# Comparative Corrosion Resistance of Electroless Ni-P/nano-TiO<sub>2</sub> and Ni-P/nano-CNT Composite Coatings on 5083 Aluminum Alloy

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Corrosion resistance was compared between electrolessly plated Ni-P/nano-TiO<sub>2</sub> and Ni-P/CNT composite coatings on 5083 aluminum alloy exposed to 3.5 wt.% NaCl solution. The composite coatings were prepared by electroless plating method that the nano-TiO<sub>2</sub> (15 nm) and carbon nano-tube (CNT, 5nm) particles were compared between eletroless Ni plating solutions with low and high concentrations (1 g/L and 10 g/L, respectively). The corrosion resistance of the nano-composite coatings were examined by both potentiodynamic polarization and immersion tests. The experimental results showed a uniform and compact surface morphology in both Ni-P/nano-TiO<sub>2</sub> and Ni-P/nano-CNT composite coatings, and these composite coatings possessed better corrosion resistance than that in the 5083 aluminum alloy substrate and in the electroless Ni-P coating. The corrosion resistance of the nano-CNT introduction. Moreover, the nano-CNT codeposited coating exhibited superior corrosion resistance compared to the nano-TiO<sub>2</sub> codeposited coating.

Keywords: Electroless plating, TiO<sub>2</sub>, CNT, Polarization, Corrosion.

# **1. INTRODUCTION**

Electroless Ni-P coatings are widely used in many industries, including the chemical, mechanical, automobile, electronics and aerospace engineering industries, for surface protection because of their excellent mechanical, magnetic and corrosion-resistant properties. Electroless plating, which is an autocatalytic technique for reducing metals and alloys without applied current, yields a fine, uniform and smooth surface that provides good protection against corrosion. The properties and structures of Ni-P coating depend mainly on the codeposited P content. Because Ni-P coatings have a

non-crystalline amorphous structure when the P content exceeds 7 wt%, they provide excellent protection for mining and chemical equipment and for structural components used in the highly corrosive environments encountered in the oil and gas industries. When applied to metal surfaces, Ni-P coatings with phosphorous content higher than 9 wt% provide effective corrosion protection because they provide a physical barrier that minimizes contact between the metallic substrate and aggressive environments [1-3].

Nanoparticles have many unique physical and chemical properties because of the quantum size effect, the small size effect and the macroquantum tunnel effect [4,5], Nanocomposite plating technique, in which nanoparticles are added to metal coatings to improve physical and mechanical properties, is one example of how nanotechnology can be applied in composite plating. Also, incorporating nanosized particles in Ni-P autocatalytic coatings greatly improves their properties and imparts new functional features that enhance their performance in different fields [6,7]. Particlereinforced composite coatings can also be formed by adding inorganic non-metal nanoparticles such as TiO<sub>2</sub> [8-11], SiC [12,13], SiO<sub>2</sub> [14,15], Al<sub>2</sub>O<sub>3</sub> [16], B<sub>4</sub>C [17], CNT [18-20], BN [21] and diamond [22]. Of these particles, TiO<sub>2</sub> has attracted the most interest because of its many applications in engineering materials. Studies show that TiO<sub>2</sub> coatings enhance wear resistance, hardness and corrosion resistance and other properties such as electrocatalysis and photocatalysis. [8-11,23]. Carbon nanotube (CNT) coatings are also under intensive study because of their novel properties and the many applications of their unique nanostructures in various fields [24-26]. The CNT exhibits excellent electronic properties, high elastic modulus, large elastic strain and fracture strain. Measurements of the Young modulus in isolated nanotubes based on the amplitude measurements of intrinsic thermal vibrations by TEM obtain average Young modulus values of 1.8 TPa and a bend strength as high as 14.2 GPa [27]. Studies of the mechanical properties of multi-walled nanotubes by atomic force microscope (AFM) confirm their superior stiffness and strength. When depositing Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings with high wear resistance, heat resistance and hardness, preserving their anticorrosion properties is essential, especially when the coatings are exposed to aggressive media for long-term periods.

Because nanoparticles easily agglomerate in plating baths, which increases the amount of particles in composite coatings, the unique properties of nanocomposite coatings may be compromised owing to the segregation and agglomeration of nano-particles with high surface energy and activity in the plating bath [14,29]. Therefore, dispersion of particles in the plating bath, which is affected by the nanoparticle concentration in the plating bath and by the stirring rate, is a key parameter [30]. However, the optimal TiO<sub>2</sub> content and CNT content remain undetermined. The CNT easily agglomerates because it is a one-dimensional nanoscale material. Thus, the behavior of CNT differs from that observed in SiC,  $Al_2O_3$  or TiO<sub>2</sub> with particle shape. Generally, different coating surface structures resulting from the varying nanoparticle content of the plating bath can change corrosion properties. The TiO<sub>2</sub> and CNT content in composite coatings can only increase when the TiO<sub>2</sub> and CNT content of the plating is maximal and when the TiO<sub>2</sub> and CNT is homogeneously dispersed.

The electroless plating technique in this study used  $TiO_2$  and CNT nanoparticles in a Ni-P plating solution to form Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings on a 5083 aluminum alloy substrate. The corrosion properties of the 5083 substrate were then compared with those of the

substrate with Ni-P coating. The surface structures of the coatings are examined by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and atomic force microscopy (AFM). The corrosion resistance is determined by both potentiodynamic polarization and immersion tests in aerated 3.5 wt% NaCl solutions.

## **2. EXPERIMENTAL**

# 2.1. Electroless coating preparation procedure

Although the AA5083 aluminum alloy (Al-4.7Mg-0.7Mn) used as a substrate material in this study had good formability, high strength, and good solderability, the intrinsic intermetallic compounds used in the alloy reduced its corrosion resistance. Rectangular ( $1.8 \text{ cm} \times 1.8 \text{ cm} \times 0.7 \text{ cm}$ ) samples of 5083 alloy were first ground with SiC abrasive papers with up to 2000 mesh and then polished with 1  $\mu$ m and 0.3  $\mu$ m Al<sub>2</sub>O<sub>3</sub> powder to achieve an acceptable surface uniformity. The pretreatment procedure consisted of ultrasonic cleaning in acetone for 5 min, washing with a 50 g/L NaOH solution for 3 min at 70°C, miro-etching with a 200 g/L HNO<sub>3</sub> solution for 1 min at room temperature, and double zincating [31]. The zincating solution consisted of 120 g/L NaOH, 20 g/L ZnO, 1 g/L NaNO<sub>3</sub> and 50 g/L C<sub>3</sub>H<sub>4</sub>(OH)(COOH)<sub>3</sub>·H<sub>2</sub>O. The zincated alloy specimen was immersed in the Ni-P plating solution at 85-88°C. The Ni-P electroless plating solution consisted of 30 g/L NiCl·6H<sub>2</sub>O, 10 g/L Na<sub>2</sub>C<sub>2</sub>H<sub>4</sub>O<sub>4</sub>·6H<sub>2</sub>O, 10 g/L NH<sub>2</sub>CH<sub>2</sub>COOH, 20 g/L NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O and 2.5 mg/L Pb(NO<sub>3</sub>)<sub>2</sub>, and additive at pH 4.0. The TiO<sub>2</sub> (with average size of 15 nm) and CNT (multi-walled naotubes with average size of 10 nm) nanoparticles were separately added to the plating solution (1 g/L and 10 g/L) for comparisons of codeposition in composite coatings. Agglomeration of the TiO<sub>2</sub> and CNT was minimized by ultrasonic dispersion of the plating solution for 15 min followed by magnetic stirring at a constant speed of 100 rpm during electroless deposition for 60 min.

#### 2.2. Coating Characterization

Coating surfaces and cross sections were characterized by scanning electron microscopy (SEM, JEOL JSM-6360) and by X-ray energy dispersive spectrometry (EDS, INCA Energy 6587). Imaging of the coating surface topography was performed by atomic force microscopy (AFM, Quesant Q-250CL) in contact mode. The average roughness ( $R_a$ ) and root mean square roughness ( $R_{ms}$ ) parameters were then measured in square regions (side length, 40 µm), and the average of five measurements for each sample was recorded.

#### 2.3. Potentiodynamic polarization tests

Electrochemical corrosion in the electroless composite coatings of the 5083 alloy substrate after exposure to 3.5 wt% NaCl solution was evaluated by potentiodynamic polarization measurements performed with a potentionstat/galvanostat (Model 273A, EG & G Instruments, USA) and a three-

electrode cell designed by the authors with an exposed area of 1 cm<sup>2</sup>. All potentials referred to a saturated calomel electrode (S.C.E.) with a platinum the counter electrode. The potentiodynamic polarization curves were scanned from 0.25 V<sub>SCE</sub> below OCP to a final potential of 1.2 V<sub>SCE</sub>, at a sweeping rate of 1 mV·s<sup>-1</sup>. Five tests were performed for each coated sample to ensure reproducibility.

## 2.4. Immersion tests

The immersion tests were performed by immersion in 3.5 wt.% NaCl solution for durations of 1 h, 7 h, 12 h, 24 h, 48 h, 72 h, 168 h, 336 h, 524 h and 720 h. Variation in corrosion potential and corrosion current density as a function of immersion time was measured by linear polarization method. Before and after each immersion test, each specimen was cleaned and weighed in accordance with ASTM G1-90 standards [32]. The wear loss was determined using an analytical balance (Precisa XS 225A) with a sensitivity of 0.1 mg. After polarization and immersion corrosion testing, corroded surfaces were observed with a SEM equipped with an EDS.

## **3. RESULTS AND DISCUSSION**

# 3.1. Coating comparisons

The surface of the 5083 substrate was highly regular after sanding with SiC abrasive paper #2000. The surface morphology of the Ni-P coating shows a spherical nodular structure. Such a structure with a phosphorous content higher than 7 wt% is often cited in the literature as an example of a Ni-P coating [1-3]. The Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings show superior fineness, uniformity and density compared to the Ni-P coating, which confirms the uniform deposition of the codeposited TiO<sub>2</sub> and CNT nanoparticles in the Ni-P matrix of nanocomposite coating (Figs. 1a, 1b).



**Figure 1.** The SEM images of surface photomicrographs of the nanocomposite coatings: (a) Ni-P/10 g/L TiO<sub>2</sub> (b) Ni-P/10 g/L CNT.

Non-porous areas of the nanocomposite coating surfaces correlated with the incorporation of TiO<sub>2</sub> and CNT in the coatings. The coating cross-sections further show no interfacial voids or defects between the coatings and the 5083 substrate, and the nanocomposite coatings such as Ni-P/10g/L TiO<sub>2</sub>  $(3.33 \pm 0.05 \ \mu\text{m})$  and Ni-P/10 g/L CNT  $(4.13 \pm 0.05 \ \mu\text{m})$  are thicker than the Ni-P coating  $(2.35 \pm 0.06 \ \mu\text{m})$ . Thus, the Ni-P/CNT nanocomposite coating at a high concentration of 10 g/L has the highest coating thickness of  $4.13 \pm 0.05 \ \mu\text{m}$  (Fig. 2). Adding nanoparticles to the plating solution increased the thickness of the nanocomposite coatings, which indicated that adding nanoparticles enhanced the coating deposition rate [18]. The CNT was superior to the TiO<sub>2</sub> because the Ni-P/CNT coatings were thicker than the Ni-P/TiO<sub>2</sub> coatings regardless of whether the nanocomposite coatings were compared at high or low concentrations of TiO<sub>2</sub> and CNT.



**Figure 2.** The SEM images of cross-sectional photomicrographs of the Ni-P/10g/L CNT nanocomposite coating.

Table 1 shows the analysis results of EDS performed for qualitative and quantitative elemental measurement of the Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings. The results show that the Ni-P coating had a phosphorous content up to 14.37 wt%, which confirmed its nodular surface morphology. This Ni-P coating exhibited an amorphous structure when its phosphorous content exceeded 7 wt% but showed a crystalline structure when its phosphorous content decreased to below 7 wt%. [13,33,34]. The data in Table 1 also confirm the presence of Ti and O elements in the Ni-P/TiO<sub>2</sub> nanocomposite coatings, and the presence of C element in the Ni-P/CNT nanocomposite coatings. Moreover, as the TiO<sub>2</sub> and CNT nanoparticles in the electroless plating solution were increased, the Ti, O and C content in the nanocomposite coatings increased, but the Ni content decreased. This indicates that codeposition of TiO<sub>2</sub> and CNT nanoparticles in the coatings occurs before codeposition of Ni ions in the electroless plating solution. Table 1 shows the results of further comparisons of P content, which revealed that adding TiO<sub>2</sub> in the Ni-P plating solution slightly decreases the P content in the Ni-P/TiO<sub>2</sub> coating. However, adding CNT nonoparticles in the Ni-P plating solution substantially increases the P content in the formed Ni-P/CNT coating. After a high CNT concentration (10 g/L) was added, the Ni-

P/CNT nanocomposite coating already had the highest P content of 17.21 wt.%. This demonstrates the beneficial effect of adding CNT nanoparticles in the electroless Ni-P plating solution, *i.e.*, promoting phosphorous ion codeposition in the Ni-P/CNT nanocomposite coatings, and thus exhibiting the higher fineness and density of the surface structure of the Ni-P/CNT nanocomposite coatings (Fig. 1b). The results can be explained by the easy deposition of phosphorous ions at the interface of the nodular granules [13], which corresponded with the incorporation of CNT refining the nodular granules therefore increasing the number of nodular interfaces.

a .		27	NI' D/				NT D/			
Specime	N; D	N1-P/			N1-P/		N1-P/	N1-P/		
n	INI-P	18	g/L TiO <sub>2</sub>	10g/L TiO <sub>2</sub>			1g/L CNT	10g/L CNT		
Element	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%
C K	_	_	_	_	_	_	17.39	49.81	19.01	50.77
Ni K	85.67	73.86	73.71	63.99	63.04	56.91	66.18	39.94	63.78	31.66
O K	_	_	12.55	18.67	20.43	20.71	_	_	_	_
РK	14.37	24.14	12.36	15.71	13.14	18.52	17.43	10.25	17.21	15.57
Ti K	_	_	1.38	1.63	3.39	3.86	_	_	_	-
Total	100.00	100.00	100.00	100.00	) 100.00	100.00	0 100.00	100.00	100.00	100.00

**Table 1.** The EDS elemental analysis results for the Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings.

Correlations between the coating structure and surface morphology were determined by atomic force microscopy (AFM). Roughness parameters  $R_a$  and  $R_{ms}$  were also determined based on the AFM images. The  $R_a$  parameter corresponds to the average of a set of individual measurements of surface peaks and valleys. The  $R_{\rm ms}$  parameter denotes the root mean square average values of deviations of the profile height from the mean line, which were recorded within the evaluation length. The incorporation of TiO<sub>2</sub> and CNT nanoparticles resulted in a significantly lower surface roughness in the nanocomposite coatings compared to the Ni-P coating. Although the increase of TiO<sub>2</sub> and CNT concentrations in the nanocomposite coatings slightly increased roughness, the increases in roughness were still smaller than those in the Ni-P coating. Moreover, the roughness the Ni-P/CNT nanocomposite coatings was significantly lower than that of the Ni-P/TiO<sub>2</sub> nanocomposite coatings containing either low or high concentrations of TiO<sub>2</sub> and CNT nanoparticles. Fluctuations in the appearance of the coating surfaces were observed in the following order:  $Ni-P/CNT < Ni-P/TiO_2 <$ Ni-P. The experimental results therefore confirm that full incorporation of the CNT nanoparticles in the Ni-P coating increases the fineness, density, continuity and smoothness of the coating surface and results in the lowest roughness values of Ra (40.1~42.4 nm) and Rms (43.6~45.2 nm). The roughness is significantly lower than that of the earlier report [35].

#### 3.2. Electrochemical corrosion testing

Figure 3 shows the potentiodynamic polarization curves for the 5083 substrate, Ni-P coating,

Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings in 3.5 wt% NaCl solution. The Ni-P coating and all nanocomposite coatings of Ni-P/TiO<sub>2</sub> and Ni-P/CNT exhibited a better corrosion behavior, and presented more noble corrosion potential and lower anodic corrosion current density compared to the 5083 substrate. The Ni-P/CNT coating conferred superior corrosion protection compared to the Ni-P/TiO<sub>2</sub> nanocomposite coating because it formed a coat with a higher density and a higher uniformity. Additionally, the cathodic curves are accelerated by the Ni-P coating and all nanocomposite coatings and the cathodic current density increased in the following order: Ni-P coating < Ni-P/TiO<sub>2</sub> nanocomposite coating < Ni-P/CNT nanocomposite coating. This result is illustrated by the fact that the cathodic evolution of hydrogen can be accelerated by the presence of these coatings. Although the Ni-P coating is a good catalysis of hydrogen evolution [36], TiO<sub>2</sub> and CNT nanoparticles in the nanocomposite coatings posses better active sites of catalysis for producing hydrogen than the Ni-P coating due to their high-surface area to volume ratio, porous structure, chemical inertness, thermal stability and high mechanical strength [37,38]. Characteristics such as corrosion potential ( $E_{corr}$ ) and corrosion current  $(i_{corr})$  are obtained from the intersection of the cathodic and anodic Tafel curves constructed by Tafel extrapolation method. Polarization resistance  $(R_p)$  was measured using the Stren-Geary equation as follows [39]:

$$R_{\rm p} = \beta_{\rm a} \cdot \beta_{\rm c} / 2.303 \cdot i_{\rm corr} \cdot (\beta_{\rm a} + \beta_{\rm c}) \tag{1}$$

where  $\beta_a$  and  $\beta_c$  are the anodic and cathodic Tafel slopes, respectively.



**Figure 3.** Potentiodynamic polarization curves for the 5083 substrate, Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings in 3.5 wt% NaCl solution.

	$E_{\rm corr}$	i <sub>corr</sub>	$\beta_a$	$\beta_c$	R <sub>p</sub>	<i>i</i> ′ <sub>corr</sub>	R'p
Specimen	(mV <sub>SCE</sub> )	$(\mu A \cdot cm^{-2})$	$(V \cdot dec^{-1})$	$(V \cdot dec^{-1})$	$(k\Omega \cdot cm^2)$	$(\mu A \cdot cm^{-2})$	$(k\Omega \cdot cm^2)$
5083 substrate	-905.4	7.38	0.0567	0.4355	2.95	3.03	7.18
Ni-P	-838.7	6.36	0.0572	0.4047	3.42	2.70	8.06
Ni-P/1g/L TiO <sub>2</sub>	-787.3	5.14	0.0607	0.2856	4.23	2.19	9.91
Ni-P/10g/L TiO <sub>2</sub>	-654.2	4.87	0.0591	0.3248	4.46	2.15	10.08
Ni-P/1g/L CNT	-561.4	3.18	0.0750	0.1507	6.84	1.88	11.58
Ni-P/10g/L CNT	-514.5	2.95	0.0622	0.2603	7.39	1.75	12.45

**Table 2.** Electrochemical characteristics of the 5083 substrate, Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings obtained from potentiodynamic polarization and immersion tests.

Note :  $i'_{corr}$  and  $R'_{p}$  calculated from immersion test.

Table 2 summarizes the results of the polarization tests, which showed that the coatings had the following relationship in terms of effectiveness of corrosion prevention: Ni-P coating < Ni-P/TiO<sub>2</sub> nanocomposite coating < Ni-P/CNT nanocomposite coating. The Ni-P/CNT nanocomposite coating formed by adding high CNT concentration of 10 g/L in the electroless Ni-P plating solution, shows the lowest corrosion current of 2.95  $\mu$ A/cm<sup>2</sup> (a 60% decrease compared with 5083 substrate), the highest polarization resistance of 7.39 K $\Omega$ ·cm<sup>2</sup> (a one and a half fold increase compared with 5083 substrate) and the most noble corrosion potential of -514.5  $mV_{SCE}$  (a 76% increase compared with 5083 substrate). The higher polarization resistance of Ni-P/TiO<sub>2</sub> and Ni-P/CNT composite coatings can be explained by the incorporation of high noble potential of TiO<sub>2</sub> and CNT nanoparticles in the coatings and forming a more homogeneous structure of small grains based upon SEM images of Fig.1, which may exhibits a high activation barrier to prevent the local anodic dissolution. The inequal values of the cathodic and anodic charge transfer coefficients for all specimens are illustrated in Table 2, in particular for 5083 substrate, where  $\beta_a = 57$  mV is less than  $\beta_c = 436$  mV indicating that the cathodic reduction reactions promote anodic polarization. The sum of both cathodic and anodic charge transfer coefficients does not amount to unity in the case of double (mixed) electrode because of its anodic and cathodic polarization curves are not symmetrical about  $E_{\text{corr}}$ . In contrast the sum of both equals exactly unity in the case of single electrode for instance an  $Al^{3+}/Al$  redox-couple due to its single-step reaction. The mixed potential theory proposed by Wagner and Traud [40], which stated that the sum of anodic oxidation currents must equal the sum of cathodic reduction current currents. The nanocomposite coatings with high corrosion resistance of TiO<sub>2</sub> and CNT nanoparticles could provide a high activation barrier and polarize to a highr  $E_{corr}$  value, obtaining a lower  $i_{corr}$  (Table 2). In the Ni-P/CNT composite coatings, their exchange current densities for cathodic hydrogen evolution may be high because of high surface area of CNT embedded in coatings, and may have a low anodic Al dissolution due to their high activation barrier. A higher charge transfer resistance value (*i.e.*, about 17.169  $\Omega \cdot cm^2$ ) was reported in a earlier study of Ni-P/nano-SiO<sub>2</sub> composite coatings exposed to the same 3.5 wt% NaCl solution [15]. This charge transfer resistance value is rather lower than that of the Ni-P/TiO<sub>2</sub> and Ni-P/CNT composite coatings analyzed in the present study. The Ni-P coating protects the substrate by preferential dissolution of nickel occurring at open circuit potential, which causes phosphorous

enrichment in the coating surface layer. By reacting with water, the enriched phosphorus surface forms a layer of adsorbed hypophosphite anions that block the supply of water to the electrode, which is the first step in the formation of soluble Ni<sup>+2</sup> species or a passive nickel film [3,41,42]. Amorphous alloys offer better corrosion resistance compared to equivalent polycrystalline materials because the glassy film that passivates their surfaces prevents grain boundaries from forming [43]. The improved corrosion protection in the presence of TiO2 and CNT can be explained by two mechanisms of the nanocomposite coatings. First, the TiO<sub>2</sub> and CNT nanoparticles act as inert physical barriers by occupying very small pores in the metal matrix, which modifies the Ni-P layer microstructure and provides a superior corrosion resistance of the composite coating in comparison with the pure alloy coating. Via this mechanism, more CNT nanoparticles than TiO<sub>2</sub> nanoparticles are incorporated in the Ni-P coating. Phosphorus has an important effect on the coating structure because the corrosion resistance of the coating improves with phosphorus content. The Ni-P/CNT (17.21~17.43 wt% P) coating provided significantly better corrosion protection compared to the Ni-P/TiO<sub>2</sub> coating because it had a significantly higher phosphorous content (12.36~13.14 wt% P) (Table 1). The second mechanism, incorporation of TiO<sub>2</sub> and CNT nanoparticles in the Ni-P coating, forms corrosion microcells in which the TiO<sub>2</sub> and CNT nanoparticles act as a cathode and nickel acts as anode since the standard potential of TiO<sub>2</sub> and CNT is higher than that of nickel. Such corrosion micro-cells facilitate the anodic polarization. Therefore, in the presence of TiO<sub>2</sub> and CNT nanoparticles, localized corrosion is inhibited, and corrosion is generally uniform [23,44]. According to this mechanism, the standard corrosion potential of CNT is nobler than that of TiO<sub>2</sub>, and incorporation amount of CNT (17.39~19.01 wt%) is significantly higher than that of  $TiO_2$  (1.38~3.39 wt%) (Table 1), which further confirmed that corrosion protection obtained by incorporation of CNT in the Ni-P coating is clearly superior to that obtained by incorporation of TiO<sub>2</sub>. The resulting increase in phosphorus content also gives it high chemical stability and high resistance to pitting attack of Cl<sup>-</sup> in the 3.5 wt% NaCl solution.

#### 3.3. Immersion testing

Immersion tests were performed in 3.5 wt% NaCl solution for durations ranging from 1 h up to 720 h for further evaluation of long term corrosion resistance in the 5083 substrate, Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings. Figure 4 shows the weight reduction in the specimens after immersion corrosion testing in 3.5 wt% NaCl solution. The data show that weight decreases as immersion time increases. The weight loss observed with the specimens immersed for various times was in the following order: 5083 substrate > Ni-P coating > Ni-P/TiO<sub>2</sub> nanocomposite coating > Ni-P/CNT nanocomposite coating. Furthermore, the weight loss of the Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coating decreases as the concentration of TiO<sub>2</sub> and CNT nanoparticles increases. The weight loss of Ni-P/CNT nanocomposite coating at a high CNT concentration of 10 g/L has the lowest value of 14.001 g/m<sup>2</sup> after 720 h immersion. Ma *et al.* [45] reported a weight loss of 4.235 g/m<sup>2</sup> in electroless Ni-P/Au nanocomposite coatings with 2.0 × 10<sup>-5</sup> mol/L of added gold nanoparticles after 46 h immersion in the same 3.5 wt% NaCl solution. This value is much higher than that observed in the Ni-P/CNT nanocomposite composite coating with a high CNT concentration of 10 g/L in the

present study after exposure to the same solution for the same immersion time  $(2.021 \text{ g/m}^2)$ . The corrosion potential (Fig. 5) and corrosion current density (Fig. 6) of the specimens were further compared at various immersion times in 3.5 wt% NaCl solution by linear polarization method. The 5083 substrate presents the most active corrosion potential and the highest corrosion current density during the varying durations of immersions.



**Figure 4.** Weight loss of the 5083 substrate, Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings after immersion in 3.5 wt% NaCl solution for varying durations.



**Figure 5.** Variations in corrosion potential of the 5083 substrate, Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings after immersion in 3.5 wt% NaCl solution as functions of immersion time.



**Figure 6.** Variations in corrosion current of the 5083 substrate, Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings during immersing in 3.5 wt% NaCl solution as functions of immersion time.

The Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings exhibit more noble corrosion potential and lower corrosion current density compared to the Ni-P coating during the varying durations of immersion. The Ni-P/CNT nanocomposite coating at high CNT concentration of 10 g/L also possesses the most noble corrosion potential and the lowest corrosion current density after varying durations of immersions. These findings of the immersion tests are consistent with those of the surface structure and potentiodynamic polarization corrosion behavior of the coatings. The polarization resistance,  $R'_{\rm p}$ from corrosion current density,  $i_{corr}$  based upon Fig. 4 and the Tafel constants based upon Fig. 3 and Table 2. The calculated results of  $i'_{corr}$  and  $R'_{p}$  from immersion test are listed in Table 2. As comparing them obtained from two methods of weight loss method and potentiodynamic polarization method, it is found that the trend of  $i'_{corr}$  and  $R'_{p}$  obtained from weight loss measurements after the immersion tests agrees well with the  $i_{corr}$  and  $R_p$  values obtained by Tafel extrapolation method. These results evidence that the estimation of corrosion rate instantaneously by means of polarization, being of special relevance the relationship between weight loss and polarization resistance, which cannot always be deduced from Tafel parameters, because the constancy of electrochemical parameters with time cannot a priori be assumed. Therefore, the two methods should be necessary and additionally applied in order to supplement the major drawback of each method. The SEM images of surface corrosion in the specimens after 72 h immersion in 3.5 wt% NaCl solution show that the 5083 alloy substrate presents severe localized pitting corrosion with numerous large and deep pits (Fig. 7a). Although the electroless Ni-P coating provides good corrosion protection for the 5083 substrate, it produced localized broken corrosion voids after 72 h immersion (Fig. 7b). At a low TiO<sub>2</sub> concentration of 1 g/L, the Ni-P/TiO<sub>2</sub> nanocomposite coating exhibits a uniform corrosion. At a high TiO<sub>2</sub> concentration (10 g/L), the nanocomposite coating shows localized cracking phenomena (Fig. 7c). However, regardless of

whether the CNT concentrations are low or high (1 g/L or 10 g/L, respectively) the Ni-P/CNT nanocomposite coatings still show the best corrosion resistance with no corrosion failures after 72 h immersion (Fig. 7d).



**Figure 7.** The SEM photomicrographs of corroded surfaces of the 5083 substrate, Ni-P coating, Ni-P/TiO<sub>2</sub> and Ni-P/CNT nanocomposite coatings after immersion in 3.5 wt% NaCl solution for 72 h: (a) 5083 substrate (b) Ni-P (c) N-P/10 g/L TiO<sub>2</sub> (d) Ni-P/10g/L CNT.

## **4. CONCLUSIONS**

(1) The Ni-P/nano-TiO<sub>2</sub> and N-P/nano-CNT composite coatings deposited by a novel electroless process on 5083 alloy substrate exhibited good corrosion protection for 5083 alloy immersed in 3.5 wt% NaCl solution for durations of up to three months.

(2) Incorporation of nano-TiO<sub>2</sub> and nano-CNT could promote codeposition of an Ni-P coating and formation of a uniform and dense coating structure. Incorporation of Nano-CNT was superior to

that of nano-TiO<sub>2</sub> and maintained a high phosphate level (17.21 wt% at high CNT concentration of 10 g/L) in the Ni-P/nano-CNT composite coating and a finer, smoother and more compact structure, which gave it the best corrosion resistance of Ni-P/nano-CNT composite coating.

(3) When CNT was added at high concentration of 10 g/L in potentiodynamic polarization tests in 3.5 wt% NaCl solution, the Ni-P/nano-CNT coating showed the best corrosion resistence behavior with lowest corrosion current of 2.95  $\mu$ A/cm<sup>2</sup> (descending 60% compared with 5083 substrate), the highest polarization resistance of 7.39 K $\Omega$ ·cm<sup>2</sup> (raising one and half folds compared with 5083 substrate) and the most noble corrosion potential of -514.5 mV<sub>SCE</sub> (raising 76% compared with 5083 substrate).

(4) Weight loss increased with immersion time in immersion testing in 3.5 wt% NaCl solution. Consequently, the electroless Ni-P/nano-CNT was superior to the Ni-P/nano-TiO<sub>2</sub> coating and the N-P coating, and the best corrosion resistance was observed in the electroless Ni-P/nano-CNT composite coating formed at a high CNT concentration of 10 g/L.

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