Indian Journal of Chemical Technology
Vol. 30, January 2023, pp. 76-84
DOI: 10.56042/ijct.v30i1.34758

Effect of electroplating time on microstructure, corrosion and wear behaviour of Ni-P-W-TiO_2 coating

Sajjad Sadeghi & Hadi Ebrahimifar*

Department of Materials Engineering, Faculty of Mechanical and Materials Engineering,
Graduate University of Advanced Technology, 7631133131, Kerman, Iran.

E-mail: h.ebrahimifar@kgut.ac.ir

Received 5 May 2020; accepted 4 August 2020

Ni-P-W-TiO_2 coating has been deposited on the AISI 304L steel substrate using the electroplating method. Electroplating has been performed at 30, 45, and 60 min, and the effect of electroplating time on microstructure, corrosion and wear behaviour has been investigated. The coatings have been characterized by use of scanning electron microscopy (SEM). In order to investigate corrosion resistance, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests have been used in 3.5% of NaCl aqueous solution. A pin on disk test has been used to test the wear resistance of uncoated and coated samples. Sample micro-hardness has also been measured by the Vickers hardness test. Examination of the microstructure has shown that the best time for deposition is 45 min. The results of potentiodynamic polarization and electrochemical impedance spectroscopy tests are also consistent with microscopic images, and the results have shown that the coating created within 45 min has the highest corrosion resistance (7058 $\Omega.cm^2$) compared to coated sample within 30 (4142 $\Omega.cm^2$) and 60 (3059 $\Omega.cm^2$) minutes. Also, the results of the wear test and micro-hardness have shown that composite coating formed within 45 minutes has the highest wear resistance and micro-hardness (677 Vickers) compared to coated sample within 30 (257 Vickers) and 60 (638 Vickers) minutes.

Keywords: Ni-P-W-TiO_2 coating, Electroplating time, Potentiodynamic polarization, Electrochemical impedance spectroscopy, Wear resistance

Stainless steels are used in numerous applications due to their good performance in different environments and their relatively low price. They are used in industrial processes related to carbochemistry, petrochemical and power plants, gasification systems, combustion, aerospace, etc.[1-5]. Nickel-based coatings are promising candidates to improve the properties of stainless steels. Nickel-based coatings have important properties such as high strength and hardness, corrosion/oxidation resistance and good wear resistance[6]. The mechanical properties of these coatings can be improved by modifying the composition of the electrolyte bath, changing the operating parameters, and by combining other metal elements, fibers, and ceramic particles in nickel. Coatings from sulfate baths, which include organic additives such as saccharin, naphthalene and sulfuric acid, are hard coatings and nickel stress strains[7-9]. One of the problems with organic sulfate compounds is the fragility of sulfur. When the coating is exposed to high temperatures, sulfur fragility occurs due to the presence of sulfur in the coating. Therefore, to solve this problem, a simultaneous session of phosphorus, cobalt, etc. was suggested during deposition. By forming a solid solution (Ni_3P) during the electroplating process, the problem of coating fragility in thermal operations is solved[5]. The hardness of nickel-phosphorus alloy coatings depends on the content of phosphorus in the coating. The hardness of nickel-phosphorus coatings varies from 0 to 28% by weight with an increase in the amount of phosphorus to 310 to 520 Vickers[7, 8]. Internal stresses in nickel-phosphorus alloy coating in are both tensile and compressive forms. High tensile stresses cause distortion and cracks in the coating and reduce fatigue strength. High compressive stresses cause blisters on the surface and distortion or detachment of the coating layer. In nickel-phosphorus deposits, the internal stresses and strength of the adhesion of the layer can be improved by controlling the *p*H and electroplating time[10-13].

Researches show that the properties and structure of nickel-phosphorus coatings are affected by various electroplating factors such as electric current density, phosphorus concentration in electrolyte, time and *p*H. One of the most important parameters that affect the concentration of deposited particles in the coating, crystal size, corrosion behaviour and mechanical properties of the coating can be referred to the electroplating time[9, 10].

In a study conducted by Ebrahimifar and Zandrahimi, the effect of deposition time on the microstructure and efficiency of the cathodic current of Mn-Co electrochemical deposition was investigated. In the investigation of the effect of time on microstructure, it was observed that in short times (10 min), some parts remained uncovered. At very long times (30 min) the coating was thick and the residual stresses in the coating led to cracking of the coating. In addition, in the long run, adverse reactions led to cracking of the coating[11].

The Ni-W/TiNnanocomposite coating was also deposited on the steel substrate in a study conducted by Li et al., and the mechanical behaviour and wear resistance of the coating were investigated. The results of their research showed that choosing the wrong coating time reduces the amount of deposited TiN particles in the coating and reduces the mechanical properties and corrosion resistance of the coating[12].

Wang and colleagues examined the effect of deposition time on the growth of ZrC/SiC composite coating. The results of their research showed that the short deposition times of only SiC carbide particles are deposited in the coating and as the deposition time increases, the ZrC carbide particles are also deposited in the coating[13].

According to previous studies and survey of literatures, no Ni-P-W-TiO$_2$ coating has been produced on the AISI 304L so far. The presence of TiO$_2$ is expected to improve the properties of Ni-P-W coatings.

In the present study, the Ni-P-W-TiO$_2$ composite coating on the AISI 304L austenitic stainless steel was deposited by electroplating. After that, the effect of electroplating time on the amount of particles in coating, microstructure, corrosion behaviour and wear behaviour of the coating was investigated. Scanning electron microscopy (SEM) was used to observe the morphology. To investigate the abrasive behaviour of these coatings, a pin on disk test was performed.

Experimental Section

In this research, AISI 304L stainless steel was used as a substrate for electroplating. The chemical composition of this steel is shown in Table 1. First, AISI 304L stainless steel sheet was cut using a wire cutter with dimensions of 3mm×10mm×10mm. A 0.7 mm diameter wire was connected to one side of the sample and the connection was insulated using thermal glue. In the next step, SiC sandpaper with numbers 60, 120, 200, 500, 800, 1000, 1200 were used to polish the samples. In order to dehydration, the sample was first washed with soap and water solution and then placed in acetone solution. To activate the surface, the samples were electropolished in a solution containing 10% phosphoric acid for 2 min at current density of 80 mA.cm^{-2}. After removing the samples from the electropolish solution, the surface was thoroughly washed with distilled water, and immediately placed in electroplating bath for coating. To prepare the bath, the metal salts were first poured into water and dissolved with the help of a full magnetic stirrer. Sodium citrate, sodium hypophosphite, boric acid, and phosphoric acid were added to the bath, respectively. Titanium oxide was eventually added to the bath. After that, the solution was stirred for 6 h to stabilize with the help of a magnetic stirrer. Sodium hydroxide and sulfuric acid was used to adjust the *p*H. All experiments were performed on 100 ml of electroplating solution. A nickel plate measuring 2mm×20mm×20mm was used as the anode, which was connected to the positive pole. Samples were electroplated at 30, 45 and 60 min. After electroplating, the samples were rinsed twice with distilled water and dried using hot air flow. The composition of the electroplating bath is given in Table 2.

Table 1 — Chemical composition of AISI 304L stainless steel based on EDX analysis

Element	C	Mn	Si	P	S	Cr	Ni	Fe
Concentration (wt.%)	0.031	2.00	0.85	0.04	0.04	19.7	10.8	Bal.

Table 2 — Chemical composition and bath conditions for Ni-P-W-TiO$_2$ composite coating.

Coating mixtures		Electrodeposition parameters/materials	
$NiSO_4.6H_2O$	180.00 g/L	Current density	20 mA.cm^{-2}
$NiCl_2.6H_2O$	20.00 g/L	pH	2
Na_2WO_4	20.00 g/L	Electroplating time	30, 45, 60 min
TiO_2	20 g/L	Electroplating temperature	60±5 °C
H_3BO_3	30.00 g/L	Cathode	AISI 304L stainless steel
H_3PO_4	50 g/L	Anode	Nickel plate
$Na_3C_6H_5O_7$	40 g/L		
$NaPO_2H_2 \cdot H_2O$	30 g/L		

The scanning electron microscope (SEM) model of Cam scan MV 2300 equipped with EDX analysis was used for morphology and microstructural analysis.

In order to perform electrochemical experiments a common three-electrode cell, including a working electrode (coated or uncoated specimen), a saturated calomel electrode (SCE) was used as the reference electrode. Platinum electrode was used as an auxiliary electrode. All experiments were performed in distilled water solution containing NaCl 3.5% at ambient temperature. Potential control and current measurements were performed using an Autolab PGSTAT302N Potentiostat. Before any testing, each sample was connected to a copper wire and then sealed with epoxy resin. The sample surface was then prepared to be exposed to the solution and the samples were thoroughly rinsed with distilled water and dried with acetone. Also, before performing the electrochemical tests, the samples were immersed in the NaCl 3.5% solution for 1 hour in order to establish the equilibrium potential conditions. EIS measurements in the corrosion potential, Ecorr, and in the 10^{-2}-10^{-5} frequency range were plotted with a excitation amplitude of 5 mV for each sample. Nova and Zview software were used in the impedance tests. Nova software is used as an interface between an impedance device and a computer, and the information obtained by the device is converted into numerical information by this software. To analyze the results obtained from Nova, the information obtained from this software was transferred to Zview software and with the help of Zview, the analysis of the data's was performed. The impedance spectra were analyzed by Zview software and finally the equivalent circuit of the corrosion process was proposed.

In order to investigate the mechanical properties of coated specimens, microhardness and wear tests were carried out. The microhardness of the samples was performed using the FUTHER-TECH CORP (Japan) FM700 microhardness tester. Microhardness test of all samples was performed at 50 gr load with a stop time of 10 s and the microhardness results were measured 3 times on average. The wear test was performed through the pin on disk method according to the ASTM G99 standard. The pin was coated samples and used disk was made of 5100 carbon steel with a hardness of 64 Rockwell and a radius of 200 mm. Before the wear test, the loading test began with a force of 2 Newtons and increased by 2 Newtons every 50 meters. The experiment continued until a significant reduction in mass was observed in the samples. The wear test was performed at a speed of 0.03 m/s and a distance of 120 m. The amount of weight loss of the samples was weighed with an electronic balance and the results of the friction coefficient were calculated using CDT125 software. In order to investigate the mechanization of wear, the wear path was examined using scanning electron microscopy images.

Results and Discussion

Effect of electroplating time on the microstructure of Ni-P-W-TiO_2 coating

Figure 1 shows the SEM image of formed Ni-P-W-TiO_2 composite coating at different electroplating times, including 30, 45, and 60 min. Table 3 shows the chemical analysis of the deposited Ni-P-W-TiO_2

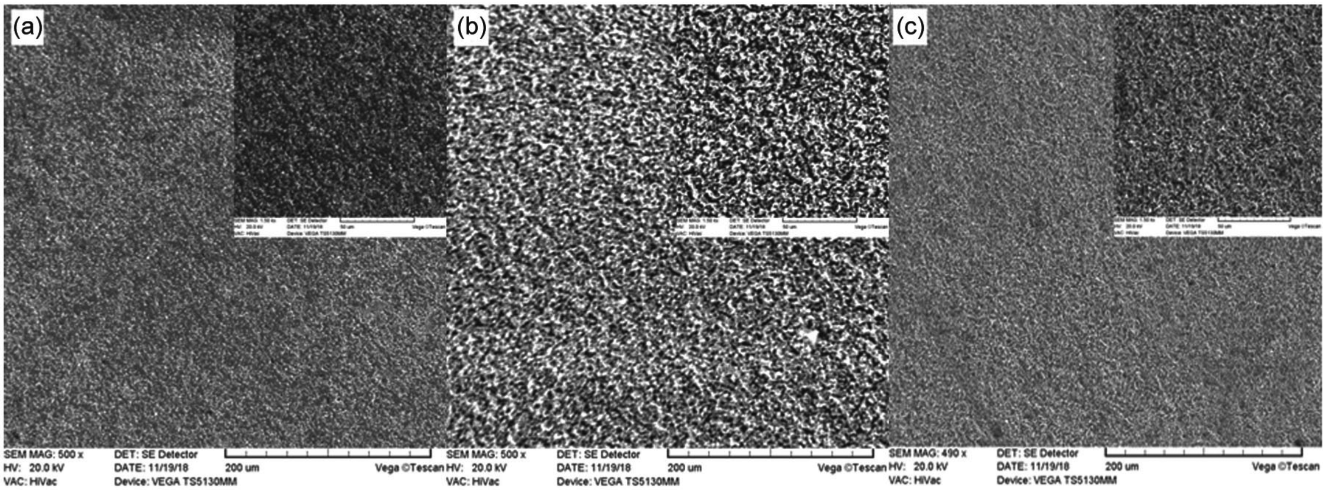

Fig. 1 — SEM surface morphology of Ni-P-W-TiO_2 coatings formed after (a) 30 min; (b) 45 min and (c) 60 min of electroplating.

Table 3 — Chemical analysis of Ni-P-W-TiO$_2$ composite coating deposited under different times.

Time (min)	Ni (wt.%)	P (wt.%)	W (wt.%)	Ti (wt.%)	O (wt.%)	Fe (wt.%)	Cr (wt.%)
30	66.32	8.02	1.04	4.32	7.29	10.37	2.63
45	68.97	7.28	2.08	7.46	14.21	-	-
60	76.94	9.67	0.1	6.98	6.41	-	-

composite coating under different time (30, 45 and 60 min). The coated sample at 30 min shows an almost uniform and continues surface [Fig. 1(a)]. There are a number of cavities on the surface of this coating. In chemical analysis of this coating, the amount of titanium deposited is 4.32 Wt.% and the amount of tungsten is 1.04 wt.% . The presence of iron and chromium elements in the chemical analysis of this coating is related to the substrate. The presence of these elements is due to the thinness of the coating, the presence of cavities and cracks in the coating. The amount of titanium deposited in this coating is 7.46 wt.% and the amount of tungsten is 2.08 wt.%, which is more than the amount of titanium and tungsten of the coating created after 30 min of electroplating. The surface of the coating created during 60 min is almost uniform, but a number of cavities are seen on the surface of this coating [(Fig. 1(c)]. The amount of titanium and tungsten deposited in this coating compared to the coating created after 45 min of electroplating is less.

The results of EDX analysis showed that with increase of electroplating time up to 45 min, caused to the increase of of titanium and tungsten. Over a longer period of time (60 min), the concentration of metal cations decreases and unwanted reactions lead to the formation of hydroxide and oxide compounds. The discoloration of the electrolyte solution is the cause of unwanted reactions that can lead to reduced current efficiency. The formed coating after 45 min of electrodeposition had the highest amount of titanium and tungsten, and iron and chromium elements were not found in the coating.

Factors such as the release of hydrogen at the cathode level and subsequent increase in *p*H near the cathode surface lead to OH^{-1} or O alignment as a precipitation of nickel-based (NH)$_2$ or NiO base hydrated salts in the coating, which leads to decrease of TiO$_2$. These intermediate phases may absorb halide ions. In the absence of halides, reactions (1), (2), and (3) can be performed to form (NiOH)$_{ads}$ on the surface of the coating. In the presence of halides at lower concentration of 0.05 M, the reaction (4) can be expressed for the formation of NiOH$^+$X^{-1} species, both of which lead to decrease of TiO$_2$ in the coating. At higher concentrations, reactions (5), (6), and (7) can be expressed for the formation of NiCl (ads) species, which leads to increase of TiO$_2$ in the coating[14-16].

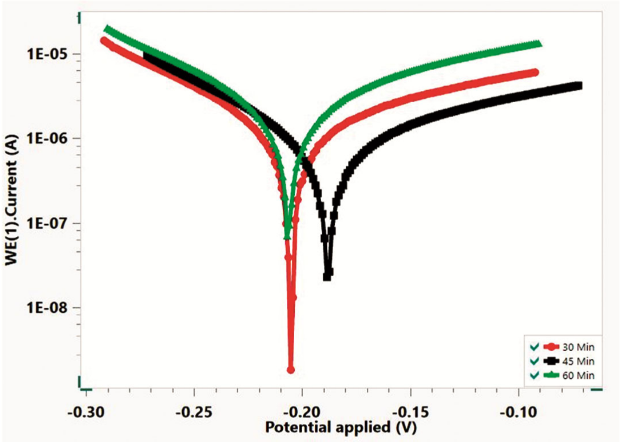

Fig. 2 — Potentiodynamic polarization curves of Ni-P-W-TiO$_2$ composite coatings formed at different times in 3.5% NaCl solution.

$$Ni^{+2} + H_2O \leftrightarrow NiOH^+ + H^+ \quad ...(1)$$
$$NiOH^+ + e^- \rightarrow (NiOH)_{ads} \quad ...(2)$$
$$(NiOH)_{ads} + H^+ \leftrightarrow Ni + H_2O \quad ...(3)$$
$$NiOH^+ + X^- \leftrightarrow NiOH^+X^- \quad ...(4)$$
$$Ni^{+2} + Cl^- \leftrightarrow NiCl^+ \quad ...(5)$$
$$NiCl^+ + e^- \rightarrow (NiCl)_{ads} \quad ...(6)$$
$$(NiCl)_{ads} + e^- \rightarrow Ni + Cl^- \quad ...(7)$$

The presence of TiO$_2$ in the composite coating reduces the residual stresses relative to the pure nickel, which depends on the particle size and the amount of particles. The thickness of Ni-P-W-TiO$_2$ composite which was coated at times of 30, 45, and 60 min was approximately 65, 150 and 135 µm. As the thickness of the deposited layer increased, the amount of internal stress decreased. The results of EDX analysis showed that the coating thickness increased with time up to 45 min.

Effect of electroplating time on corrosion behavior of Ni-P-W-TiO$_2$ coating

Figure 2 shows the potentiodynamicpolarization curves for Ni-P-W-TiO$_2$ composite coatings formed at different times of electroplating (30, 45, and 60 min)

Table 4 — Electrochemical parameters obtained from the polarization curve of Ni-P-W-TiO_2 composite coating formed at different times.

Time (min)	30	45	60
i_{Corr}(µAcm^{-2})	1.8	1.21	3.0395
E(V)	-0.20513	-0.17780	-0.2063
Corrosion rate (mm/year)	0.02093	0.014059	0.035319
Polarization resistance (Ω)	18764	27286	10589
βa (V/dec)	0.14647	0.15506	0.13866
βc (V/dec)	0.073419	0.075805	0.07938

in NaCl 3.5% solution. The corrosion parameters obtained from these graphs are obtained by linear polarization of anodic and cathodicTafel curves in the ±50 mV open circuit potential. The polarization resistance was also obtained using Stern-Geary relation[12]:

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{Corr} (\beta_a + \beta_c)} \quad \ldots (8)$$

In this regard, Rp is the resistance of polarization, βa and βc are the slopes of anodic and cathodicTafel curves, respectively, i_{Corr}, current density of corrosion. The obtained electrochemical parameters from the polarization test are given in Table 4.

The coated sample at 30 min has a corrosion current density of 1.8 µAcm^{-2}. As the electroplating time increased, the corrosion current density decreased from 1.8 µAcm^{-2} to 2.21 µAcm^{-2} in 45 minutes. Corrosion potential also shifted toward positive potentials. By reducing the electroplating time to 60 min, the corrosion current density increased to 3.0395 µAcm^{-2}. The difference between corrosion behaviors in short times is attributed to the presence of large defects in the coating and in long times is attributed to the creation of stress and defects due to high thickness[17].

As the electroplating time increased from 30 to 45 min, the corrosion current density decreased and the corrosion potential increased to positive values. This is due to the higher amount of titanium oxide in the coating. Also, the presence of cavities in the coating created within 45 min led to less corrosion resistance of this coating. Also, with increasing electroplating time, the corrosion current density increased from 45 to 60 min. As the concentration of titanium oxide particles decreased, the corrosion resistance decreased. The presence of oxide particles on the surface of the coatings increased the corrosion resistance of the surface due to the creation of a protective layer against corrosion. Also, the deposition of oxide particles in the coating prevented the expansion of cavities for corrosion and improved corrosion resistance[18].

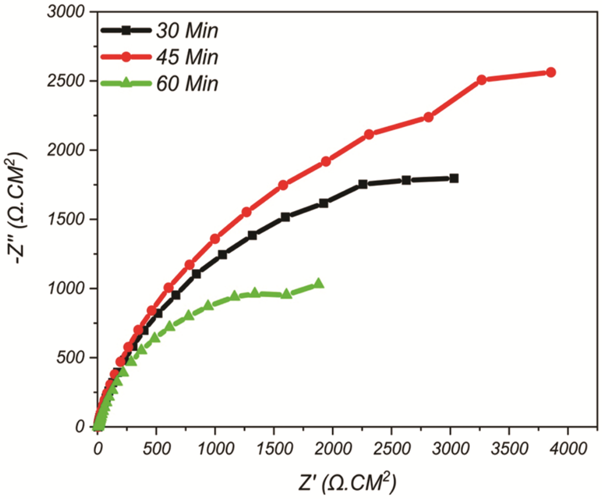

Fig. 3 — Nyquist diagram of Ni-P-W-TiO_2 composite coatings formed at different times in 3.5% NaCl solution.

The presence of TiO_2 oxide particles increased the corrosion resistance of nickel-phosphorus-tungsten composite coatings. In composite coatings, the presence of TiO_2 oxide particles in the coating structure is improved by mechanisms such as: reduction of effective surface, reduction of grain size by TiO_2 oxide particles and change in microstructure coating[16, 19].

The presence of non-conductive and noble titanium oxide particles in the composite matrix of nickel-phosphorus-tungsten coating and covering part of the coating surface with these noble particles reduced the amount of surface that was exposed to corrosive environment. These nanoparticles also sank into holes and filled micron holes and fissures. Naturally, nanoparticles have a good chance of filling these holes. This reduced the anodic dissolution and improved the corrosion resistance of the nanocomposite coatings[23, 24].

In order to study the corrosion behaviour more accurately, impedance electrochemical test was used to investigate the corrosion behaviour of Ni-P-W-TiO_2 composite coatings. Nyquist curves for coated specimens at different electroplating times are given in 3.5% sodium chloride solution in Fig. 3. Figure 4(a) and Fig. 4(b) also show bode and bode-phase curves for the tested samples, respectively. All curves are plotted in the frequency range 0.01 Hz to 10 KHz.

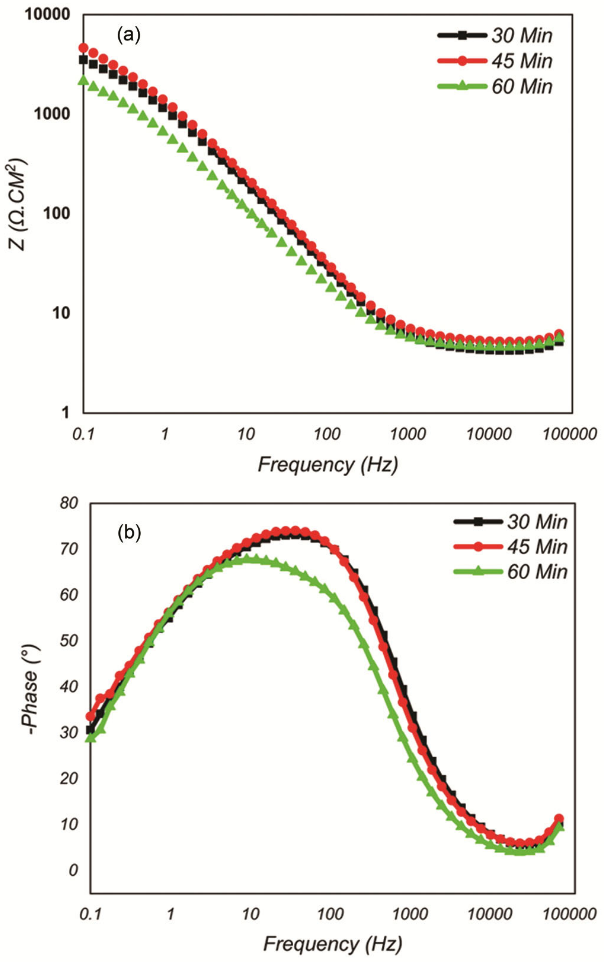

Fig. 4 — Curves of (a) Bode and (b) Bode phase for Ni-P-W-TiO$_2$ composite coatings formed at different times in 3.5% NaCl solution.

Table 5 — Electrochemical parameters obtained from electrochemical impedance for samples coated at different times.

Time (min)	R_S ($\Omega.cm^2$)	R_c ($\Omega.cm^2$)	CPE1-T ($F.cm^{-2}$)	CPE1-P ($F.cm^{-2}$)
30	3.843	4142	0.00017377	0.75175
45	4.922	7058	0.00016389	0.8381
60	4.39	3059	0.00035344	0.74833

As shown in Fig. 3, the Ni-P-W-TiO$_2$ coating, which was coated at 45 min, has the largest diameter of the semicircular. The Nyquist curve of the formed coating in 45 min at higher frequencies shows better coating performance than other coatings, indicating an increase in corrosion resistance in the composite coating. In this diagram, it is clear that the impedance of the formed coating in 45 minutes for all frequencies is better than the other coatings. Table 5 demonstrate the obtained information from the impedance curve at different times of electroplating; that R_S indicates the resistance of the solution and CPE is attributed to the capacitive ring of the charge transfer. Due to the presence of heterogeneity or microscopic roughness of the coating surface in the solid-solution joint with a constant phase element (CPE) in the circuit, the pure double layer capacitor is displaced in the circuit to provide more accurate matching[25]. R_P represents the charge transfer resistance, the value of which determines the electron transfer across the coating surface and is directly related to the corrosion rate[26].

The presence of a wide peak in the phase angle diagrams in terms of the frequency of the coated samples indicates the existence of two time constants where one of the time constants is not clearly seen. In other words, in these samples, due to the discontinuity of the coating and, of course, the contact of the corrosive environment with the underlying layer, two active electrochemical cells are formed on the surface of the coating. The first time constant at high frequencies is related to the response of the Ni-P-W-TiO$_2$ composite coating to the corrosive environment. While the second time constant at low frequencies associated with the corrosion process which is occurring in the interface of metal/solution in the cavities in the Ni-P-W-TiO$_2$ composite coating[27].

The results of fitting the equivalent circuits using the Zview software are given in Table 5. As it turns out, the impedance results are well consistent with the Tafel polarization results. In the Table 5, R_S is the solution resistance, R_P is the resistance of the coating charge transfer against the penetration of electrolyte through the defects and pores in the coating, and CPE is the constant phase element of the double layer, which is used instead of the simple capacitor. Due to the fact that the charge transfer resistance (R_C) is the same as the coating resistance (R_P), the coating formed in 45 minutes has a higher polarization resistance and, of course, a higher corrosion resistance. CPE-P is the surface disorder factor and ranges from 0.5 to 1. The CPE-P parameter is related to surface roughness, and lower values indicate higher surface roughness[27, 28]. This parameter is the lowest value for the coating formed at 60 min, so this coating creates the highest surface roughness[29, 30]. Higher CPE-T values indicate more porosity in the coating. The coating formed within 60 min has more CPE-T than other coatings, so the coating has more porosity and it is easier for electrolyte to penetrate into it. The coated sample has the lowest CPE-T value at 45 min compared to other coatings, so it has the lowest amount of porosity.

The shape of the Nyquist curves describes the type of electrochemical reactions that occur on the surface of the electrode. The similarity of the shape of this curve for different samples indicates that their corrosion mechanism is the same. The larger diameter of curvature of the Nyquist curve, for example, covered in 45 min, compared to the rest of the Ni-P-W-TiO_2 composite coatings, indicates smaller hole and porosity that interferes with the penetration of electrolyte into the coating[31]. In fact, by forming local micro-cells in the Ni-P-W composite coating containing TiO_2 ceramic particles, the corrosive environment is required to cross the semicircular path around the TiO_2 ceramic particles to reach the substrate and thus prolong the corrosion path[32]. TiO_2 ceramic particles in the matrix of Ni-P-W lead to smaller grains. Due to the long and complex corrosion path in fine grain structure compared to large grain structure, corrosion rate will be lower in fine grain state[32]. The higher the polarization resistance for the coated sample at 45 min than other samples indicates better protective properties of this coating compared to other coatings.

Effect of electroplating time on the wear resistance of Ni-P-W-TiO_2 coating

Micro-hardness of Ni-P-W-TiO_2 composite coating was measured based on the described procedure in experimental procedure. The highest hardness was related to the sample that has been electroplated for 45 min (677 Vickers). The sample, which has been electroplated for 30 min, had the hardness of 257 Vickers due to its low thickness. The 60 min electroplated sample also had the hardness of 638 Vickers. As can be seen, the value of micro-hardness increased with increasing electroplating time from 30 to 45 min, and then decreased with increasing time up to 60 min. The highest micro-hardness was related to the formed coating after 45 min of electroplating.

The hardness and wear resistance of Ni-P-W-TiO_2 composite coatings can be affected by two factors, one is TiO_2 oxide particles and the other is Ni-P-W matrix hardness. Many factors are involved in the hardness and wear resistance of coatings, such as grain size, coating thickness, and type of composition. However, the effect of TiO_2 oxide particles on the hardness and wear resistance of the coating can be divided into two types of mechanisms; first: dispersion and the amount of TiO_2 particles present in the coating; and second: hardness and size of TiO_2 particles[33, 34]. The amount of deposited TiO_2 particles on the coating formed in 45 min are more than the coating created at 30 and 60 min. That's why the hardness of the coating created in 45 min is more than other coatings. Also the measured average grain size based on the SEM images (Fig. 1) for coated samples at times of 30, 45, and 60 min was approximately 5, 2 and 3 μm. The sample that has been electroplated for 45 minutes has the lowest grain size.

The weight loss changes after the wear test for the uncoated and coated samples at different times was also measured. The weight loss of the coated sample at 30 min was equal to 30 g^{-4} and with increasing electroplating time up to 45 min, weight loss decreased. The coated sample at 45 min had the lowest weight loss (4 g^{-4}) and the weight loss increased with increasing the electroplating time (60 min) increases. The weight loss of coated sample at 60 min was 16 g^{-4}. TiO_2 particles can be removed from the surface during wear and reduce the contact surface between the pin and the composite coating. These particles play a solid lubricant role [22]. As a result, the wear resistance of the coating decreases with decreasing TiO_2. On the other hand, by increasing electroplating time (60 min), the hardness is reduced and this leads to the decrease of wear resistance. The highest weight loss was related to the 304 steel substrate and the lowest weight loss was related to the sample electroplated in 45 min. The lower weight loss of the coated specimen at 45 min after 120 m of wear is due to the more presence of the TiO_2 oxide phase in the coating.

One of the factors that affect the wear resistance is the coefficient of friction[35]. Figure 5 demonstrates the effect of electroplating time on the friction coefficient of coated samples. The highest coefficient of friction was related to the 304 steel, and electroplated sample at 45 minutes had the lowest coefficient of friction. The friction coefficient the electroplated sample at 30 minutes was unstable. This is due to the thickness of the coating and the roughness of the surface. Cracks and cavities on the surface reduce the adhesive of the coating to the substrate and the weak coating layer is broken during the wear test and fine particles are produced that are hard and abrasive. Similarly, after the production of such particles, wear performs with higher rate. This has been observed in other studies [9, 10].

This suggests that nickel, phosphorus, tungsten, and titanium oxide coatings have lower friction coefficients than steel substrates. The electroplated sample at 45 minutes showed the lowest coefficient of friction. Then, as the coating time increases, the solid lubrication decreases and the coefficient of friction increases, due to the decrease in the amount of TiO_2 particles[36, 37].

Figure 6 shows the SEM image of the Ni-P-W-TiO_2 composite coated samples at different electroplating time after wear test. The wear surface for the coated sample at 30 min had a higher depth and width than other samples. In this sample, wear grooves can be seen in some places, but in most areas the surface of the coating is seriously damaged, which is fully consistent with the micro hardness and wear diagrams. The wear mechanism for electroplated sample in 30 min is delamination. The width of the wear path is reduced by increasing the electroplating time from 30 to 45 min. The wear mechanism for the coated samples at 45 min is abrasive. As the electroplating time increased from 45 to 60 min, the wear resistance decreased due to the reduction of TiO_2 particles.

The results of Gadari's research showed that with increasing the concentration of particles inside the electrolyte, the volume percentage of the deposited particles in the coating increased, which increased the hardness of these coatings. However, in high concentrations of TiO_2 particles, due to agglomeration, the slope of hardness has decreased[38].

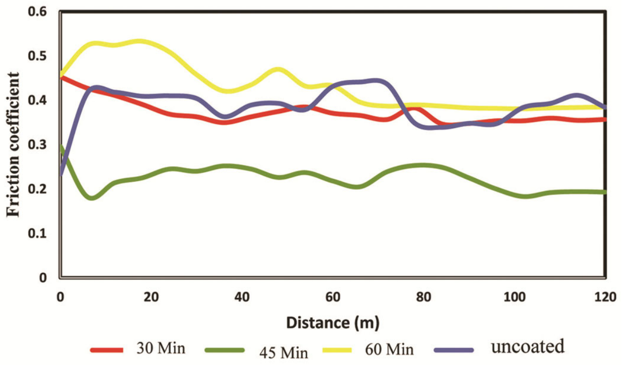

Fig. 5 — Friction coefficient as a function of wear distance for uncoated and coated samples at different times

Another factor that increases the wear resistance of nickel-based coatings is the presence of elements such as tungsten. Mohsenifar[39] and colleagues reported that adding alloying elements to Nickel's electric precipitate could improve properties such as corrosion, hardness and wear resistance. The coated sample at 45 minutes has the highest amount of tungsten and titanium compared to the other coated samples. Palanipa and colleagues have examined the wear behavior of Ni-P and Ni-P-W coatings. Their research has shown that Ni-P-W coatings have higher hardness and wear resistance than Ni-P coating. Also, the results of their research showed that the higher the amount of tungsten in the coating, the higher the wear resistance and hardness[40].

Conclusion

The Ni-PW-TiO_2 composite coating is fabricated on the AISI 304L stainless steel trough electroplating method, and the effect of deposition time (30, 45 and 60 min) on the microstructure, corrosion behaviour and mechanical properties has been investigated and the following results were obtained :

1. By increasing the deposition time to 45 min, the amount of precipitation of ceramic particles and tungsten in the coating increased and then decreased.

2. The created coating after 45 min of electroplating showed a uniform surface, without cracks and cavities.

3. The created coating after 45 min of electroplating showed the lowest corrosion current density (1.21 μAcm^{-2}) and the highest corrosion resistance (27286 Ω). In addition, the decrease in coating capacity

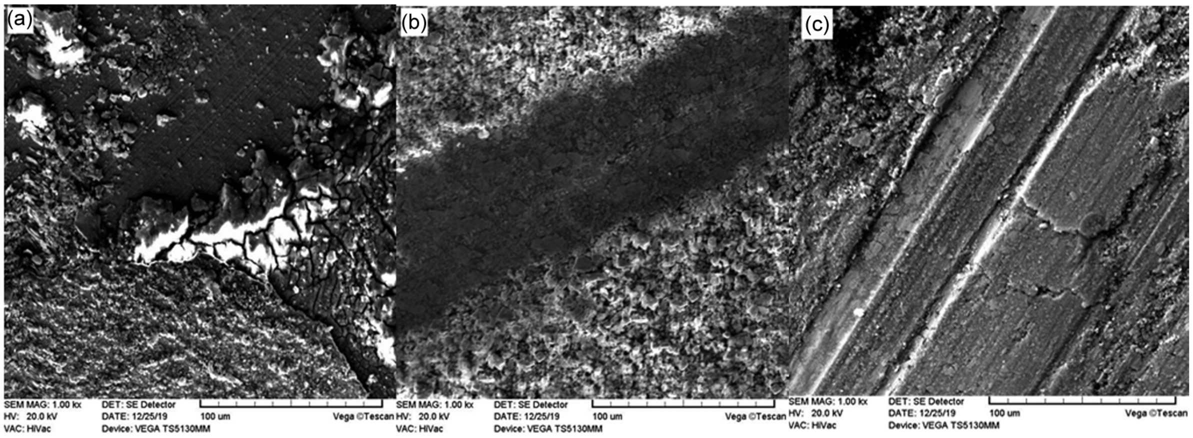

Fig. 6 — SEM image after wear test of Ni-P-W-TiO_2 coatings formed at different times of (a) 30 min, (b) 45 min and (c) 60 min.

with increasing concentration of titanium oxide particles in the electrochemical impedance test indicates a decrease in porosity and pores due to the presence of titanium oxide particles, which reduced the penetration of electrolyte into the coating and increases the corrosion resistance of the coating.

4. By increasing the deposition time to 45 min, the hardness of the composite coating increased and then decreased.

5. The created coating after 45 min of electroplating showed the lowest weight loss and the highest wear resistance. The higher presence of titanium oxide in the coating and the reduction of the friction coefficient led to an increase in hardness and wear resistance.

References

1 Keong K G & Sha W, *Surf Coat Technol*, 168 (2003) 263.
2 Ebrahimifar H, Zandrahimi M, Nikrooz B & Sedighi M, *Indian J Chem Technol*, 20 (2012) 40.
3 Varmaziar S, Atapour M & Hedberg Y S, *Mater Degrad*, 6 (2022) 1.
4 Zandrahimi M, Vatandoost J & Ebrahimifar H, *Oxid Met*, 76 (2011) 347.
5 Limooei M B, Ebrahimifar H & Hosseini S, *Indian J Eng Mater Sci*, 20 (2013) 513.
6 Rajabi T, Atapour M, Elmkhah H & Nahvi S M, *Thin Solid Films*, 753 (2022) 139288.
7 Mosavi A & Ebrahimifar H, *Int J Hydrogen Energy*, 45 (2020) 3145.
8 Wang S C & Wei W C J, *Mater Chem Phys*, 78 (2003) 574.
9 Ebrahimifar H, *Oxid Met*, 91 (2019) 417.
10 Gul H, Kilic F, Usal M, Aslan S, Apl A & Akbulut H, *Appl Surf Sci*, 258 (2012) 4260.
11 Ebrahimifar H & Zandrahimi M, *Bull Mater Sci*, 40 (2017) 1273.
12 Li B, Li D, Chen W, Liu Y, Zhang J, Wei Y, Zhang W & Jia W, *Ceram Int*, 45 (2019) 4870.
13 Wang F, Chen L, Wang Y, Yao M, Hao S, Ouyang J & Huang Z, *Ceram Int*, 43 (2017) 2853.
14 Mortezanejad E, Atapour M, Salimijazi H, Alhaji A & Hakimizad A, *J Mater Eng Perform*, 30 (2021) 4030.
15 Tsuru Y, Nomura M & Foulkes F, *J Appl Electrochem*, 30 (2000) 231.
16 García I, Conde A, Langelaan G, Fransaer J & Celis J P, *Corros Sci*, 45 (2003) 1173.
17 Ashassi-Sorkhabi H & Rafizadeh S H, *Surf Coat Technol*, 176 (2004) 318.
18 Sadreddini S & Afshar A, *Appl Surf Sci*, 303 (2014) 125.
19 Zhang X, Wang F & Du Y, *Surf Coat Technol*, 201 (2007) 7241.
20 Zhang S, Li Q, Yang X, Zhong X, Dai Y & Luo F, *Mater Charact*, 61 (2010) 269.
21 Sadeghi A, Khosroshahi R & Sadeghian Z, *J Surf Invest X-Ray Synchrotron Neutron Tech*, 5 (2011) 186.
22 Baghery P, Farzam M, Mousavi A & Hosseini M, *Surf Coat Technol*, 204 (2010) 3804.
23 Li Q, Yang X, Zhang L, Wang J & Chen B, *J Alloys Comp*, 482 (2009) 339.
24 Szczygieł B & Kołodziej M, *T I Met Finish*, 83 (2005) 181.
25 Fini M H & Amadeh A, *T Nonferr Metal Soc China*, 23 (2013) 2914.
26 Abdel-Gaber A, Abd-El-Nabey B, Sidahmed I, El-Zayady A & Saadawy M, *Corros Sci*, 48 (2006) 2765.
27 Srivastava M, Selvi V E, Grips V W & Rajam K, *Surf Coat Technol*, 201 (2006) 3051.
28 Amin M A, Khaled K, Mohsen Q & Arida H, *Corros Sci*, 52 (2010) 1684.
29 Saeidpour F, Zandrahimi M & Ebrahimifar H, *Corros Sci*, 153 (2019) 200.
30 Bajat J, Mišković-Stanković V, Popić J & Dražić D, *Prog Org Coat*, 63 (2008) 201.
31 Wang Y, Zhou Q, Li K, Zhong Q & Bui Q B, *Ceram Int*, 41 (2015) 79.
32 Song L, Wang Y, Lin W & Liu Q, *Surf Coat Technol*, 202 (2008) 5146.
33 Sadeghi S & Ebrahimifar, *Indian J Eng Mater Sci*, 29 (2022) 108.
34 Wang Y, Wang S J, Shu X, Gao W, Lu W & Yan B, *J Alloys Compd*, 617 (2014) 472.
35 Alirezaei S, Monirvaghefi S M, Salehi M, Saatchi A & Kargosha M, *Surf Eng*, 21 (2005) 60.
36 Staia M, *Surf Coat Technol*, 86 (1996) 598.
37 Sadeghi S & Ebrahimifar, *Int J Mater Res*, 112 (2020) 474.
38 Gadhari P & Sahoo P, *Mater Today Proceedings*, 2 (2015) 2367.
39 Moshrefifar M, Ebrahimifar & Hakimizad A, *Coatings*, 12 (2022) 1438.
40 Palaniappa M & Seshadri S, *Wear*, 265 (2008) 735.