21].

As it is seen from table 4. Ni-P/ZnO coating shows a higher charge transfer resistance in comparison to Ni-P coating, which is in agreement with the polarization results. This increase in corrosion resistance via incorporation of ZnO nano-particles may be due to a decrease in the electrochemically-active area of the coating surface [22].

Table 3. Corrosion current and potential of the coatings.

Sample	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)
Ni-P	-641/52	0/000493
Ni-P/nanoZnO	-605/35	0/0000443

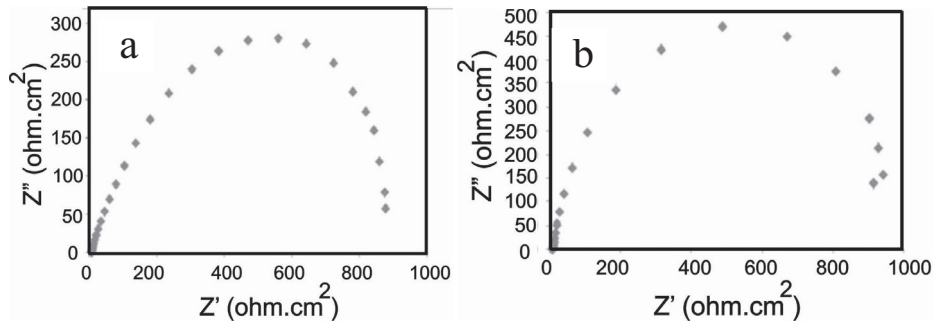


Fig. 6. Nyquist diagrams of the Ni-P (a), and Ni-P/ZnO coatings (b).

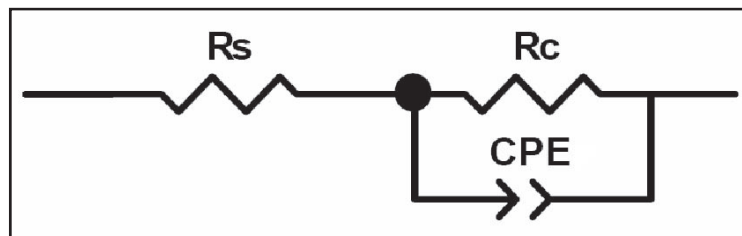


Fig. 7. Equivalent circuit used to obtain the electrochemical corrosion parameters from EIS results.

Table 4. Electrochemical corrosion parameters obtained from EIS results for Ni-P and Ni-P/ZnO coatings.

coatings	CPE		R_c	R_s
	CPE-P	CPE-T		
Ni-P	0/64562	$7/0646 \times 10^{-5}$	91/05	4/658
Ni-P/nanoZnO	0/8789	$6/23 \times 10^{-5}$	7/946	7/803

4. CONCLUSIONS

1. Since bath decomposition occurs at higher concentrations of nano-ZnO, the maximum possible amount of ZnO nano-particles, which can be added to the electroless nickel phosphorous plating bath is 2 g/L;
2. By incorporating ZnO nano-particles in electroless Ni-P coatings, surface morphology changes from smooth to an uneven profile; this effect is intensified with the excess nano-particles incorporated in the coating;
3. Incorporation of ZnO nano-particles does not change the coating structure and XRD analysis shows an amorphous phase in the presence and absence of ZnO nano-particles;
4. Incorporation of ZnO nano-particles increased the corrosion resistance which may be due to the decrease in the electrochemically-active area of the coating surface.

REFERENCES

1. Huang, C. Y., Mo, W. W., Roan, M. L., "Studies on the influence of double-layer electroless metal deposition on the electromagnetic interference shielding effectiveness of carbon fiber/ABS composites", *Surf. Coat. Technol.*, 2004, Vol. 184, pp. 163-169.
2. Paunovic, M., "Fundamentals of electrochemical deposition", Wiley, 2006, pp. 46-57.
3. Apachitei, L., Tichelaar, F. D., Duszczuk, J., Katgerman, L., "Solid-state reactions in low-phosphorus autocatalytic NiP-SiC coatings", *Surf. Coat. Technol.*, 2001, Vol. 148, pp. 284-295.
4. Grosjean, A., Rezrazi, M., Takadom, J., "Hardness, Friction and wear characteristics of nickel-SiC electroless composite deposits", *Surf. Coat. Technol.*, 2001, Vol. 137, pp. 92-96.
5. Balaraju, J. N., Sankara Narayanan, T. S. N., Seshadri, S. K., "Electroless Ni-P composite coatings", *Appl. Electrochem.*, 2003, Vol. 33, pp. 1241-1242.
6. Wang Ye, R., Ma, W. C., Wang, C., "Preparation and characterization of nanodiamond cores coated with a thin Ni-Zn-P alloy film", *Mater. Character.*, 2008, Vol. 59, pp. 108-111.
7. Stojak, J. L., Fransaer, J., Talbot, J. B., "Review of electrocodeposition", *Advances in Electrochemical Science and Engineering (AESE)*, 2002, Vol. 7, pp. 78-86.
8. Li, Z. H., Wang, X. Q., Wang, M., Wang, F. F., Ge, H. L., "Preparation and tribological properties of the carbon nanotubes-Ni-P composite coating", *Tribol. Int.*, 2006, Vol. 39, pp. 953-957.
9. Wang, L. Y., Tu, J. P., Chen, W. X., Wang, Y. C., Liu, X. K., Olk, C., Cheng, D. H., Zhang, X. B., "Friction and wear behavior of electroless Ni-based CNT composite coatings", *Wear*, 2003, Vol. 254, pp. 1289-1293.
10. Chen, X. H., Chen, C. S., Xiao, H. N., Liu, H. B., Zhou, L. P., Li, S. L., Zhang, G., "Dry friction and wear characteristics of nickel/carbon nanotube electroless composite deposits", *Tribol. Int.*, 2006, Vol. 39, pp. 22-28.
11. Balaraju, J. N., Sankara Narayanan, T. S. N., Seshadri, S. K., "Evaluation of the corrosion resistance of electroless Ni-P and Ni-P composite coating by electrochemical impedance spectroscopy", *Solid. State. Electrochem.*, 2001, Vol. 5, pp. 334-338 .
12. Kalavati, J. N., Rajam, K. S., "Influence of particle size on the microstructure, hardness and corrosion resistance of electroless Ni-P-Al₂O₃ composite coatings", *Surf. Coat. Technol.*, 2006, Vol. 200, pp. 3933-3941.
13. Huang, Y. S., Zeng, X. T., Hu, X. F., Liu, F. M., "Corrosion resistance properties of electroless nickel composite coatings", *Electrochim. Acta.*, 2004, Vol. 41, pp. 4313-4319.
14. Bigdeli, F., Allahkaram, S. R., "An investigation on corrosion resistance of as-applied and heat treated Ni-P/nanoSiC coatings", *Mater. Des.*, 2009, Vol. 30, pp. 4450-4453.
15. Novakovic, J., Vassiliou, P., "Vacuum thermal treated electroless NiP-TiO₂ composite coatings". *Electrochim. Acta.*, 2009, Vol. 54, pp. 2499-2503.
16. ASTM International", Standard practice for preparing, cleaning, and evaluating corrosion test specimens", In: ASTM, G1, 1999.
17. Balaraju, J. N., Rajam, K. S., "Electroless deposition and characterization of high phosphorus Ni-P-Si₃N₄ composite coatings", *Int. J. Electrochem. Sci.*, 2007, Vol. 2 , pp. 747-761.
18. Novakovic, J., Vassiliou, P., Samara, K. L., Argyropoulos, T., "Electroless NiP-TiO₂ composite coatings: their production and properties", *Surf. Coat. Technol.*, 2006, Vol. 201, pp. 895-901.
19. Elsener, B., Crobu, M., Scorciapino, M. A., Rossi, A., "Electroless deposited Ni-P alloys: corrosion resistance mechanism", *J. Appl. Electrochem.*, 2008, Vol. 38, pp. 1053-1060.
20. Hosseini, M., Mertens, S. F. L., Arshadi, M., "Synergism and antagonism in mild steel corrosion inhibition by sodium dodecylbenzenesulphonate and hexamethylenetetramine", *Corros. Sci.*, 2003, Vol. 45, pp. 1473-1459.
21. Ma, H., Cheng, X., Li, G., Chen, S., Quan, Z., Zhao, S., Niu, L., "The influence of hydrogen sulfide on corrosion of iron under different

- conditions”, *Corrosion Science*, 2000, Vol. 42, pp. 1668-1683.
22. Rabizadeh, T., Allahkaram, S. R., “Corrosion resistance enhancement of Ni-P electroless coatings by incorporation of nano-SiO₂ particles”, *Materials and Design*, 2011, Vol. 32, pp. 132-138.