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Short Communication

Corrosion Resistance of Nickel-Phosphorus/Nano-ZnO Composite Multilayer Coating Electrodeposited on Carbon Steel in Acidic Chloride Environments

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In this study, a multilayer nickel-phosphorus (Ni-P)/nano-ZnO composite multilayer coating electrodeposited on carbon steel (CS) substrate was investigated for higher corrosion resistance and surface hardness. Scanning electron microscopy, X-ray diffraction and energy-dispersive X-ray spectroscopy analysis were employed to consider the microstructure, surface morphology and composition of the samples. The polarization and electrochemical impedance spectroscopy (EIS) tests were used to measure the corrosion resistance of the Ni-P/n-ZnOcomposite multilayer coated CS and its heat treatment in acidic chloride environment. The results showed that the multilayer ZnO nanostructures and Ni-P coatings on CS substrates indicated an excellent corrosion protection behavior because of the ceramic protective barrier and higher hardness on the metal surface. The corrosion protection of heat-treated Ni-P/n-ZnO coated CS revealed a lower I_{corr} and higher E_{corr} than the other samples which can be related to the considerable enhancement of hardness in the Ni-P/n-ZnOcomposite multilayer coating by heat treatment.

Keywords: Electrodeposition; Multilayer coating; Carbon steel; Heat treatment; Corrosion behavior

1. INTRODUCTION

Corrosion is the metal deterioration because of its reaction with a corrosive media, such as carbon dioxide, fluorine, chlorine, oxygen, etc[1, 2]. Damages to steel structures and alloys can lead to economic consequences such as replacement, loss of materials, repair, environmental pollution and safety [3]. Carbon steel (CS) is a widely used material and a very important material which plays a significant role as fundamental material in the metallurgical industries [4]. There are many methods to protect CS against corrosion in corrosive environments. In order to protect metal from corrosion, organic material depositions have been extensively used in the industry [5, 6]. Coatings as a considerable technique which indicates excellent corrosion resistance in various industrial environments. Due to good electrical and thermal properties of semiconductor materials, many researchers have focused on their corrosion resistance ability as coating materials [7]. Furthermore, they have better resistant to erosion, wear, oxidation and corrosion then metals in aggressive and high temperature environments [8, 9]. Hence, metal oxide films such as alumina, silica, Titania and ZnO can be coated on metal substrates to advance their surface properties [10]. Electrodeposition method of Ni-P coatings is a well-known commercial route that has found many applications in numerous fields because of its excellent properties in coatings such as good lubricity, high wear resistance, high corrosion resistance, acceptable ductility and high hardness [11].

Electrochemical techniques have been broadly used by many researchers to investigate the corrosion resistance of materials. These systems like electrochemical impedance spectroscopy (EIS) method, have been revealed to be a compelling and efficient tool for considering corrosion behavior of coated steel substrates [12, 13]. Composite multilayer coatings on carbon steel have been investigated to enhance corrosion protection behavior in corrosive environments. However, enhancing the corrosion resistance by multilayer coating semiconductor based materials remains a challenge.

In this study, the Nickel-Phosphorous (Ni-P) electrodeposited on ZnO/CS substrate was investigated for higher corrosion resistance and surface hardness. SEM, XRD, EDX analysis were employed to consider the micro structure, surface morphology and composition of the samples. The polarization and EIS tests were used to measure corrosion resistance of the Ni-P/n-ZnO coated CS and its heat treatment in acidic chloride environment.

2. MATERIALS AND METHODS

An AISI 1045 carbon steel (CS) substrates as a cathode with a 20×20 mm dimension were used for electrodeposition process. Before electrodepositing, the samples were continuously ground with SiC sheets down to 2500#. Then, the substrates were degreased by acetone in an ultrasonic cleaner and washed in distilled water for 30 min., and finally dried by a hot air stream.

A potentiostatic technique was used to grow ZnOcoatedon CS substrates. A standard three electrode electrolytic cell was employed which contained CS substrate, a saturated calomel electrode and pure zinc as the working, reference and counter electrodes, respectively. The ZnO coated on substrate was gained in a stirred (200 rev min^{-1}) solution of 0.1 M $Zn(NO_3)_2$.6H2O at 90 ^{o}C. The applied potential and deposition time were kept at -0.9 V and 30 min, respectively. After deposition, the specimens were rinsed with DI water and cleaned in ethanol solution.

Table 1. Electrodeposition conditions and bath compositions

$NiSO_4.6H_2O$	**75 g/L**
$NiCl_2.6H_2O$	25 g/L
H_3PO_3	20 g/L
H_3PO_4	35 g/L
Temperature	80 ^{o}C
pH	1
Deposition time	30 min
Current density	0.1 A/cm^2

In order to prepare Ni-P/n-ZnO/CS sample, the ZnO/CS substrate, a platinum plate and a saturated calomel electrode were utilized as the working electrode, counter electrode and reference electrode, respectively. The electrodeposition conditions and bath composition are revealed in Table 1.

In order to study of heat treatment effect, the Ni-P/n-ZnO/CS were located in a tube furnace by an argon gas flow to avoid the oxidation of the sample. The sample was maintained at 500 ^{o}C for 60 min at a 3 ^{o}C/min heating/cooling rate to reach maximum hardness. Then, the sample was cooled to ambient temperature.

Electrochemical analysis of the samples was carried out by electrochemical impedance spectroscopy (EIS) technique. A conventional three-electrode cell was applied for the measurements which contain the coated CS substrate as working electrode, a platinum wire as a counter electrode and a saturated calomel electrode as the reference electrode with acidic chloride environments (3 wt% NaCl + 1.0 M HCl) as the working electrolyte. The EIS analysis was done in a frequency range of 0.01 Hz to 0.1 MHz.The potentiodynamic polarization (CorrTest Instruments Corp., Ltd., China) measurement was performed at 1 mV/s scanning rate from 0.25V. The morphology of the Ni-P/n-ZnO/CS substratewas analyzed by scanning electron microscopy (SEM, Zeiss Supra 40VP). Crystallinity analysis of the coated CS was performed with Xpert Pro X-ray diffractometer with 1.5404 Å (Cu Kα) in wavelength and 40KV/30 mA in power.

3. RESULTS AND DISCUSSION

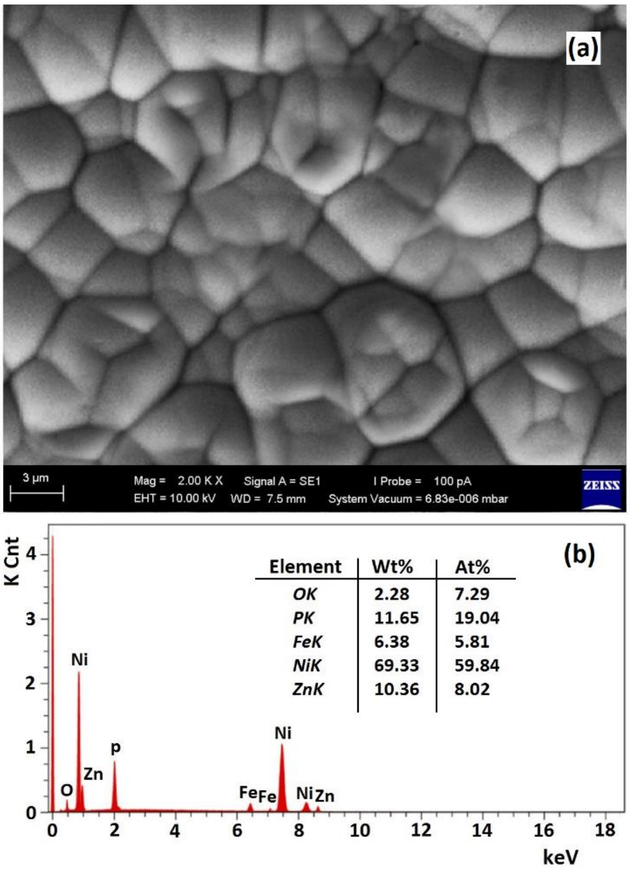

Figure 1. (a) FESEM image and (b) EDX spectrum of Ni-P/n-ZnO composite multilayer coated on CS

Figure 1 shows the surface morphology results and EDX analysis of Ni-P/n-ZnOcomposite multilayer coating electrodeposited on CS. As shown in figure 1a, the coating is composed of uniform, smooth, compact, and grayish bright without noticeable defects such as peeling, cracking, bubbling, pitting, or peeling. Furthermore, the electrodeposited Ni-P/n-ZnOcomposite multilayer coatings show good adherence on the CS substrate. Figure 1b indicates the EDX results of the sample which proved the presence of nickel, phosphorus, oxygen and zinc in the thin layer coating. As shown in figure 1b, the atomic ratio between Ni and P to be close to 3:1. The presence of Fe in the film can be attributed to the substrate effect to eliminate charging effects.

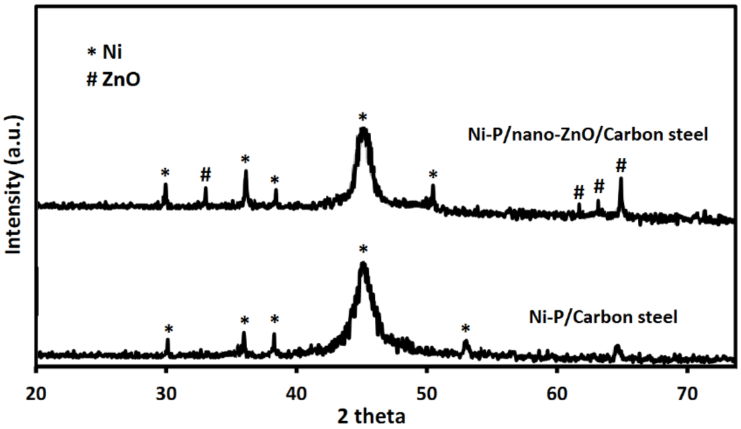

Figure 2. XRD pattern of the Ni-P/CS and Ni-P/n-ZnO/CS substrate

The XRD diffraction of Ni-P and Ni-P/n-ZnOcomposite multilayer coated on CS substrate are shown in figure 2. In the XRD pattern, the peaks revealed the Ni-P and Ni-P/n-ZnOcomposite multilayer prepared under the same experimental conditions in 20-75° angle range. The XRD pattern of the samples exhibited amorphous nature of the Ni-P coating on the CS substrates.

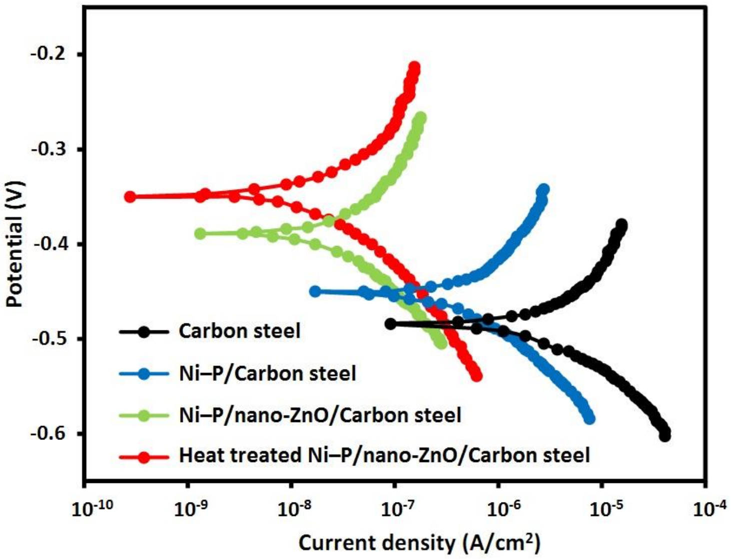

Figure 3. Polarization plots of uncoated CS, Ni-P/CS, Ni-P/n-ZnO/CS samples and heat-treated Ni-P/n-ZnO/CS sample

The polarization plots attained for uncoated CS, Ni-P/CS, Ni-P/n-ZnO/CS specimens and heat-treated Ni-P/n-ZnO/CS sample are indicated in Figure 3. As shown in figure 3 , the anodic polarization curves are considered by passive zones at all samples, indicating that the passive layers have obviously shaped on the surface of coated CS substrate in acidic chloride environments [14]. Besides, a considerable shift had occurred in corrosion potential to a positive direction which exhibited that the dissolution of anodic metal was effectively retarded using the coating materials [15]. The electrochemical parameters achieved from the polarization diagrams such as corrosion current density (I_{corr}), corrosion potential (E_{corr}) and cathodic and anodic Tafel slopes (b_c&b_a) are shown in Table 2. As shown, the corrosion potential (E_{corr}) of the Ni-P/n-ZnOcomposite multilayer coated sample is - 0.386 V, which was more positive than Ni-P coated and uncoated specimens. It can be attributed to the more thermodynamically steady structure than the others [16]. In the cathodic domain, as seen in Table 2, the values of b_c show small changes with coating layers on CS, which indicates that the addition of the Ni-P and n-ZnO layers hindered the acid attack on the CS. In anodic domain, the values of b_a decreases with coating Ni-P and n-ZnO layers on CS. The shift in the anodic Tafel slope b_a might be attributed to the modification of anodic dissolution process due to the adsorption of inhibitor molecules on the active sites [17].

Table 2. I_{corr},E_{corr}, b_c *and* $b_a$of uncoated CS, Ni-P, Ni-P/n-ZnO coated samples and heat-treated Ni-P/n-ZnO/CS sample

Samples	I_{corr}(μA/cm^2)	E_{corr} (V)	b_c(mVdec^{-1})	-b_a (mVdec^{-1})
Uncoated CS	3.4	-0.486	202.2	162.4
Ni-P/CS	0.85	-0.448	214.1	144.1
Ni-P/n-ZnO/CS	0.06	-0.386	195.2	105.6
Heat-treated Ni-P/n-ZnO/CS	0.02	-0.348	188.9	87.2

CS was found to be active in dissolution state and had the maximum cathode current density. Ni–P coating significantly decreased the cathodic and anodic current density of the CS substrate. This indicated that a problem occurred with the migration contribution of electroactive species to the steel surface. Thus, it can be proposed that the coating of Ni-P can block the steel surface and act as a strong dielectric strength [18]. Furthermore, the corrosion protection of coating layer can be related to the inactivation and amorphous nature of Ni-P sediments [19]. Amorphous steels have better corrosion resistance than the multicrystalline materials because they do not have grain boundaries which results in the formation of a glassy passive layer on their surfaces. The more reduction of cathodic/anodic current densities were observed in Ni-P/n-ZnO/CS specimen than that of Ni-P which may be accredited to the less accessible metallic region for the corrosive environment in Ni-P/n-ZnO/CS specimen. Metallic sites are appropriate places to reduce active species, especially in acidic environments. Therefore, reduction of some metallic sites leads to a reduction in the amount of sites which are ready to be dissolved, resulting a decrease in anodic reactions. Moreover, it was found that Heat-treated Ni-P/n-ZnO/CS indicated a lower $I_{corr}$and higher E_{corr} than the other samples. It can be related to the considerable enhancement of hardness in the Ni-P/n-ZnOcomposite multilayer coating by heat treatment which resulted ina bettercorrosion resistance [20]. Due to the particle hardening, the heat-treated Ni-P/n-ZnOcomposite multilayer coatings obtained higher values of microhardness than the as-deposited sample. It can be attributed to the large number of Ni3P intermetallic precipitates [21]. According to the literature [22, 23], it is obvious that the size of Ni_3P phase and the chemical composition can affect the hardness and microstructure of the Ni-P coating.

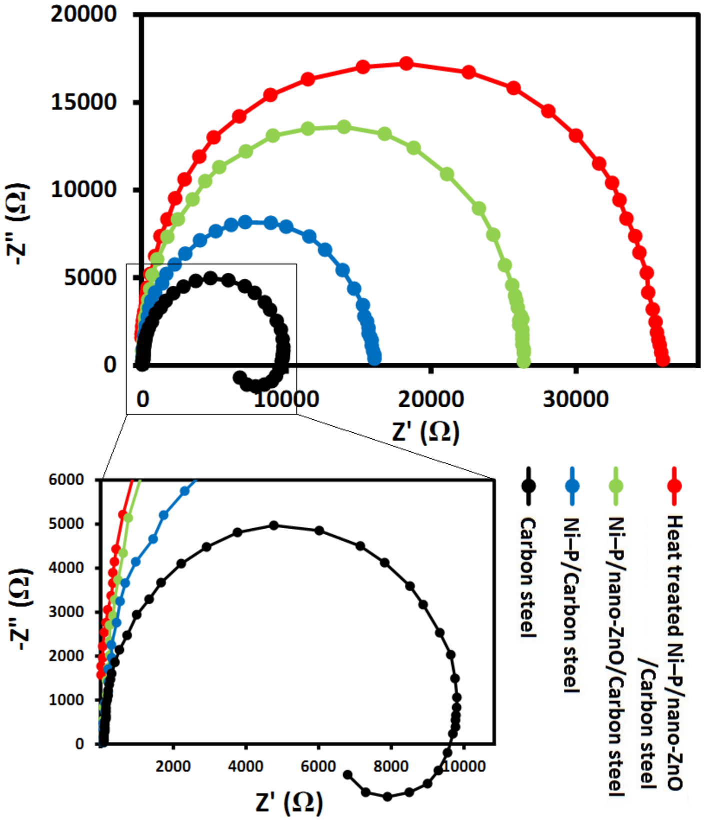

Figure 4. Nyquist plots of bare CS, Ni-P/CS, Ni-P/n-ZnO/CS samples and heat-treated Ni-P/n-ZnO/CS sample

Figure 4 reveals Nyquist plots of uncoated CS, Ni-P/CS, Ni-P/n-ZnO/CS and heat-treated Ni-P/n-ZnO/CS sample in acidic chloride environment. The key difference between the EIS curves of the uncoated and coated CS is the occurrence of an induction loop in the uncoated specimen, which shows the formation of $FeCO_3$ as corrosion products on the steel surface [24, 25]. The Nyquist diagrams for uncoated CS, Ni-P/CS, Ni-P/n-ZnO/CS samples and heat-treated Ni-P/n-ZnO/CS sample contain only one single semicircle at high frequency suggesting the occurrence of the charge-controlled reactions. Furthermore, the existence of only one semicircle indicates that the corrosion procedure of the coated specimens includes one-time constant demonstrating the occurrence of a double-layer in electrolyte/ coating interface [26]. The Bode diagrams attained from the EIS results were revealed in Figure 5. As shown in Figure 5, heat-treated Ni-P/n-ZnO/CS sample indicates the best performance to inhibit the corrosion behavior in acidic chloride environment. The appearance of a maximum phase angle and an inflection point in the Bode plots confirm that the process includes a single time constant which is in agreement with the reports by other researchers [27].

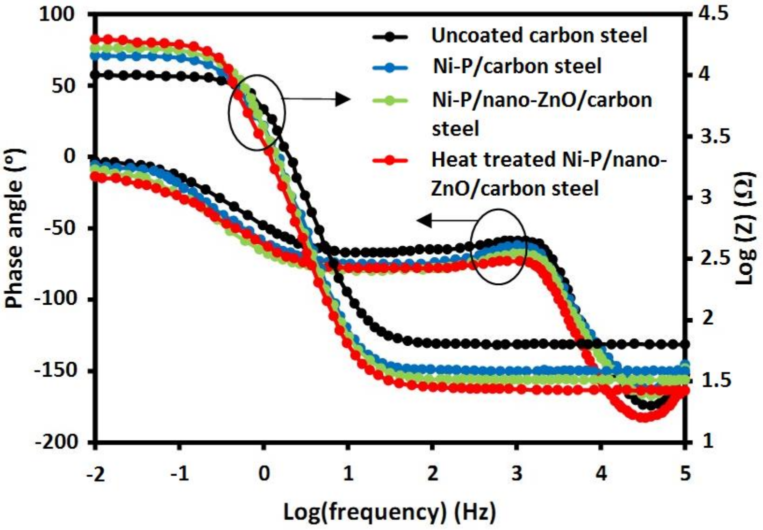

Figure 5. Bode plots of uncoated CS, Ni-P/CS, Ni-P/n-ZnO/CS samples and heat treated Ni-P/n-ZnO/CS sample

The preferential dissolution of Ni as a proposed mechanism had led to the enrichment of P in the surface layer which had a reaction with water to form an adsorption configuration of hypophosphite anions [28]. This layer prevents water from reaching the electrode surface, thus stopping the hydration process of Ni, which was investigated the first step in forming a passive Ni film [29]. The equivalent circuit model used is indicated in Figure 6.

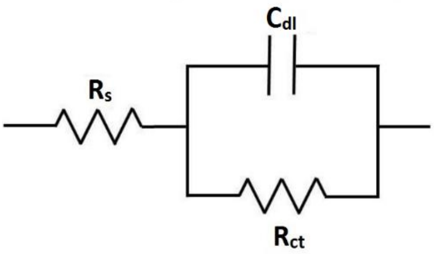

Figure 6. Equivalent circuit model

Where R_s is the resistance of solution [30].R_{ct} and C_{dl} are charge transfer resistance in steel surface and double-layer capacitance, respectively [31]. The R_{ct}observed for uncoated CS, Ni-P/CS, Ni-P/n-ZnO/CS and heat-treated Ni-P/n-ZnO/CS sample were 10.58, 16.7, 27.6 and 36.8 kΩcm^2, respectively. The results show a better performance of corrosion resistance for Ni-P/n-ZnOcomposite multilayer coating sample compared to uncoated and Ni–P coated CS which may be related to the reduction of the effective metallic region prone to corrosion.

Moreover, the higher values obtained from R_{ct} in the heat-treated Ni-P/n-ZnO/CS sample indicated that the coating had more ability in corrosion protection.

The C_{dl} observed for uncoated CS, Ni-P/CS, Ni-P/n-ZnO/CS and heat-treated Ni-P/n-ZnO/CS sample were 7.2, 5.6, 3.8 and 1.7 µFcm^{-2}, respectively. The smaller $C_{dl}$for heat treated Ni-P/n-ZnO/CS sampleindicated that the annealing treatment had shown more improvement in the corrosion resistance ability of the Ni-P/n-ZnO coating. These findings are in good accordance with the polarization results.

4. CONCLUSIONS

An electrochemical technique was used to grow ZnO and Ni-P multilayer coatings on CS substrates to investigatethe corrosion behavior and surface hardness on steel. SEM, XRD and EDX analysis were employed to consider the micro structure, surface morphology and composition of the samples. The polarization and EIS tests were used to measure corrosion resistance of the Ni-P/n-ZnOcomposite multilayer coated on CS and its heat treatment in acidic chloride environment. The corrosion potential of the Ni–P/n-ZnO coated sample was -0.386 V, which was more positive than Ni-P coated and uncoated steel substrates which can be attributed to the more thermodynamically steady structure than the others. The electrochemical results showed that the heat-treated Ni-P/n-ZnO/CS indicated a lower I_{corr} and higher E_{corr} than the other samples which can be related to the considerable enhancement of hardness in the Ni-P/n-ZnOcomposite multilayer coating by heat treatment due to the large number of Ni3P intermetallic precipitates.

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References

1. J.T. Bauer, X. Montero, M. Schütze and M.C. Galetz, *Surface and Coatings Technology*, 285(2016)179.
2. V.J. Pulikkottil, S. Chidambaram, P. Bejoy, P. Femin, P. Paul and M. Rishad, *Journal of pharmacy & bioallied sciences*, 8(2016)S96.
3. A. Kahyarian, B. Brown and S. Nesic, *Corrosion Science*, 129(2017)146.
4. F. Ma, Y. Zhang, H. Wang, W. Li and B. Hou, *International Journal of Electrochemical Science*, 13(2018)235.
5. J. Mosa, N. Rosero-Navarro and M. Aparicio, *RSC Advances*, 6(2016)39577.
6. F. Husairi, J. Rouhi, K. Eswar, A. Zainurul, M. Rusop and S. Abdullah, *Applied Physics A*, 116(2014)2119.
7. Y. Xiao, J. Gu and J. Zhang, *Arabian Journal for Science and Engineering*, 42(2017)4273.
8. H. Wang, J. Xie, X. Jiang, Z. Zhu, Y. Wang, M. Chamas, M. Duan and J. Tang, *International Journal of Electrochemical Science*, 11(2016)10278.
9. J. Rouhi, S. Mahmud, S.D. Hutagalung and S. Kakooei, *Journal of Micro/Nanolithography, MEMS, and MOEMS*, 10(2011)043002.
10. I. Santana, A. Pepe, E. Jimenez-Pique, S. Pellice, I. Milošev and S. Ceré, *Surface and Coatings Technology*, 265(2015)106.
11. L. Elias, K.U. Bhat and A.C. Hegde, *RSC Advances*, 6(2016)34005.
12. Y. Qian, Y. Li, S. Jungwirth, N. Seely, Y. Fang and X. Shi, *International Journal of Electrochemical Science*, 10(2015)10756.
13. R. Dalvand, S. Mahmud and J. Rouhi, *Materials Letters*, 160(2015)444.

14. R. Antunes, M. De Oliveira and I. Costa, *Materials and Corrosion*, 63(2012)586.
15. S. Kakooei, J. Rouhi, E. Mohammadpour, M. Alimanesh and A. Dehzangi, *Caspian Journal of Applied Sciences Research*, 1(2012)16.
16. L. Song, Y. Wang, W. Lin and Q. Liu, *Surface and Coatings Technology*, 202(2008)5146.
17. A. Ehsani, M.G. Mahjani, R. Moshrefi, H. Mostaanzadeh and J.S. Shayeh, *RSC Advances*, 4(2014)20031.
18. J. Balaraju, T.S. Narayanan and S. Seshadri, *Journal of solid state electrochemistry*, 5(2001)334.
19. J. Balaraju, V.E. Selvi, V.W. Grips and K. Rajam, *Electrochimica acta*, 52(2006)1064.
20. F. Husairi, J. Rouhi, K. Eswar, C.R. Ooi, M. Rusop and S. Abdullah, *Sensors and Actuators A: Physical*, 236(2015)11.
21. P.I.A.N. JEKLA, *Heat Treatment*, 413(2017)417.
22. K. Keong, W. Sha and S. Malinov, *Surface and Coatings Technology*, 168(2003)263.
23. M. Buchtík, M. Krystýnová, J. Másilko and J. Wasserbauer, *Coatings*, 9(2019)461.
24. M.A. Chidiebere, E.E. Oguzie, L. Liu, Y. Li and F. Wang, *Journal of Dispersion Science and Technology*, 36(2015)1115.
25. J. Rouhi, C.R. Ooi, S. Mahmud and M.R. Mahmood, *Electronic Materials Letters*, 11(2015)957.
26. A.M. Kumar and Z.M. Gasem, *Progress in Organic Coatings*, 78(2015)387.
27. Y. Lin, A. Singh, E.E. Ebenso, Y. Wu, C. Zhu and H. Zhu, *Journal of the Taiwan Institute of Chemical Engineers*, 46(2015)214.
28. A. Barba-Pingarrón, R. Valdez-Navarro, F. Sánchez-De Jesus, A.M. Bolarín-Miró, R. González-Parra, A. Covelo-Villar, M.Á. Hernández-Gallegos and C. Domínguez-Ríos, *Journal of Surface Engineered Materials and Advanced Technology*, 7(2017)86.
29. A. Buyuksagis, S. Kara and A. Aksut, *Protection of Metals and Physical Chemistry of Surfaces*, 51(2015)155.
30. K.M. Emran and H. AL-Refai, *International Journal of Electrochemical Science*, 12(2017)6404.
31. N. Naderi, M. Hashim, K. Saron and J. Rouhi, *Semiconductor Science and Technology*, 28(2013)025011.