Structural, Mechanical and Corrosion Behavior of Ni-P-TiO₂ Composite Coatings: Effect of Current Density

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Ni-P-TiO₂ composite coatings are important in engineering due to their properties such as good resistance to wear and corrosion, magnetic properties, electrical and thermal conductivity. In this paper, the effect of current density on electrodeposited Ni-P-TiO₂ composite coatings was investigated for the first time. Ni-P-TiO₂ composite coatings were deposited with applied current densities (1, 3, 5, 7 and 9 A·dm⁻²) on copper substrates. X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and microhardness analysis were used to study the morphological, microstructural and mechanical properties. On the other hand, the corrosion performance of the coatings was evaluated using Tafel polarization and electrochemical impedance spectroscopy (EIS). XRD results indicate that the inclusion of TiO₂ nanoparticles into the coatings alters the relative intensity of Ni peak as well as peak breadth. In addition, microhardness of the coatings noticeably increased with current densities. Ni-P-TiO₂ composite coating electrodeposited at 3 A·dm⁻² exhibits the best microhardness and corrosion resistance.

1. INTRODUCTION

Surface properties of materials may change due to wear, corrosion and fatigue [1]. Therefore, the surface of a material is the most important engineering part. The use of surface modification technologies in the manufacturing process is inevitable. Coatings are used to improve the properties of metals, such as corrosion resistance, hardness, etc., by depositing an appropriate material over the surface by several techniques [2]. Thin film coating by electrodeposition method is attractive because of its simplicity, uniform and controllable deposition rate, operation at ambient temperature, the possibility to obtain multilayer coatings and cover large surfaces of different shapes at low cost, their homogeneous deposition nature and good adhesion to materials even in complex geometries [3]. Ni-P coatings are used for various industrial applications, including automotive, aerospace, decorative, etc., due to their important properties such as corrosion resistance, good solderability, high electrical conductivity, smooth surface formation and symmetry, low coefficient of friction, electrical activity and paramagnetic properties obtained by simple electrochemical processes, and also due to their shiny and smooth appearance, unlike the Ni deposit [4-6]. The electrodeposition process plays a crucial role in the formation of thin films on materials through the electrochemical reduction of metal ions in electrolytic solutions. Up to date, two mechanisms including direct and indirect have been proposed for the co-deposition of phosphorus with nickel, which are presented elsewhere [7]. Nevertheless, the structural properties of Ni-P coatings depend on the phosphorus content, while some coatings have an amorphous structure and others have a crystalline structure [8]. Recent studies have shown that co-deposition of insoluble second-phase particles into a coating improves its mechanical, tribological, and corrosion-related properties [9, 10]. For example, ceramic and polymer carbides (WC, TiC, SiC), nitrides (Si₃N₄, AlN), sulfides (MoS₂), metal oxides (Al₂O₃, ZrO₂, TiO₂, NiO, La₂O₃), boron, and recently also metal powders (W, Al, Ti, Mo, V, Co), intermetallics (RuAl, NiAl), silicon, organic compounds (polytetrafluoroethylene (PTFE) or polyethylene (PE)) can be incorporated into the Ni-P alloy matrix as reinforcing elements [11]. This technology is used due to its desirable features such as low cost, ease of use, and versatility. To improve the various properties of Ni-P alloy deposits, more studies have been conducted in recent decades on electrodeposited Ni-P nanocomposites, which are successful examples that have attracted attention owing to their improved properties over the original Ni-P coatings, TiO₂ [11], SiC [12], Al₂O₃ [10], MWCNT [13]. Nickel and nickel-phosphorus matrix composite coatings reinforced with TiO₂, SiC and WC particles were produced under direct and pulse current in an additive-free Watts type bath. The incorporation of ceramic particles modified the nickel electrocrystallization process in different ways, while the Ni-P amorphous matrix was not affected by particle occlusion.

The present work investigates the effects of current density on the phase structure, morphology, chemical composition, microhardness, and corrosion behavior of Ni-P-TiO₂ coatings.

2. EXPERIMENTAL

2.1 Preparation of Coatings

In this work, Ni-P-TiO₂ composite coatings were deposited by electrodeposition on copper sheet substrates (20 mm×10 mm×1 mm). The substrates were mechani-

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cally polished using 120- up to 1200-grit silicon carbide paper. They were rinsed with distilled water, degreased in a solution of 50 g/l Na_2CO_3 and 15 g/l NaOH, then pickled in 10 % HCl solution to remove oxide traces and finally washed with bidistilled water. A copper substrate positioned between two anodes of nickel plates (30 mm×10 mm×3 mm) was placed in a cell containing a bath. The bath composition and operating parameters are shown in Table 1. Before deposition, the plating bath was magnetically stirred for 72 h.

Table 1 – Electrodeposition bath chemical composition and working conditions

Bath composition	Concentration
$NiSO_4$, $7H_2O$	28 g/l
$NiCl_2$	5 g/l
NaH_2PO_2, $2 H_2O$	15.5 g/l
H_3PO_3	5 ml/l
H_3BO_3	10 g/l
NaCl	28.5 g/l
TiO_2	10 g/l
$Na_3C_6H_5O_7$	22.6 g/l
NH_4Cl	5 g/l
Conditions	
Temperature	80 °C
Current density	1-9 $A \cdot dm^{-2}$
pH	2
Deposition time	1 h
Stirring rate	200 rpm

2.2 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 [14]. Surface morphology of the coatings was observed by an environmental scanning electron microscope (FEI QUANTA 200), and the preferred orientation of the coating growth was evaluated by X-ray diffraction (XRD, Mini Flex 600, Rigak). Data from $2\theta = 10$-90° were measured with a step size of 0.04 (2θ). The microhardness of the deposits was measured by a Vickers microhardness tester (Wilson 402UD Wolpert) with an applied load of 100 g for 10 s. The reported values are average of five measurements.

The corrosion phenomenon was investigated at ambient temperature in 3.5 wt. % NaCl solution. Using potentiodynamic polarization technique, the tests were carried out in a three-electrode cell filled with 300 ml of 3.5 wt. % NaCl solution, with a working electrode (Ni-P-TiO$_2$ composite coating), an auxiliary Pt electrode and a calomel reference electrode, the scan rate was 1 mV/s and in the potential range was from – 600 up to – 300 mV. All potentials are reported vs. SCE for potentiodynamic polarization.

3. RESULTS AND DISCUSSION

3.1 Effect of Current Density

3.1.1 Phase Structure

Fig. 1 shows the XRD patterns for Ni-P-TiO$_2$ composite coatings prepared at different current densities. As seen, the patterns present five main diffraction peaks assigned to TiO$_2$, NiO, NiTi and Ni phases: at 25.24° for TiO$_2$, 43.32° for NiO, 44.50° for Ni, 50.38° for NiTi, and 74.05° for TiO$_2$. The crystallographic planes of the corresponding peaks are (011), (012), (111), (220) and (017), respectively. In addition, diffraction peaks of NiO and NiTi disappear at a current density above 2 $A \cdot dm^{-2}$. No diffraction peaks of NiO and NiTi were detected by XRD of the sample with current densities, but the diffraction peak of TiO$_2$ was detected. Since an increase in the current density leads to an increase in the number of electrons on the cathode surface, this leads to the attraction of nickel ions, their reduction to atoms, and their subsequent adhesion to the cathode. It is assumed that the current density has a certain influence on electrodeposited Ni-P-TiO$_2$ composite coatings and does not change the phase in composite coatings but changes their relative abundances and affects the position of NiTi and TiO$_2$ peaks; however, it can vary the peak width and relative intensity. The result shows that the full width at half maximum (FWHM) of the diffraction peak of Ni in Ni-P-TiO$_2$ composite coatings at 2 $A \cdot dm^{-2}$ is smaller than that in Ni-P-TiO$_2$ composite coatings at 4-7 $A \cdot dm^{-2}$. According to Scherrer formula, this implies that the current density refines the size of crystalline Ni grains, which is consistent with the SEM result observed above.
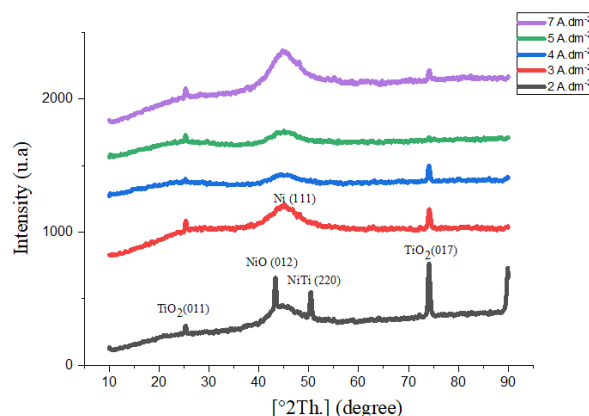

Fig. 1 – XRD spectra of Ni-P-TiO$_2$ composite coatings as a function of different current densities

3.1.2. Surface Morphology

Surface morphology of Ni-P-TiO$_2$ composite coatings electrodeposited at different current densities is shown in Fig. 2. It is seen that all electrodeposited coatings are compact, crack-free and contain numerous globular grains. In addition, titanium particles appeared as white spherical spots, and the black area (darker) is the Ni-P matrix. The coatings show a typical spherical nodular structure, and second-phase titanium particles are uniformly distributed over the Ni-P matrix. Surface morphology of these coatings changed with increasing applied current density. The specimens that were realized at current densities of 2 and 3 $A \cdot dm^{-2}$ have a fine and homogenous structure with small nodules on their surfaces. But the coating realized at a current density of 4-7 $A \cdot dm^{-2}$ has a rough morphology with large nodules. The TiO$_2$ content increased with increasing current densities. These results are similar to those of other

researchers on the incorporation of various types of hard/soft composite particles into the Ni-P matrix [15, 16]. From Fig. 2, it is confirmed that the presence of titanium particles increased in the coating with a current density of $4\,A\cdot dm^{-2}$ compared to other coatings.
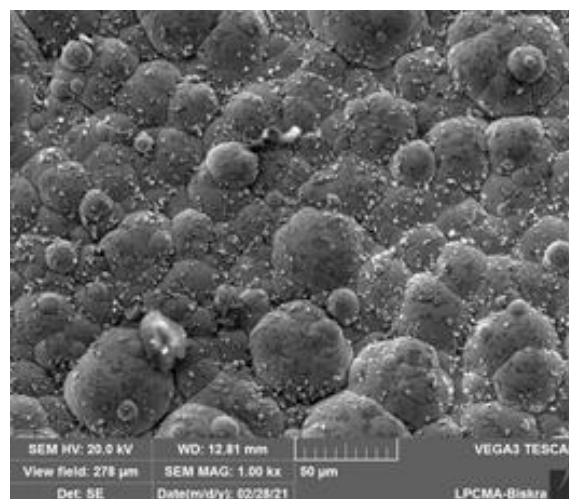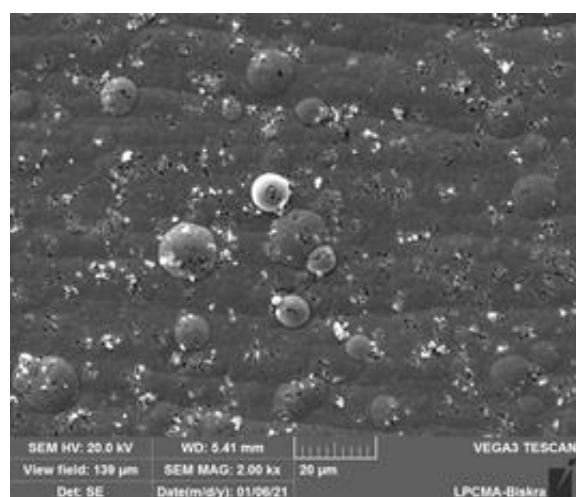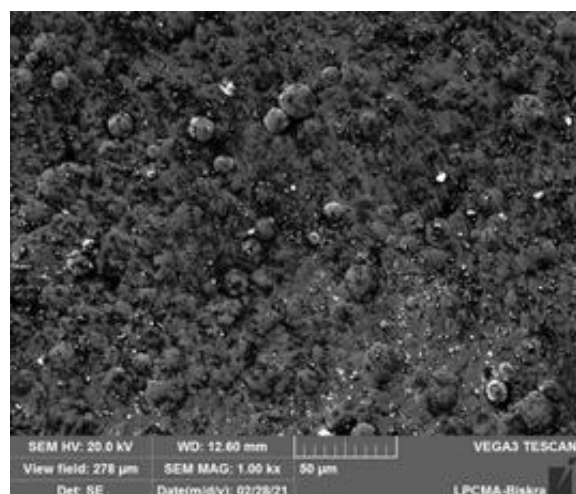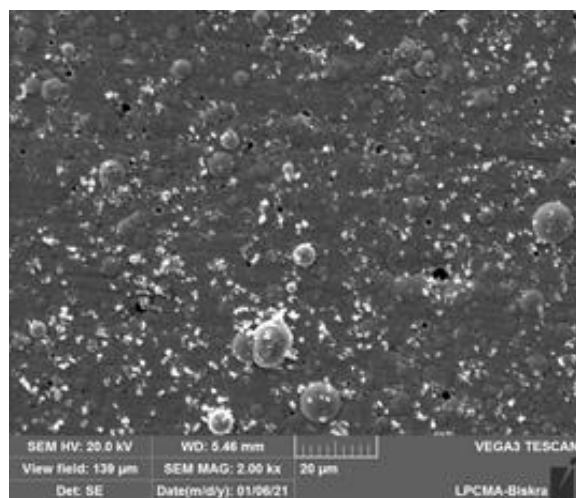

Fig. 2 – Surface morphology of Ni-P-TiO$_2$ composite coatings electrodeposited at different current densities (in $A\cdot dm^{-2}$): (a) 2, (b) 3, (c) 4, (d) 5, and (e) 7

3.1.3. Mechanical Properties of Coatings

Microhardness plays an important role in mechanical properties such as improving tool life. Fig. 3 shows the Vickers microhardness of composite coatings as a function of applied current density. The highest Vickers value appears in the composite coating electrodeposited at $3\,A\cdot dm^{-2}$, then it slightly decreases at a current density of $4\,A\cdot dm^{-2}$. There are many factors affecting the microhardness of composite coatings: 1) the high hardness of Ti and P themselves may be the main reason for the microhardness of the composite coating, 2) the microhardness of the composite coating tends to decrease when the current density exceeds $5\,A\cdot dm^{-2}$, since the Ni-P matrix is deposited by TiO$_2$ particles with increasing current density.

3.1.4 Corrosion Test

3.1.4.1 Polarization Curves

The polarization curves of Ni-P-TiO$_2$ composite coatings as a function of the applied current density are shown in Fig. 8. Corrosion parameters of the coatings obtained from Tafel linear fitting are listed in Table 2.
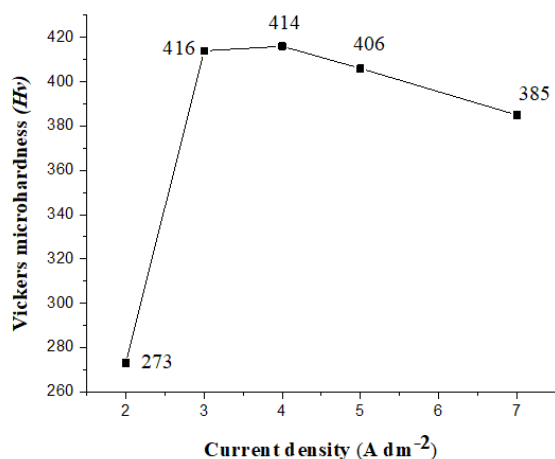
Fig. 3 – Microhardness values of Ni-P-TiO₂ composite coatings at different current densities

Table 2 – Corrosion electrochemical parameters of Ni-P-TiO₂ composite coatings

Current densities ($A \cdot dm^{-2}$)	$E\ (i = 0)$, (mV)	R_p, $\Omega \cdot cm^2$	I_{corr}, ($\mu A\ cm^{-2}$)	T_{corr}, ($\mu m\ y^{-1}$)
2	− 464.5	578.32	15.7650	184.3
3	− 504.0	$2.99 \cdot 10^3$	4.0053	46.84
4	− 502.3	$1.6 \cdot 10^3$	9.1122	106.5
5	− 491.5	$3.16 \cdot 10^3$	4.3395	50.75
7	− 503.2	$1.65 \cdot 10^3$	7.5959	88.84

Fig. 4 and Table 2 show that with increasing applied current density to prepare Ni-P-TiO₂ composite coatings, corrosion potential, corrosion current density and corrosion rate first increase and then decrease. Thus, at an applied current density of $2\ A \cdot dm^{-2}$, the corrosion potential of the composite coating is − 495 mV and the corrosion current density is $15.7650\ \mu A\ cm^{-2}$, indicating a low corrosion resistance of the coating due to the presence of pores (Fig. 2a). When the current density increases up to $3\ A \cdot dm^{-2}$, the composite coating corrosion potential is − 504 mV and the corrosion current density is $4.0053\ \mu A \cdot cm^{-2}$. Corrosion resistance is better, the corrosion rate is $46.84\ \mu m \cdot y^{-1}$. The results of the poten-

tiodynamic polarization curve and the analysis of corrosion parameters show that the composite coating realized at a current density of $3\ A \cdot dm^{-2}$ gives the best protective coating against corrosion and high microhardness. In general, particles incorporated into the nickel matrix can reduce the passivation and corrosion resistance of the composite coating [17].
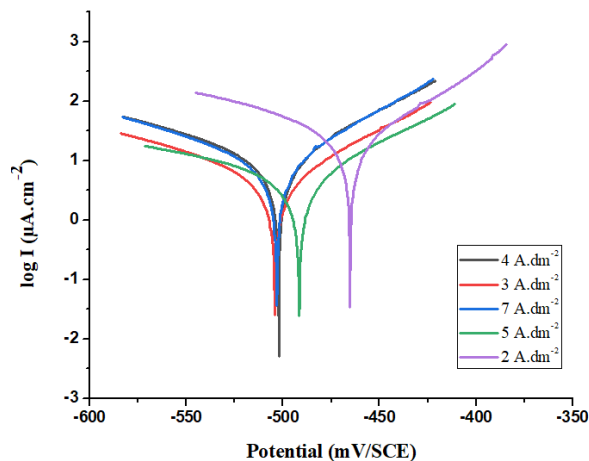

Fig. 4 – Potentiodynamic polarization curves of electrodeposited Ni-P-TiO₂ composite coatings for various current densities

4. CONCLUSIONS

In the present study, the influence of the applied current density on the surface morphology, phase structure, microhardness, and corrosion resistance of Ni-P-TiO₂ composite coatings was assessed. The most important results can be drawn as follows:

1) The thermal shock test revealed that deposited Ni-P-TiO₂ composite coatings have good adhesion to copper substrate.

2) The distribution of TiO₂ particles in the coatings was more uniform, and the content of TiO₂ particles increased with increasing the current density.

3) Ni-P-TiO₂ composite coating electrodeposited at $3\ A \cdot dm^{-2}$ exhibited superior microhardness and corrosion resistance due to a fine and homogenous structure with small nodules on its surface.

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Структурна, механічна та корозійна поведінка композитних покриттів Ni-P-TiO₂: вплив густини струму

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Композитні покриття $Ni-P-TiO_2$ важливі для техніки завдяки таким властивостям, як стійкість до зносу та корозії, електро- та теплопровідність, магнітним властивостям. У роботі вперше досліджено вплив густини струму на електроосаджені композитні покриття $Ni-P-TiO_2$. Композитні покриття $Ni-P-TiO_2$ осаджувалися на мідні підкладки з густинами прикладеного струму, рівними 1, 3, 5, 7 та 9 А·дм$^{-2}$. Для дослідження морфологічних, мікроструктурних та механічних властивостей використовували рентгеноструктурний аналіз (XRD), скануючу електронну мікроскопію (SEM), енергодисперсійну спектроскопію (EDS) та аналіз мікротвердості. З іншого боку, корозійні властивості покриттів оцінювали за допомогою поляризаційної та електрохімічної імпедансної спектроскопії (EIS). Результати XRD показують, що включення наночастинок TiO_2 в покриття змінює відносну інтенсивність піку Ni, а також його ширину. Крім того, мікротвердість покриттів помітно збільшується з густиною струму. Найкращу мікротвердість і корозійну стійкість демонструє композитне покриття $Ni-P-TiO_2$, нанесене електроосадженням при 3 А·дм$^{-2}$.

Ключові слова: Густина струму, Композитні покриття $Ni-P-TiO_2$, Корозійна стійкість, Мікротвердість, XRD.