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Property anti corrosion Ni-P-TiO_2 composite coatings in an aggressive environment (H_3PO_4)

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ABSTRACT

The realization of the deposits of composite with nickel, on copper substrata, as well as their characterization were made essentially at the level of the Laboratory of electrochemistry, corrosion and environment, Faculty of science, university IBN TOFAIL KENITRA MOROCCO. Knowing that Morocco's largest producer of phosphoric acid in the world. The barrels used for storage and transportation of this product are subject to severe corrosion. For this reason we have sought to develop Ni-P-TiO_2 composite coatings on copper substrates. The corrosion resistance of the composite Ni-P-TiO_2 composite coatings was estimated in a very aggressive environment 4 mol/L (4M) of H_3PO_4 by using the techniques of polarization and the spectroscopy of impedance confirmed by those obtained by using non-electrochemical methods (Energy of dispersal of the X-rays and the electronic microscopy with sweeping). The results showed that the incorporation of TiO2 in the cover pulls an increase of the corrosion resistance and the improvement of the morphology of surface.

Keywords: Corrosion, composite, titanium oxide, electrodeposition.

INTRODUCTION

Electrodeposition is a method for producing a coating on a metal to protect it from oxidation at high temperature or corrosion in aggressive environments. A Such a coating consists of particles that can be hard oxide or carbide such as: TiO_2[1], SiO_2[2], NiO[3], Sc_2O_3[4],Fe_2O_3[5], RuO_2[6-7]or Al_2O_3[8-9]were incorporated as composite components other chemicals can also be co-deposited with the nickel matrix, for example SiC[10], PTFE[10-11]or Talc[12].

Many of work in this area have been achieved and the results were evaluated in various aqueous solutions according to the needs for which these studies were conducted as follows:

Hosseini and Bodaghi [13] have studied the corrosion resistance of composite coatings Ni-P-TiO2 in 3.5 wt% NaCl aqueous solution, obtained by optimizing the chemical process parameters using the Taguchi method.

D. Gierlotka et al [1] have prepared the Ni-P-TiO_2 coatings by simultaneous electrodeposition of Ni and TiO_2 on a Cu substrate from a solution in which TiO_2 particles were suspended by stirring. It was ascertained that the introduction of TiO_2 to the amorphous Ni–P layers leads to an increase in the rate of hydrogen evolution in comparison with conventional Ni–P layers irrespective of environment.

In this study we will try to make the deposit by electrodeposition which allows the development of Ni-P-TiO_2composite coatings nickel base on the copper substrate in acidic medium. Then, we will examine the influence of Titanium in the bath on the coatings resistance obtained, while fixing the TiO_2 content in the bath and cathodic current density and we vary the pH of the bath.

The corrosion resistance of Ni–P–TiO_2 composite films plated on copper substrate was evaluated in a very aggressive environment 4M H_3PO_4 by using polarization technique and spectroscopy of impedance were corroborated with those obtained by using non-electrochemical methods (Energy dispersive X-ray analysis and scanning electron microscopy). The results showed that incorporation of TiO_2 in coating causes an increase of corrosion resistance and improves surface morphology.

MATERIALS AND METHODS

Pretreatment and activation of substrate

For the realization of chemical deposits we used copper plates of dimensions (L = 2 cm, l = 1 cm and h = 0.2 cm) which are polished using abrasive paper of different grain sizes: 180-240-320-400-600-1200 and then rinsed with distilled water. Then substrates have been degreased in a solution of ethanol and rinsed in distilled water. Substrates have been activated in a solution of sulfuric acid 33% and then rinsed in distilled water.

Bath coating deposition

The bath of Ni-P-TiO_2 whose formulations are illustrated by the table .1 contain nickel sulfate as a source of metal ions, the hypophosphite as a reducing agent, the sodium acetate as buffering agent, the boric acid to lower the surge required the filling, the ammonium chloride (NH_4Cl) provides stability for the electrolyte as well as the titanium dioxide to improve the quality of filing and the remedy for the problem pores.

The pH was measured using a pH Meter, and adjusted by addition of acetic acid which plays a buffer role. The temperature of bath in veneer was maintained at 25 ± 2 ° C using a controlled heating plate. The amounts of TiO_2 powder have been added in the bath and under constant agitation during the plating process for the coating of Ni-P-TiO_2.

Table 1. Composition of the bath and electrodeposition conditions

Electroplating solution composition	
$NiSO_4$, $6H_2O$	51 g/L
NaH_2PO_2, H_2O	29 g/L
NH_4Cl	10.7 g/L
CH_3COONa	10 g/L
H_3BO_3	8 g/L
TiO_2	100-200 g/L
jdép	8 mA/cm^2
pH	5-7
Température	25± 2 °C

Surface investigation

The surface morphology of the as-deposited Ni-P-TiO_2 composites on copper was studied using scanning electron microscopy SEM attached to an EDX unit.

Electrochemical processing

The electrochemical experiments were performed using a potentiostat/ Voltalab PGZ100, which were by a personal computer, calculates and displays the corrosion rate in µm/yr. The reference and auxiliary electrodes were a saturated calomel electrode (SCE) and a platinized platinum electrode, respectively. The electrolyte used was a 4mol/L H_3PO_4 solution.

Corrosion current density Icorr was determined using Equation.1 [14].

$$i_{corr} = \frac{\beta a \times \beta c}{2.303(\beta a \times \beta c)} \times \frac{1}{R_p} \qquad \text{Equation (1)}$$

Or, ßa and ßc (mV) are respectively the anodic and cathodic Tafel slope. The values of ßa and ßc were determined separately by respective polarization of the substrates in the anodic and cathodic directions (± 200mV corrosion potential). Rp (Ω.cm^2) is the polarization resistance, which was calculated as the slope of the curve between the current density and the potential swept within ± 20 mV of the open circuit potential

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyzer, over the frequency range from 100 kHz to 0.01 Hz with10 points per decade. The applied amplitude of AC signal was 10 mV rms. All experiments were performed at the open circuit potential.

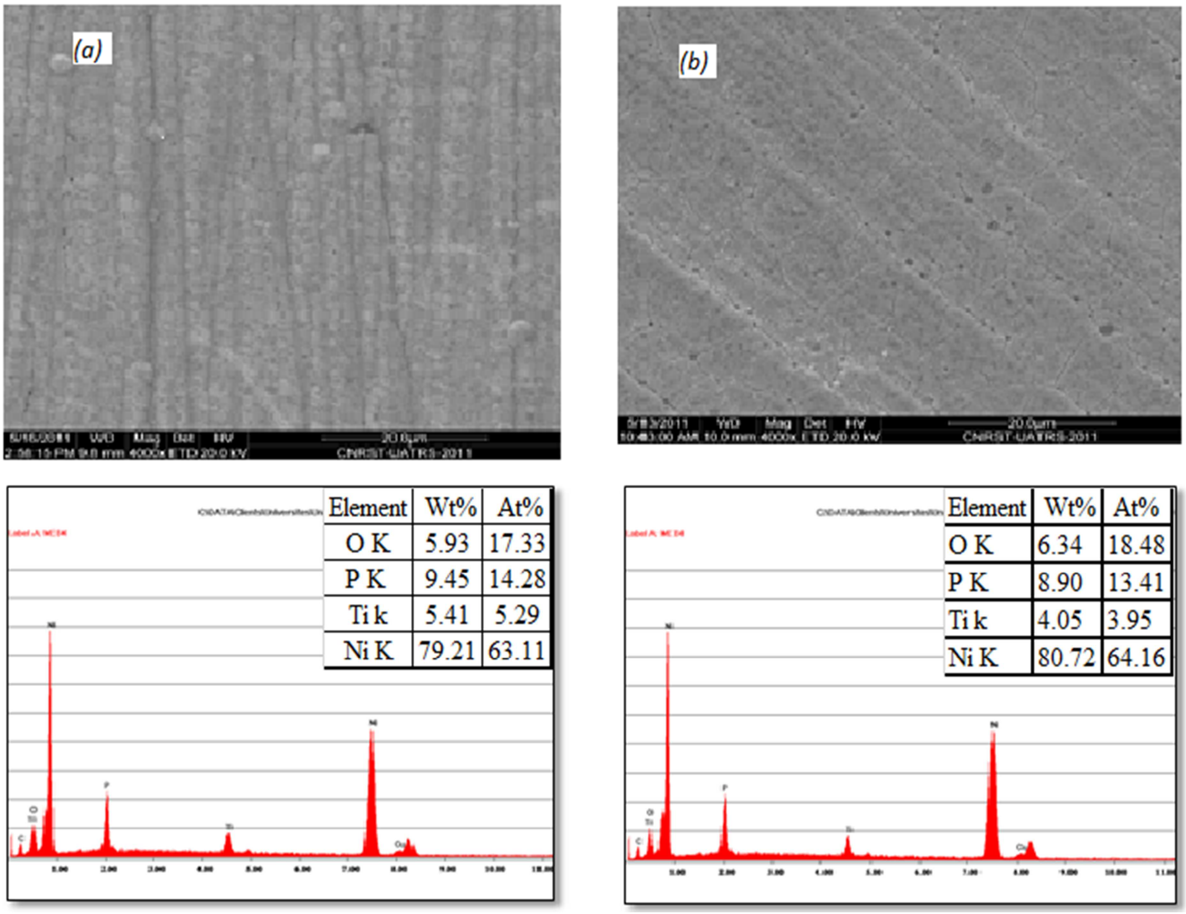
RESULTS AND DISCUSSION

Characterization of the coatings

To better understand the microstructural variations depending on the titanium dioxide content. The following coatings were characterized by scanning electron microscopy, a significant change in the morphology of the coatings according to the insertion of titanium dioxide (TiO_2) is confirmed.

a. Acid solution (pH = 5)

In an acid solution (pH = 5), **i**ncreasing TiO_2 content improves significantly the appearance of the coating: Rough, less porous and without cracking.



Element	Wt%	At%
O K	5.93	17.33
P K	9.45	14.28
Ti k	5.41	5.29
Ni K	79.21	63.11

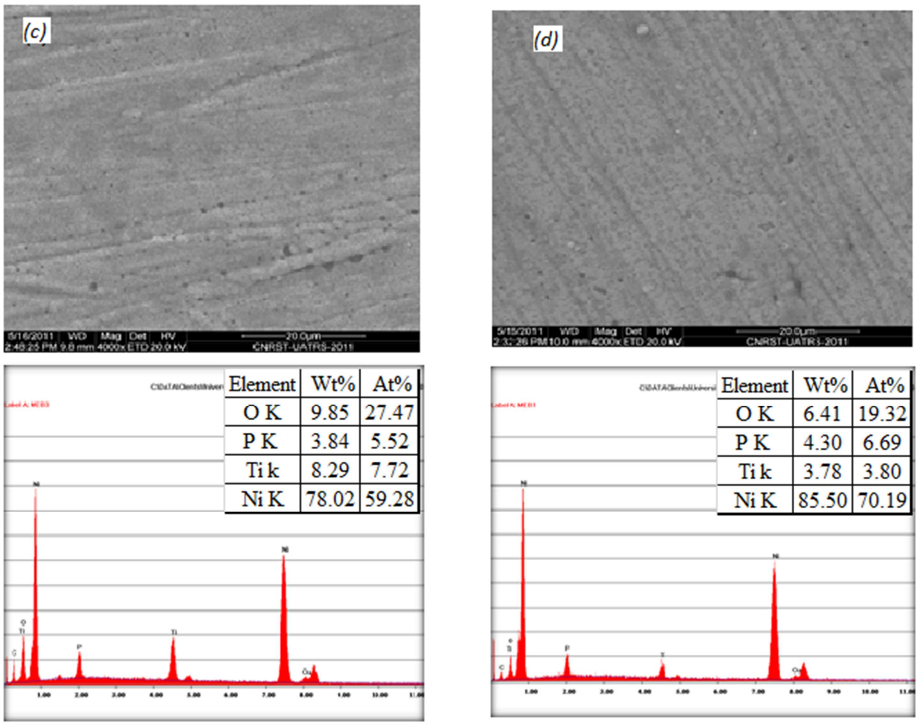
Element	Wt%	At%
O K	6.34	18.48
P K	8.90	13.41
Ti k	4.05	3.95
Ni K	80.72	64.16

Figure 1:SEM surface Morphology and EDX spectrum of Ni-P-TiO_2 composite coatings of (a) Ni-P-200g/L TiO_2 and (b) Ni-P-100g/L TiO_2

The figures (2a) and (2b) show sequentially the spectrum of Ni-P-TiO_2 composite coatings obtained for concentrations of 200g/L and 100g/L of titanium dioxide in the nickel bath to pH=5.We see that there is a reduction of the atomic percentage of nickel and an increase in that of the titanium with the increase in the concentration of titanium dioxide in the bath. This is probably due to a more compact structure of Ni-P- 200 g/LTiO_2 relative toNi-P-100 g/LTiO_2.[13].

b.Neutral solution (pH = 7)

In neutral solution (pH=7), we note that with the reduction of the TiO_2 content, the coatings are very smooth with few nodules and less porous.



Element	Wt%	At%
O K	9.85	27.47
P K	3.84	5.52
Ti k	8.29	7.72
Ni K	78.02	59.28

Element	Wt%	At%
O K	6.41	19.32
P K	4.30	6.69
Ti k	3.78	3.80
Ni K	85.50	70.19

Figure 2: SEM surface Morphology and EDX spectrum of Ni-P-TiO_2 composite coatings of (c) Ni-P-200g/L TiO_2 and (d) Ni-P-100g/L TiO_2

The figures (2d) and (2c) show sequentially the spectrum of Ni-P-TiO_2 composite coatings obtained for concentrations of 200g/L and 100g/L of titanium dioxide in the nickel bath to pH=7.

EDX spectra analysis of Ni-P-TiO_2 composite coatings letting conclude thatthe increase of titanium dioxide in the bath affect the reduction of nickel ions, the atomic percentage items in Ni-P-200g/L TiO2 is (Ni=59.28, Ti=7.72) whereas for Ni-P-100g/L TiO_2 the composition is (Ni=70.19, Ti=3.80).

Polarization curves

The current-voltage curve is a stationary technique widely exploited in electrochemistry, it allows us to estimate the corrosion rate and to understand the formation of a coating. The anodic and cathodic areas of the copper coated with a layer of Ni-P and Ni-P-TiO_2 (Figure3.).

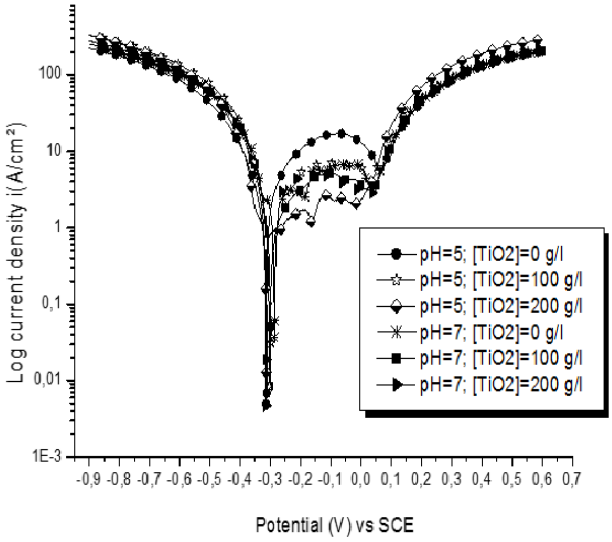


Figure 3: Polarization curves of Ni-P coating and Ni-P-TiO_2 composite film immersed in 4M, H_3PO_4 solution

The interpretation of the polarization curves in the logarithmic form by nonlinear regression allowed us to obtain the kinetic parameters of the corrosion process and values are presented in Table 2.

Table 2. Comparison of corrosion resistance between Ni-P coating and Ni-P-TiO_2 composite film immersed in 4 M H_3PO_4 solution

	idép=8mA/cm2		
	[TiO2] g/l	**Ecorr (V)**	**icorr(mA/cm2)**
pH=5	0	-291	4,55
	100	-292	3,43
	200	-312	1,92
PH=7	0	-277	2,46
	100	-300	2,08
	200	-300	3,41

These result indicates us a reduced electrochemical activity and a bigger corrosion resistance in the case of the composite deposit (Ni-P-200g / L TiO_2, pH 5) with regard to the other deposits being confirmed the beneficial effect of the incorporation of the TiO_2 in the matrix N-P.

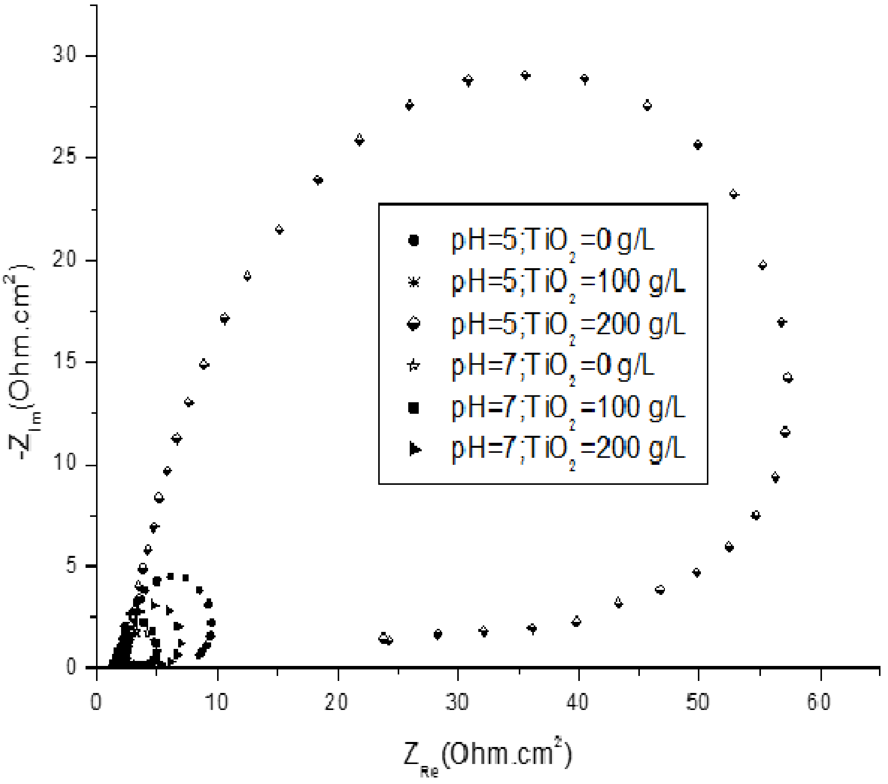


Figure 4: Impedance data, of the copper coated of the Ni-P and Ni-P-TiO_2 in 4M H_3PO_4 solution

The bad results obtained in the case of 100 g/L TiO_2 in the bath can be explained By the training of the defects and the dislocations or the chemical heterogeneous nesses in the metallic matrix either by a not uniform incorporation of particles owed the formation of agglomerates.

The analysis of parameters obtained by the interpretation of polarization curves showed value of Ecorr less negative, a smaller value icorr for composite coating (Ni-P-200g/L TiO_2, pH =5) (Table2).

To confirm this result we are going to use the passing techniques: the spectroscopy of impedance.

Measures by electrochemical impedance spectroscopy

The Figure4.Represents the impedance in the plane of Nyquist diagrams the coatings composites-solution interface, obtained the potential of abandonment in 4 M H_3PO_4 solution to different concentrations of TiO_2 performed after 30 min of immersion at room temperature. There also, graphs of impedance were separated into two curves of different colors for clarity.

The Nyquist diagram of copper coated with a layer of composite "Ni-P-TiO_2" for different concentrations of TiO_2 in the acid and neutral medium "pH=5-7» Figure4**.**

The values of charge transfer resistance (Rt) and the double layer capacitance (Cd) calculated are summarized in Table 3.

Table 3. Impedance parameters of de corrosion for the copper coated of the Ni-P and Ni-P-TiO_2 in 4M H_3PO_4 solution

	idép=8mA/cm2		
	[TiO2] g/l	**Cd (mF/cm²)**	**Rt (ohm*cm²)**
pH=5	0	63,71	3,947
	100	15,46	4,109
	200	2,399	66,31
PH=7	0	40,5	0,786
	100	1,318	7,631
	200	4,596	7,032

Electrochemical impedance spectra allowed deciphering the behavior of composite coatings in corrosive solution of 4 M H_3PO4. The incorporation of the TiO_2 particles determines the growth of the corrosion resistance of the Ni-P deposition.

According to the shape of the impedance diagrams the mechanism associated with the greatloop is predominant. Indeed, after immersion in 4M H_3BO_4 solution, we are witnessing a displacement of the points of the capacitive arc toward the low frequencies and an increase of its diameter(Cd= 2,399 mF/cm^2 and Rt = 66, 31 ohm.cm²).

Then, there is an increase of the values of charge transfer resistance, Rt, while the ability of the double layer, Cd, decreases relative to the deposition of pure Ni-P, which can be explained by the decrease of the active surface into direct contact with the corrosive medium, as a result of incorporation of the particles, where the growth of the thickness of the layer of corrosion products [15].

We can observe that as to the corrosion current density an optimum has been reached for the composite Ni-P-TiO2 coating for (pH=5 and[TiO_2]=200g/L).The results are quite correct.

CONCLUSION

In this work an experimental study of the composite covers Ni-P-TiO_2 was led. For that purpose, the influence of the concentrations of TiO_2 on the structural and anticorrosive properties was studied.

Coatings were realized by electroplating on copper substrate beforehand handled.

Thanks to this study, interesting results were obtained and conclusions were pulled:

- The morphology of the deposits, examined by electronic microscopy with scanning, possesses a homogeneous and compact metallic structure. Furthermore, for coversco-deposited, it seems that in the conditions of elaboration chosen, a high degree of co-deposition is obtained. While the substrate is coated homogeneously;
- The results obtained after the tests of corrosion indicate us a reduced electrochemical activity and a big corrosion resistance in the case of the composite deposits Ni-P-TiO_2 compared with the deposit of Ni-P, being confirmed the beneficial effect of the incorporation of the TiO_2 in the matrix of N- P, better results are obtained for a concentration of 200 g/L from TiO2, pH=5.

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