

Deposition Rate and Electrochemical Corrosion Behavior of Nickel-Based Composite Coatings

F. Lekmine^{1,2,*}, I. Zidani³, A. Chala², H. Ben Temam²

¹ University Abbes Laghrour, 40000 Khenchela, Algeria

² Physics Laboratory of Thin Layers and Applications, Biskra University, BP 145RP, Biskra 07000, Algeria

³ University Hadj Lakhdar, Batna-1, Algeria

(Received 27 July 2022; revised manuscript received 20 December 2022; published online 27 December 2022)

Metal corrosion control is technically, economically, environmentally and aesthetically important. The best option is to use coatings to protect metals and alloys from corrosion. Nickel plating is one of the most widely used methods for protecting less noble metal surfaces since the turn of the century. The need for improved coatings with better wear and corrosion resistance has led to the development and use of composite electrostatic deposits. In this paper, Ni-P-TiO₂ composite coatings were fabricated by direct current electrodeposition on copper substrates. X-ray diffraction (XRD) analysis and energy dispersive spectroscopy (EDS) were employed to determine the average particle size of coatings elemental chemical composition. The electrochemical corrosion behavior of Ni-P-TiO₂ composite coatings in 3.5 wt. % NaCl was characterized using a potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS). The results indicate that TiO₂ nanoparticles are included in the coatings. The deposition rate increased with increasing current density; the microhardness of the coatings noticeably increased with current density. Corrosion tests have shown that 3 A.dm⁻² is the optimal value of the applied current density in terms of the lowest value $E_{corr} = -504$ mV and the best charge transfer resistance $R_p = 114.7 \Omega \cdot \text{cm}^2$.

Keywords: Current density, Ni-P-TiO₂ composite coatings, Average particle size, Corrosion resistance, Microhardness.

DOI: [10.21272/jnep.14\(6\).06005](https://doi.org/10.21272/jnep.14(6).06005)

PACS numbers: 81.65.Rv, 82.45.Bb, 62.20.Qp, 81.65.Kn

1. INTRODUCTION

Coatings are used to improve the properties of metals as corrosion resistance, hardness, etc., by depositing an appropriate material over the surface by several techniques [1-3]. Thin film coating by electrodeposition is an attractive method because of its simplicity, the uniform and controllable deposition rate, operation at ambient temperature, and good adhesion with materials even in complex geometries [3, 5]. Ni-P coating is used for corrosion protection in deferent environments, as it acts as a barrier coating protecting the substrate, insulating it from corrosive environments. Recently, much attention has been given to the corrosion behavior of Ni-P coatings and their characteristics including the content and distribution of phosphorus, as well as surface morphology and structure [6, 7]. Nevertheless, corrosion resistance of the electrodeposited Ni-P coating depends on several factors, namely current densities, phosphorus content, degree of crystallinity, grain size, structural variation, thickness and coating porosity. The study of the performance of these coatings in different environments as a function of different phosphorus content is addressed by several researchers [8-10]. Raicheff and Zaprianova [11] suggested that the higher corrosion resistance of amorphous electroless Ni-P coatings is due to their homogeneous structure and the absence of grain boundaries, dislocations, kink sites and other surface defects. In recent years, studies have shown that the co-deposition of insoluble second-phase particles into the coating increases its mechanical, tribological, and corrosion-related properties [12, 13]. If nickel and nickel-phosphorous matrix composite coatings reinforced with

TiO₂, SiC and WC particles were produced under direct and pulsed current conditions from an additive-free Watts bath, the embedding of ceramic particles modifies in various ways the nickel electrocrystallization process, while the Ni-P amorphous matrix is not affected by the occlusion of these particles.

Ni-P-TiO₂ coating has been widely studied on steel substrates, which exhibited poor corrosion performance, resulting in improved properties with the application of the coating. Nevertheless, its behavior on copper has been little studied. Therefore, the present work investigates the corrosion behavior of Ni-P-TiO₂ coatings with a high phosphorus content on a copper substrate in 3.5 % aqueous NaCl solution using electrochemical techniques to determine corrosion resistance.

2. EXPERIMENTAL

2.1 Coating Fabrication

Ni-P-TiO₂ composite coating was deposited by electrodeposition on a copper substrate. The bath composition and procedure conditions used for preparation of the coatings are reported in our previous study [14].

2.2 Deposition Rate Determination

The coating plating speed is measured by the weighing method. The masses before and after plating were measured by Sertorius BL 60S electronic analytical balance. The formula to determine the plating rate was:

$$V = \frac{\Delta m \cdot 10^4}{\rho St}, \quad (1)$$

* farid.lekmine@univ-khenchela.dz

where V , ρ , S , t , and Δm represent the deposition rate ($\mu\text{m/h}$), density of the Ni-P coating ($\sim 7.9 \text{ g/cm}^3$), surface area of the copper substrate (cm^2), deposition time (h), and coating weight (g), respectively.

2.3 Deposits Characterization

In order to test the coatings adhesion, the samples were heated for 30 min at 250°C and then immersed in water at room temperature [15].

The microhardness of the deposits was measured with a Vickers microhardness tester (Wilson 402UD Wolpert) with an applied load of 100 g for 10 s. The reported values are the average of five measurements.

The corrosion phenomenon was investigated at ambient temperature in 3.5 wt. % NaCl solution. Using the potentiodynamic polarization technique, the tests were carried out in a three-electrode cell filled with 300 ml of 3.5 wt. % NaCl solution with working electrode (Ni-P-TiO₂ composite coating), Pt auxiliary electrode and calomel reference electrode, a scan rate of 1 mV/s and in a potential range from -600 up to -300 mV. All potentials are reported vs. SCE for potentiodynamic polarization.

3. RESULTS AND DISCUSSION

3.1 Chemical Composition of Coatings

The weight (wt. %) of nickel, phosphorus, titanium and oxygen is given in Table 1. Compositional analysis of coatings confirms that the number of phosphorus and titanium particles in the coating increases with increasing current density, which affects the surface roughness characteristics of the composite coating. These results show behavior similar to that reported by Mir Saman Safavi et al. [16], who attributed the adsorption behavior of TiO₂ nanoparticles on the cathode surface at different current densities passing through three different phases as: (1) absorption on the cathode surface of TiO₂ nanoparticles is large at $0\text{-}5 \text{ A}\cdot\text{dm}^{-2}$; (2) absorption decreases for TiO₂ nanoparticles at $5\text{-}10 \text{ A}\cdot\text{dm}^{-2}$, (3) enhance the tendency of TiO₂ nanoparticles to be adsorbed on the cathode at $10\text{-}15 \text{ A}\cdot\text{dm}^{-2}$. There are several different studies on the effect of current density on the amount of incorporated reinforcements in the Ni-P alloy matrix, such as Al₂O₃ particles in the Ni-P matrix increasing linearly with increasing current density from 5 to $20 \text{ A}\cdot\text{dm}^{-2}$. Hansall et al. [17] showed the opposite, since the number of precipitated SiC particles decreases with increasing current density from 10 to $25 \text{ A}\cdot\text{dm}^{-2}$.

Table 1 – Elemental chemical composition (wt. %) of the Ni-P-TiO₂ composite coating at different current densities

Current density ($\text{A}\cdot\text{dm}^{-2}$)	Ni (wt. %)	P (wt. %)	Ti (wt. %)	O (wt. %)
2	80.17	11.86	4.27	2.69
3	80.08	11.95	4.73	3.24
4	78.68	12.32	4.95	3.75
5	76.9	11.62	6.25	5.23
7	78.25	10.96	7.42	6.37

3.2 Average Particle Size of Coatings

The effect of the current density on the average particle size of the coatings is shown in Fig. 1 and Table 2. With an increase in current density from 2 to $3 \text{ A}\cdot\text{dm}^{-2}$, the average particle size of the coatings decreases (from 59.30 to 4.29 nm), and the current density increases up to $4 \text{ A}\cdot\text{dm}^{-2}$, which has the opposite effect on the average size (7.02 nm), then decreases.

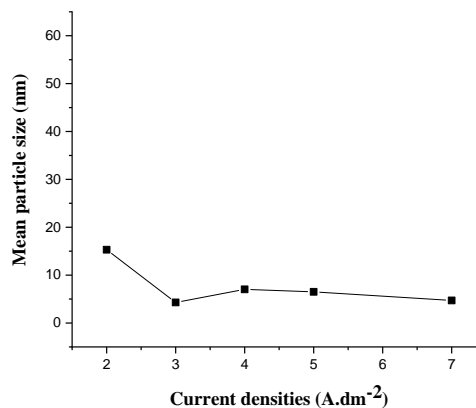


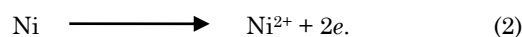
Fig. 1 – Effect of the current density on the average particle size of the coatings

Table 2 – Average particle size of Ni-P-TiO₂ composite coatings at different current densities

Current density ($\text{A}\cdot\text{dm}^{-2}$)	FWHM	Mean particle size (nm)
2	0.32577	59.30
3	8.90058	4.29
4	6.11065	7.02
5	6.00714	6.51
7	8.10176	4.70

3.3 Deposition Rate

The values of the coatings deposition rate are average values of five tests. Fig. 2 and Table 3 represent the impact of the applied current density on the deposition rate of Ni-P-TiO₂ composite coatings. From the obtained results, we notice that the current density affects the deposition rate to a great extent. This could be due to the fact that when the current density increases, the anode (nickel) oxidizes according to Eq. (2), and the number of electrons on the cathode surface increases, which leads to an increase in the cathodic polarization potential and, consequently, an increase in the electric field strength near the coated sample. The concentration of Ni²⁺ increases near the cathode, which greatly increases the reduction and deposition rates.



3.4 Microhardness of Coatings

Microhardness plays an important role in mechanical properties such as tool life. Fig. 3 shows the Vickers microhardness of composite coatings as a function of applied current densities. The highest Vickers value appears during the electrodeposition of composite coatings at $3 \text{ A}\cdot\text{dm}^{-2}$, then it slightly decreases at a current

density of $4 \text{ A}\cdot\text{dm}^{-2}$. There are many factors governing the microhardness of composite coatings: 1) the high hardness of Ti and phosphorous contents themselves can be the main reason for the microhardness of the composite coating; 2) the microhardness of the composite coating tended to decrease when the current density exceeded $5 \text{ A}\cdot\text{dm}^{-2}$, since the Ni-P matrix was deposited with TiO_2 particles with increasing current density.

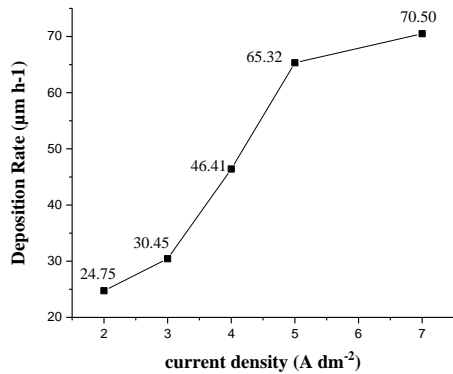


Fig. 2 – Effect of the current density on the deposition rate

Table 3 – Plating rate

Current density (A·dm ⁻²)	Δm (g)	Area (cm ²)	Deposition rate (µm·h ⁻¹)
2	0.17	8.7	24.75
3	0.21	7.75	30.45
4	0.27	7.56	46.41
5	0.48	9.28	65.32
7	0.50	9	70.50

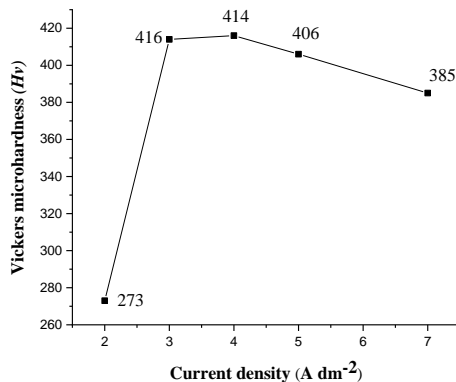


Fig. 3 – Microhardness values of the Ni-P-TiO₂ composite coatings at different current densities

3.5 Corrosion Test

3.5.1. Electrochemical Impedance

The Nyquist diagrams obtained for different Ni-P-TiO₂ deposits (Fig. 4 and Table 4) show that the size of the capacitive loops increases with an increase in the current density of the deposit up to $J = 3 \text{ A}\cdot\text{dm}^{-2}$ and then decreases. Fig. 5 gives an equivalent circuit model (Randles circuit) utilized to analyze the Nyquist plots and simulate a metal/solution interface. The featured elements shown in the circuit are a constant phase element (CPE) that is in parallel with the polarization resistance (R_p), both of which are in series with the

solution resistance (R_s). The CPE resembles a capacitor, which is usually used to explain the inhomogeneous system and some distribution (dispersion) of the value of physical property of the system that is used instead of the electric double layer capacitance (C_{dl}).

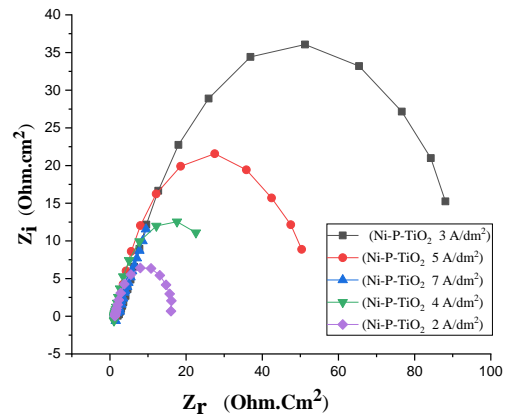


Fig. 4 – Nyquist diagrams of Ni-P-TiO₂ composites deposited with different current densities in 3.5 % NaCl medium

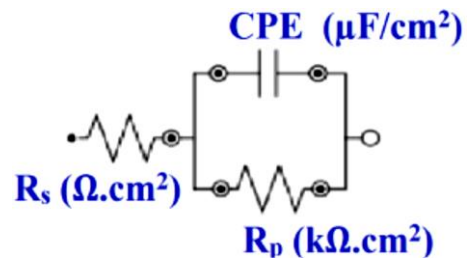


Fig. 5 – Equivalent circuit used to fit the experimental data of EIS plots

This type of diagram is generally interpreted as a charge transfer mechanism on a heterogeneous surface. The values of the load transfer resistances, determined from the low frequency limits on the Nyquist diagrams, confirm a satisfactory protective capacity for a current density of $3 \text{ A}\cdot\text{dm}^{-2}$. Extrapolation of capacitive loops on the real axis made it possible to estimate the charge transfer resistance (R_{ct}) and then calculate the double layer capacitance (C_{dl}) using the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} \times R_{tc}} \quad (3)$$

Table 4 – Corrosion parameters of Ni-P-TiO₂ composite coatings, deduced from impedance measurements, in aggressive 3.5 % NaCl

Current density (A·dm ⁻²)	R_s (Ω·cm ²)	R_{ct} (Ω·cm ²)	C_{dl} (µF·cm ⁻²)
2	2.457	15.76	780.32
3	1.875	114.7	277.2
4	3.694	28.36	422.60
5	4.789	92.79	320.68
7	2.965	49.91	402.56

3.5.2. Polarization Curves

Polarization curves of Ni-P-TiO₂ composite coatings as a function of the current density applied are shown

in Fig. 6. The coatings corrosion parameters obtained from Tafel linear fit method are listed in Table 5.

Table 5 – Corrosion electrochemical parameters of Ni-P-TiO₂ composite coatings

Current density (A·dm ⁻²)	$E(i=0)$ (mV)	R_p Ω·cm ²	I_{corr} (μA·cm ⁻²)	T_{corr} (μm·y ⁻¹)
2	-464.5	578.32	15.7650	184.3
3	-504.0	2.99×10 ³	4.0053	46.84
4	-502.3	1.6×10 ³	9.1122	106.5
5	-491.5	3.16×10 ³	4.3395	50.75
7	-503.2	1.65×10 ³	7.5959	88.84

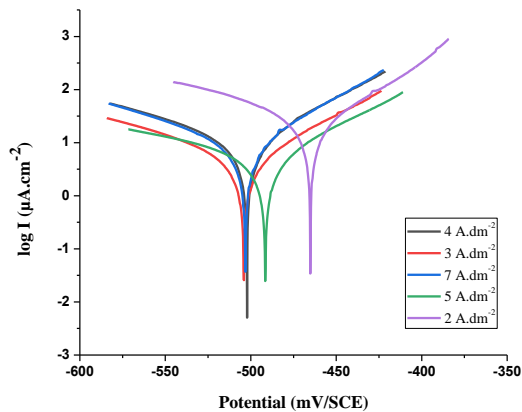


Fig. 6 – Potentiodynamic polarization curve of electrodeposited Ni-P-TiO₂ composite coatings for various current densities

Fig. 6 and Table 5 show that with increasing current density applied to prepare Ni-P-TiO₂ composite coating, corrosion potential, corrosion current density and corrosion rate first increase and then decrease. Such as, at an applied current density of 2 A·dm⁻², the corrosion potential of the composite coating is -495 mV and the corrosion current density is 15.7650 μA·cm⁻², indicating that the coating has low corrosion resistance due to the existence of pores (Fig. 2a). When the cur-

rent density increases up to 3 A·dm⁻², the composite coating corrosion potential is equal to -04 mV, and the corrosion current is 4.0053 μA·cm⁻². The resistance to corrosion is better; the corrosion rate is 46.84 μm·y⁻¹. The results of the potentiodynamic polarization curve and the analysis of the corrosion parameters show that the composite coating realized at 3 A·dm⁻² current density gives the best protection against corrosion and a high microhardness. In general, the particles incorporated into the nickel matrix can reduce the passivation and corrosion resistance of the composite coating [19].

4. CONCLUSIONS

In the present study, the influence of current density on the microhardness and corrosion resistance of Ni-P-TiO₂ composite coatings has been evaluated. The most important results can be drawn as:

1) The thermal shock test reveals that the deposition of Ni-P-TiO₂ composite coatings has good adhesion to the copper substrate.

2) The deposition rate increases with increasing current density. When the current density is 7 A·dm⁻², the fastest deposition speed is 70 μm·h⁻¹.

3) The chemical composition of the Ni-P-TiO₂ alloy varies nonlinearly and shows that the TiO₂ content in the alloy is represented as traces.

4) The microhardness test shows that the Ni-P-TiO₂ alloy coating is harder than the copper substrate. The current density at 3 A·dm⁻² exhibits the superior microhardness.

5) Electrochemical corrosion behavior of Ni-P-TiO₂ composite coatings in 3.5 wt. % NaCl solution reveals a significant decrease in the anodic current density and a positive shift of the corrosion potential with the application of the coating on the copper substrate, indicating an excellent corrosion resistance of the coated samples. The Ni-P-TiO₂ composite coating obtained by electrodeposition at 3 A·dm⁻² exhibits superior corrosion resistance due to a fine and homogeneous structure with small nodules on the surface.

REFERENCES

1. S. Arulvel, A. Elayaperumal, M.S. Jagatheeshwaran, *Eng. Fail. Anal.* **90**, 310 (2018).
2. M.S. Jagatheeshwaran, A. Elayaperumal, S. Arulvel, *Surf. Coat. Technol.* **304**, 492 (2016).
3. S. Arulvel, A. Elayaperumal, M.S. Jagatheeshwaran, *J. Solid State Chem.* **248**, 87 (2017).
4. B. Daniel Falola, I. Ian Suni, *Curr. Opinion Solid State Mater. Sci.* **19**, No 2, 77 (2015).
5. A.M. Pillai, A. Rajendra, A.K. Sharma, *J. Coat. Technol. Res.* **9**, 785 (2012).
6. P. Lo, W. Tsai, J. Lee, M. Hung, *Surf. Coat. Technol.* **67**, 27 (1994).
7. N. Martyak, S. Wetterer, L. Harrison, M. Mcneil, R. Heu, A. Albert Neiderer, *Plat. Surf. Finish* **6**, 60 (1993).
8. G. Lu, G. Zangari, *Electrochim. Acta* **47**, 2969 (2002).
9. R. Raicheff, V. Zaprianova, *J. Mater. Sci. Lett.* **19**, 3 (2000).
10. P. Bai, Y. Chuang, C. Hu, *Mater. Chem. Phys.* **82**, 93 (2003).
11. Yu.E. Sknar, O.O. Savchuk, I.V. Sknar, *Appl. Surf. Sci.* **423**, 340 (2017).
12. M. Saman Safavi, A. Rasooli, *Surf. Eng.* **35** No 12, 1070 (2019).
13. F. Lekmine, M. Naoun, A. Gana, H. Ben Temam, *J. Nano-Electron. Phys.* **14** No 1, 01009 (2022).
14. F. Lekmine, H. Ben Temam, M. Naoun, M. Hadjadj, *J. Nano-Electron. Phys.* **12** No 1, 01001 (2020).
15. M.S. Safavi, A. Rasooli, *Surf. Coat. Technol.* **372**, 252 (2019).
16. H. Shahbazi, M. Mahdavi, S. Alirezaei, F. Tabatabaei, *Mater. Res. Exp.* **6** No 8, 085076 (2019).
17. W.E.G. Hansal, G. Sandulache, R. Mann, P. Leisner, *Electrochim. Acta.* **114**, 851 (2013).

Швидкість осадження та електрохімічна корозійна поведінка композитних покриттів на основі нікелю

F. Lekmine^{1,2}, I. Zidani³, A. Chala², H. Ben Temam²

¹ *University Abbes Laghrour, 40000 Khenchela, Algeria*

² *Physics Laboratory of Thin Layers and Applications, Biskra University, BP 145RP, Biskra 07000, Algeria*

³ *University Hadj Lakhdar, Batna-1, Algeria*

Контроль корозії металу є важливим з технічної, економічної, екологічної та естетичної точок зору. Оптимальним варіантом є використання покриттів для захисту металів і сплавів від корозії. Нікелювання є одним із найпоширеніших методів захисту менш благородних металевих поверхонь з початку століття. Потреба в покращених покриттях з кращою стійкістю до зносу та корозії призвела до розробки та використання композитних електростатичних покриттів. У статті композитні покриття Ni-P-TiO₂ були виготовлені електроосадженням при прямому струмі на мідних підкладках. Для визначення середнього розміру частинок і елементного хімічного складу покриттів використовували рентгеноструктурний аналіз (XRD) та енергодисперсійну спектроскопію (EDS). Електрохімічна корозійна поведінка композитних покриттів Ni-P-TiO₂ у 3,5 мас. % NaCl характеризували за допомогою потенціодинамічного поляризаційного тесту та електрохімічної імпедансної спектроскопії (EIS). Результати показують, що наночастинки TiO₂ включені в покриття. Швидкість осадження зростала зі збільшенням густини струму; мікротвердість покриттів помітно зростала зі збільшенням густини струму. Випробування на корозію показали, що 3 А.дм⁻² є оптимальним значенням прикладеної густини струму з точки зору найменшого значення $E_{corr} = -504$ мВ і найкращого опору передачі заряду $R_p = 114,7$ Ом.см².

Ключові слова: Густина струму, Композитні покриття Ni-P-TiO₂, Середній розмір частинок, Корозійна стійкість, Мікротвердість.