The Effect of the Carbon Nanotube Content on the Corrosion Behaviour of Ni-P-CNT Composite Coating

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Abstract

In the present study, Ni-P-CNT composite coating was successfully fabricated via electroless plating. Scanning electron microscopy (SEM) was used to characterize the coatings. The effect of CNTs concentration in the bath on its content in the composite coatings was studied. Furthermore, the corrosion behaviour of the coatings with different contents of CNTs was evaluated using Tafel polarization and electrochemical impedance spectroscopy (EIS) methods in 3.5 wt.% NaCl aqueous solution at the room temperature. The results showed that the corrosion resistance of the Ni–P-CNT composite coatings was excellent in comparison with that of the Ni-P coatings and the content of incorporated CNTs played a key role in the passivation and corrosion resistance.

Keywords: Carbon nanotubes, Electroless plating, Composite coating, Corrosion resistance.

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1. Introduction

Since corrosion and abrasion are the two most significant reasons for the degradation of industrial parts, extensive researches have been conducted in order to develop the methods of reducing them and their inflicted costs. In this context, electroless composite coating process is a well-known method used for enhancing the durability of the parts and even making them reusable [1]. Electroless deposited Ni-P alloy coatings have wide applications in industry due to their unique properties such as corrosion resistance, wear resistance, non-magnetism, improved microhardness and coating thickness uniformity [2,3]. It is known that the incorporation of particles onto the Ni-P matrix improves tribological or corrosion properties of the coating, depending on the particle nature. In this regard, adding some unsolved particles such as diamond, PTFE, B_4C, TiO_2, SiO_2, Si_3N_4 or Al_2O_3 particle to Ni-P plating bath has been developed [1,4-9].

Various models have been proposed for explaining the high corrosion resistance of Ni-P coatings. The formation of a phosphorus-rich film at the deposit/solution interface because of rapid and selective nickel dissolution is expressed as the main reason for corrosion resistance of Ni-P coatings [10-13]. Formation of this film can act as diffusion barrier against active dissolution of the deposit [10,12], or by adsorption of hypophosphite ions, it can form a barrier layer which prevents the dissolution of nickel atoms at the deposit surface (called "chemical passivity") [11,12].

According to Diegle et al. [11], the passivity of an Ni-P alloy is due to the phosphorus enrichment of the coating, which is because of the preferential Ni dissolution. They postulated that the enriched phosphorus surface reacted with water to form a layer of adsorbed hypophosphite anions ($H_2PO_2^-$). Chemical passivation could block the supply of water to the electrode surface, thereby preventing hydration of the nickel. Hydration of nickel is, therefore, considered the first step to form either soluble Ni^+ species or a passive Ni film [11-13].

Carbon nanotubes (CNTs) are believed to be the ideal reinforcing agent for making advanced composites because of their attractive properties such as large aspect ratio, high Young's modulus, excellent flexibility, unique conductivity and chemical stability [14-17]. The effect of CNTs in composite coatings on the hardness [14,17], corrosion [8,18,19], mechanical and wear properties [16,17] has been studied during recent years. However, corrosion properties were not studied in detail. Some reports have been published on corrosion properties of nickel matrix composite coatings. These reports indicated that incorporation of the CNTs in the composite coatings was advantageous for forming a passive film and it could lead to a better corrosion performance [8,14].

The present work aims to prepare electroless Ni-P-CNT composite coatings with various contents of carbon nanotube and evaluate its corrosion resistance.

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2. Experimental procedure

Pristine CVD-grown multi walled carbon nanotubes, 10-30 μm in length and 10-20 nm in diameter with special surface areas (SSA) of about 200 m^2/g, were purchased from Neutrino Corporation.

The homogeneous dispersion of the CNTs throughout the matrix is a critical factor in determining the properties of the CNT-strengthened composites. In this sense, the length to diameter ratio of the CNTs is a key in order to disperse them in aqueous electrolyte solution [19]. For this reason, the as-received CNTs were milled for 8 hours in an acetone liquid using a planetary ball mill machine at the rotating speed of 400 rpm. Ball to powder ratio was kept at 50:1. Milling made the CNTs straight and shortened, and therefore, improved the dispersion of the CNTs in the electroless bath. Then, ball milled CNTs were subjected to the following acid treatment for dissolving any metallic contaminants and ensuring better dispersion in the electroless bath [20].

The ball milled CNTs were immersed in 70% HNO$_3$ solution for 1 h to remove any metallic contaminants. The samples were then exposed to a mixture of HNO$_3$ and H$_2$SO$_4$ (volumetric 1:3) under high power sonication for 3 h in an ultrasonic bath (POWERSONIC405-HWASHIN). This procedure shortened and exfoliated the CNTs. After this period, a small amount of HCl was added into the suspension, which resulted in the formation of carboxyl functional groups on the end of the CNTs. The CNTs were subsequently rinsed with distilled water until a neutral suspension was formed as indicated by a pH meter.

After grinding up to 600-grit SiC emery paper, all substrates were pretreated by the combination of organic solvents and alkaline degreasing with intermediate water rinses.

The commercial SH490L5 nickel-phosphorus electroless bath (Scholter, Germany), which consisted of 7g/l nickel and 30g/l H$_2$PO$_2^-$, was used. Bath conditions for the fabrication of the Ni-P-CNT electroless composite coating are shown in Table 1. After the Ni-P coating, the interlayer with the deposit thickness of 5μm was obtained, and the Ni-P-CNT composite coating was deposited on the interlayer with the thickness of 25 μm. The as-prepared coating was implanted into deionized water with ultrasonic vibration and then dried naturally.

Table 1. Bath conditions for the fabrication of the Ni-P-CNT electroless composite coating

Parameter	Condition
Temperature	88 ± 2 (˚C)
pH	4.7
Magnetic agitation	850 (rpm)
Surfactant (CTAB)	200 - 300 (mg/lit)
Treated CNTs	0.5, 1, 1.5, 2 and 2.5 (gr/lit)

Microstructure evaluation was carried out by scanning electron microscopy (SEM, Philips XL30). Energy dispersive spectroscopy (EDS, SERON-AIS2100) was employed to identify the composition of coatings.

Tafel polarization tests were conducted in a three-electrode system. The counter electrode was a platinum wire and the reference electrode was a standard calomel electrode (SCE). The tests were performed in 3.5% NaCl solution using an AMETEK Potentiostat (model PARSTAT 2273) at the scan rate of 1 mV s^{-1}. Corrosion potentials as well as corrosion current densities were extracted from the plots using Tafel extrapolation method. Electrochemical impedance spectroscopy (EIS) measurements were also carried out using the mentioned corrosion cell and equipment. The impedance values were recorded in the frequency range from 100 kHz to 10 mHz. The voltage amplitude was 10 mV with respect to the open circuit potential. The analysis of the spectra was performed using Zview software.

3. Results and discussion
3.1. Characterization of coatings

At the deposition process, the Ni-P coating was formed in terms of autocatalysis reaction and the precipitates of CNTs co-deposited within the matrix to form the adherent Ni-P-CNT composite coating. Figure 1 shows the cross-section and surface morphology of the Ni-P-CNT composite coating obtained from bath containing 2 gr/lit CNTs. It can be observed from Fig. 1a that a uniform and continuous coating with the thickness of about 30μm was formed and the surface of the sample was uniformly covered with the electroless deposition. These results could be highly beneficial to corrosion resistance of the composite coating. The surface of the deposit was compact, exhibiting a nodular shape with a typical cauliflower-like morphology (Figure 1(b)). The SEM micrograph of the corroded surface of the composite coating is depicted in Figure 1(c). The Ni-P-CNT composite coating was corroded in the liquid solution with nitric acid (1M) and sulfuric acid (1M). As a result of this treatment, Ni-P matrix was partially dissolved, causing the CNTs, which were covered by the Ni-P deposit, to be revealed. As can be seen, the CNTs were uniformly embedded in the Ni-P matrix and parts of them were protruded from the surface.

The effect of the CNTs concentration in the plating bath on the incorporation of CNTs in the electroless Ni-P-CNT composite coating is shown in Figure 2. It can be seen that there was a critical concentration at which these particles exhibited saturation in incorporation.
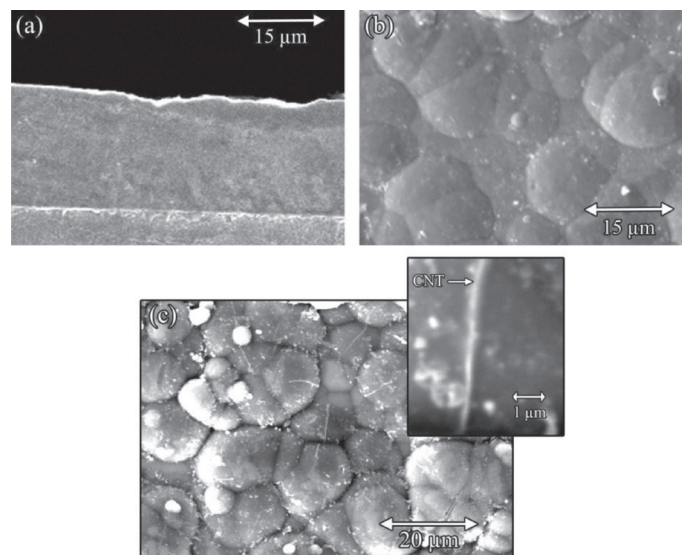
Fig. 1. The SEM micrographs of the Ni-P-CNT composite coating (a) cross-section morphology, (b) surface and (c) corroded surface.
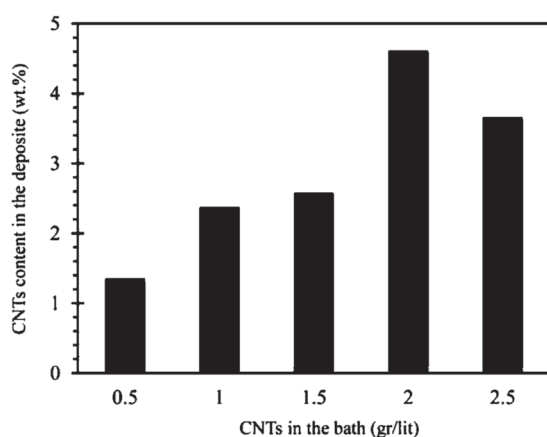

Fig. 2. The effect of the CNTs concentration in the plating bath on the incorporation of CNTs in the coating.

Below this concentration, as the content of CNTs in the bath was increased to 2 g/lit, the weight percent of CNTs in the coating was also increased to 4.6 wt.%. The reason for this increase seems to be related to the increased physical collisions of particles with the surface, following the trapping of more particles in the mechanical locks of the coating [1,21]. However, above the critical concentration, a slight decrease in the incorporation percentage was observed. This may be attributed to several reasons. First of all, above this concentration, the strong van der Waals interaction between the nanotubes led to the agglomeration of CNTs [15,22]. Since the agglomerated CNTs were hard to deposit at substrate surface and tended to settle down before the electroless depositing process, the available number of particles adjacent to the electrode surface for incorporation was decreased. Second, electroless baths are very sensitive to contaminants [23]; therefore too high concentrations of CNTs could have very deleterious effects on electroless

bath and obstruct the autocatalytic reactions. Third, above the critical concentration, some CNTs were physically adsorbed on the electrode surface, making available the smaller number of active spots for incorporation on the substrate surface. A similar co-deposition behaviour was observed earlier in some electroless composite system [1,21,24].

3.2. Corrosion tests
3.2.1. Tafel polarization

The corrosion behaviour of the electroless Ni-P and Ni-P-CNT coatings was evaluated using potentiodynamic polarization technique. Tafel polarization plots for the Ni-P and Ni-P-CNT coatings with different contents of CNTs in the as deposited condition in 3.5% NaCl solution are illustrated in Figure 3. The corrosion parameters such as corrosion potential (E_{corr}) and corrosion current density (i_{corr}), were obtained from the polarization curves using Tafel extrapolation method, as summarized in Table 2. It is obvious that as the content of CNTs in the bath was increased, the corrosion potential was first increased and then decreased. This behaviour seems to be related to the change in the content of incorporated CNTs in the composite coating. Due to the low hydrogen overvoltage on CNTs [25,26], with increasing CNTs in the coating, the rate of cathodic half reaction (most probably hydrogen evolution) was increased, and therefore corrosion potential was shifted towards a more noble direction.

Also, according to Table 2, by increasing the concentration of CNTs in the plating bath, corrosion current density values were initially decreased and then increased. The improvement of corrosion resistance of composite coating with increasing the CNTs concentration in the bath to 1.5 g/lit can be attributed to the increase in the incorporated CNTs in

the coating. More incorporated CNTs increased the rate of hydrogen evolution and enhanced the anodic dissolution of the Ni-P matrix that caused augmented preferred nickel dissolution. Consequently, the formation of the phosphorus-rich passive film at the coating/solution interface was accelerated and the corrosion current density was decreased. On the other hand, the increase in CNTs content of composite coatings led to the decrease in the effective metallic area prone to corrosion and thereby, corrosion resistance was improved [19].

Although with the further increase in the concentration of CNTs in the plating bath to 2 and 2.5 g/lit content, incorporated CNTs were increased, corrosion resistance was aggravated.

This can be ascribed to two reasons. First, the presence of a too high concentration of CNTs in the plating bath obstructed the electroless autocatalytic reactions and increased micro-defects density in the composite coatings. Since the defects known as a high energy sites, they can be easily corroded and are suitable for initiate localized corrosion. Second, too high content of CNTs in the composite coating resulted in the increase in the internal stress of the coating, thereby increasing the free energy of the coating. The coatings with higher free energy values were more susceptible to corrosion.
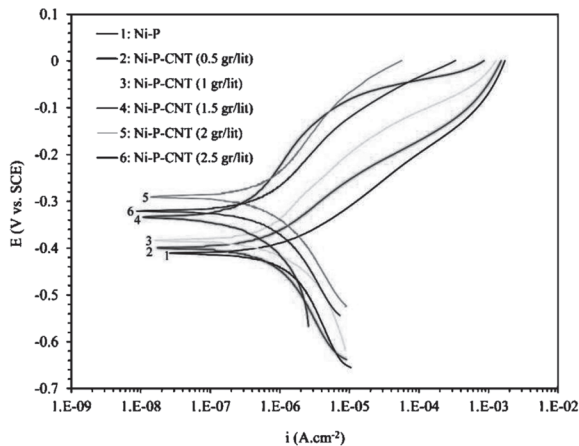

Fig. 3. The polarization curves of the coatings in 3.5% NaCl solution.

3.2.2. Electrochemical Impedance Spectroscopy (EIS)

Figure 4 shows the Nyquist plots obtained for as deposited electroless Ni-P and Ni-P-CNT coatings with different contents of CNTs in 3.5% NaCl solution at their respective open circuit potentials. All the curves appeared to be similar, consisting of a single semicircle signifying the charge controlled reaction. However, it should be noted that although these curves appeared to be similar with respect to their shape, they differed considerably in their size. This indicates that the same fundamental processes had to occur on all these coatings but over a different effective area in each case.

In order to further understand the corrosion mechanisms, the corresponding equivalent circuits for EIS tests of the coatings are shown in Figure 5. In this figure, R_s is solution resistance and R_{ct} is charge transfer resistance, which is proportional to the corrosion resistance. Constant Phase Element (CPE) was used in place of ideal capacitors to which a phenomenological constant was often attached to fit impedance behaviour at electrode/electrolyte interface, which showed deviation from the real capacitor behavior. The plots were fitted using Zview software. The results are listed in Table 2. A good correspondence between the fitted and measured spectra was obtained.

According to Table 2, as the concentration of CNTs in the bath was increased, charge transfer resistance and n_{dl} values were initially increased and then decreased while CPE_{dl} was shown to follow a inverse trend. These results were in accordance with Tafel polarization results, stating that at the concentration of 1.5 g/lit CNTs in the bath, the corrosion resistant of the coating was found to be maximized. As stated above, the increase in the concentration of CNTs in the bath to 1.5 gr/lit increased incorporated CNTs in the composite coating and therefore, enhanced the charge transfer resistance due to the facilitation of chemical passivation and rapid formation of a thicker P-rich film with low ionic conductivity properties. In addition, since the nanoscale deposited CNTs reduced the surface and structural defects by filling the crevices, gaps and micron holes of the coating [14,18] were

Table 2. Corrosion resistance values evaluated by potentiodynamic polarization and EIS studies

	E_{corr} (V vs. SCE)	i_{corr} ($\mu A.cm^{-2}$)	R_S ($\Omega.cm^2$)	R_{ct} ($k\Omega.cm^2$)	CPE_{dl} ($\mu f.s^{1-n}.cm^{-2}$)	n_{dl}
Ni-P	-430	0.64	130.9	23.12	51.2	0.75
0.5 gr/lit	-397	0.47	106.4	24.33	22.2	0.87
1 gr/lit	-383	0.37	112.3	31.01	21.7	0.86
1.5 gr/lit	-340	0.18	146.3	49.95	16.6	0.90
2 gr/lit	-297	0.29	138.2	45.10	30.3	0.87
2.5 gr/lit	-386	0.39	163.2	30.49	32.24	0.79

increased in the incorporated CNTs content, leading to the formation of a denser and more homogenous coating that caused the decrease in CPE_{dl} and the increase in n_{dl} values. According to the literature [8,27-29], CPE_{dl} and n_{dl} values can be related to the porosity and surface inhomogeneity of the coating.

Further increase in the concentration of CNTs in the bath tended to increase the porosity and defect densities of composite coating. Therefore, it can be concluded that n_{dl} value was increased while CPE_{dl} value was decreased. These changes indicate that the CNTs play a key role in the passivation and modification of the structure of Ni-P-CNT composite coating.
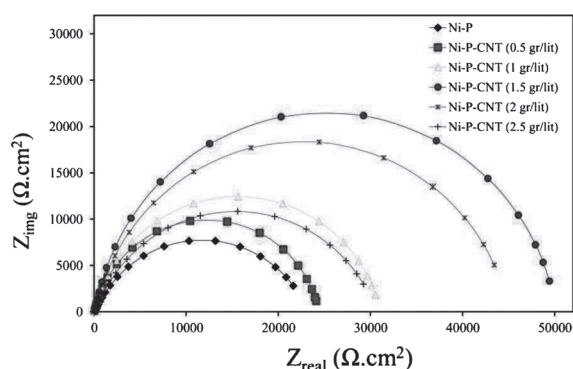

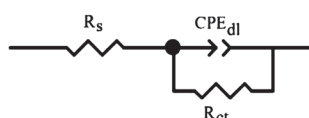*Fig. 4. The Nyquist plots of the coatings in 3.5% NaCl solution.*

Fig. 5. Equivalent electrical circuit model used to analyze the EIS data.

4. Conclusions

Electroless Ni-P-CNT composite coatings with different contents of incorporated CNTs were successfully deposited. The following conclusions can be drawn:

1. There was a critical concentration at which CNT particles exhibited saturation in incorporation.
2. With increasing CNTs in the composite coating, the corrosion potential was shifted towards a more noble direction.
3. By increasing the concentration of CNTs in the plating bath, corrosion current density values were initially decreased and then increased.
4. The content of incorporated CNTs in the composite played a key role in the passivation and corrosion resistance.

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