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Preparation of electroplated Ni-P-ultrafine diamond, Ni-P-carbon nanotubes composite coatings and their corrosion properties

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Ni-P-ultrafine diamond (UFD) and Ni-P-carbon nanotubes (CNTs) composite coatings were deposited by electroplating at 76°C. The relation between the content of the incorporation and the amount of the UFD and CNTs in the electroplating solution was investigated. The corrosion behavior of the composite coatings was evaluated by polarization curves and electrochemical impedance spectroscopy in 0.1 M NaCl and 0.5 M H_2SO_4 solutions. It was found that increasing the UFD content in the coatings displays better corrosion performance, while a contrary result for the CNTs incorporated alloys was found due to the special structural state. The results show the incorporation of UFD and CNTs in Ni-P coatings is advantageous for forming better passive films.

1. Introduction

With the increasing demand from industries for improved performance, development of better surface coatings with higher wear and corrosion resistance has become imperative. Electroplated Ni-P coatings are widely used in modern technology to improve corrosion resistance, wear resistance and hardness of various materials [1–7]. Current trends of coating techniques involve composite coatings, such as multilayer or multiphase coatings, which are expected to have tailor-made properties for specific applications. Recent progress is the co-deposition of solid particles into coatings. Consequently, functional composite coatings with highly specific characteristics can easily be produced by choosing suitable particulate materials. These solid particles can be hard materials (such as SiC, Al_2O_3 and diamond) [8–10] to enhance the hardness and the wear resistance of the deposits, or can be dry lubricants (such as MoS_2, PTFE and graphite) [11–13] to impart lubricity and reduce the coefficient of friction. In this paper, an attempt was made to incorporate ultrafine diamond (UFD) and carbon nanotubes (CNTs) into a Ni-P alloy matrix by electroplating because of their most frequently studied and applied excellent wear resistance and tribological properties [14, 15]. The effect of the incorporation ultrafine diamond and carbon nanotubes on the corrosion properties of Ni-P coatings was evaluated mostly by electrochemical methods.

2. Experimental

The basic bath for plating Ni-P binary alloy deposits was as follows: $NiSO_4{\cdot}6H_2O$ (180 g/L), H_3PO_4 (20 ml/L), H_3PO_3 (20 g/L), $NiCl_2$ (10 g/L) and citric acid (100 g/L). UFD (provided by Lingyun Nanomaterial Company, Co. Ltd., GanSu, China, average diameter of 5–10 nm) and CNTs (prepared by CVD method, CH_4 as the carbon source, 900°C, 2 h) (of weight percentage) were added, ultrasonically dispersed with the help of surfactants. The process was carried out at 76°C and a current density 20 A dm^{-2} for 20 min. All the chemicals used were analytically pure. The substrates used were 5 cm^2 copper sheets. Before plating, they were cleaned, degreased and polished with methylbenzene and propanone, and 0.4 M NaOH solution at 90°C for 10 min. Then, they were activated in a 50 ml 5% H_2SO_4 solution for 2 min at room temperature and then washed fully with deionised water.

The content of the incorporation was examined with an Elementar Analysensysteme (GmbH VarioEL). The morphology was determined by means of scan electron microscopy (SEM). The obtained coatings was investigated by anodic polarization curves and electrochemical impedance spectroscopy carried out in a three-electrode vessel using an electrochemical workstation (CHI 614). The reference electrode was a saturated calomel electrode (SCE), and the auxiliary electrode was a platinum grid. Tests were conducted in both 0.1 M NaCl solution and 0.5 M H_2SO_4 solution at room temperature, open to air. The scan rate of the polarization curves was 2 mV S^{-1}. The amplitude of the impedance spectra was 10 mV and the frequency ranged from 100000 to 0.03 Hz.

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TABLE I Relation between the content of the incorporation and the amount of the UFD and CNTs in the electroplating solution

Composite alloys	The amount of particles in the plating electrolyte (wt%)	The C content of incorporation in the alloy (wt%)
Ni-P-UFD	5	1.083
	1	0.949
	0.5	0.336
Ni-P-CNTs	0.5	0.247
	0.1	0.531

Note. The amount of the incorporation in all the graphs is corresponding to the weight percentage of the particles in the plating electrolyte.

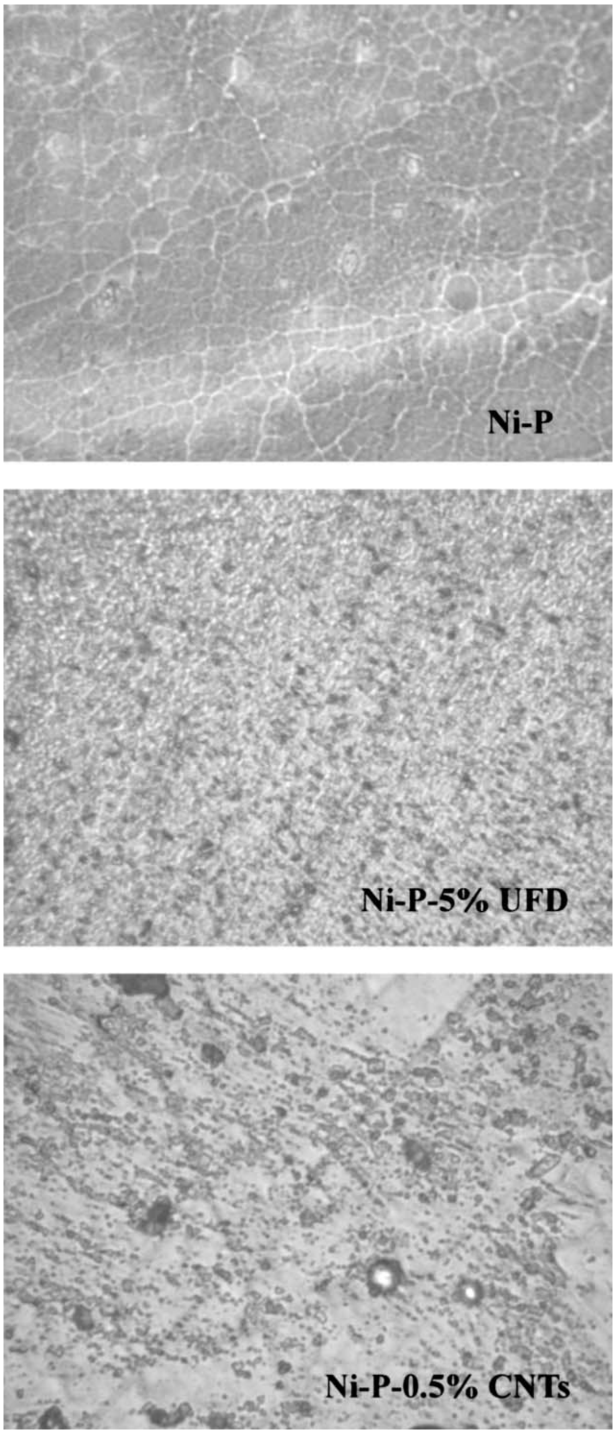

Figure 1 Metallographic photographs of the composite alloys. Magnification: ×1000.

3. Results and discussion

3.1. Relation between the content of the incorporation and the amount of the UFD and CNTs in the electroplating solution

The electrolytic composite layers exhibit good adherence to the copper substrates and can be deposited up to a thickness of 25 μm. Table I presents, as a function of the amount of UFD and CNTs in the plating electrolyte, the results of the chemical analysis of carbon content corresponding to UFD and CNTs in the alloy deposits. It should be noted that carbon content increases with increasing mount of UFD, however, is inversely proportional to the amount of the CNTs. The reason was suggested to be that carbon nanotubes in possession of highly active surface energy tend to aggregate and therefore dispersion is harder when the quantity in the plating electrolyte increases. This means that the concentration of diamond can be increased continually, while the content of CNTs has already been saturated, and excess CNTs in the electroplating solution are harmful for the incorporation.

3.2. Morphology of the composite coatings

The morphology of the deposits shows no significant dependence on the mount of the incorporation, which is supported by the metallographic study of the structure. Fig. 1 displays three typical photographs of the alloys. It is possible to note that the morphology reveals microcracks for the Ni-P alloy and granular for the Ni-P-UFD deposits. Electroplated Ni-P-CNTs composite coatings exhibit the porosity with some spherulites shaped as hemispheres. It is known [16] that the formation of composite electroplates is accompanied by the development of dislocation structure near the dispersed articles and the formation of effective barriers (the location walls, for example) preventing the dislocation motion. The presence of UFD and CNTs in the Ni-P layer affects heterogeneity of the surface and increases the number of boundaries between Ni and other particles in the matrix.

3.3. Electrochemical characterization of the corrosion resistance of the alloys

Potentiostatic anodic curves were obtained in 0.1 M NaCl solution. The effect of the amount of incorporation on the anodic behavior of Ni-P is seen in Fig. 3. The free corrosion potential (E_{cor}) doesn't present an obvious rule with the amount of the UFD and varies a little. For the UFD incorporated alloy, a current plateau is observed, which can be associated with a passivation process [17–22]. The constant current value extends from −320 mV to −80 mV for 5% UFD incorporation and is followed by an increase in the current with anodic polarization, while there was no passivation range in the Ni-P alloy by our experiment, different from that reported by Parente *et al.* [23]. However, in the range of −300 mV to 600 mV, the Ni-P alloy displays the highest current value at the same potential. As the UFD content

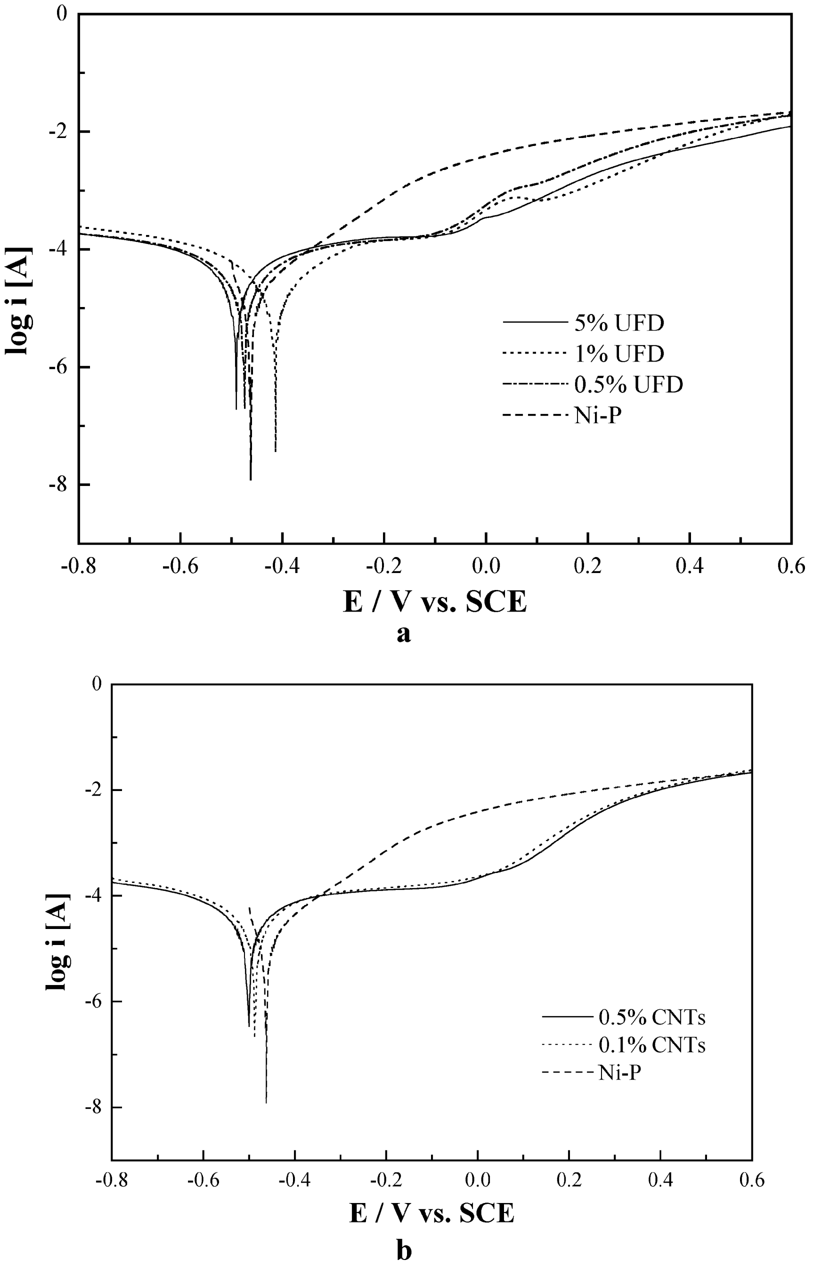

Figure 2 Anodic polar curves of (a) UFD-incorporated Ni-P alloy and (b) CNTs-incorporated Ni-P alloy in 0.1 M NaCl electrolyte.

in the deposit increases, the plateau is broadened and the current decreases. This suggests a more efficient passivation process on Ni-P-UFD alloy. A similar behavior was detected for the CNTs incorporated alloy. The broad plateau is from −300 mV to −30 mV. The E_{cor} moves a little negatively with the little incorporation and much lower current is observed. This behavior indicates that the presence of UFD and CNTs in the alloy deposits provides better corrosion resistance performance in the medium studied. The role of the UFD and CNTs is manifested in the 0.5 M H_2SO_4 electrolyte. The E_{cor} moves obviously to higher value for the incorporated alloy and the current value gets smaller with the increasing content of incorporation. In the far anodic potential range, the dispersed particles of CNTs incorporated into the coatings have no pronounced effect on the corrosion resistance. Since no pitting was observed at the end of the tests, one can suggest dissolution through the passive structure of the alloy for all the samples polarized to high anodic values. Such an effect of the carbon concentration on the anodic dissolution of Ni-P coatings can be explained by the formation of a barrier layer. We consider that because diamond can be a semiconductor with a broad bandgap, the formed grain barrier is effective. However, for the CNTs alloy, the large quantity of the incorporation decreases the corrosion resistance due to its good conductivity, as well as to its porous structure which is often considered to cause corrosion. The result points to the fact that the structural state of the alloy is of primary importance as far as the ability of the passivation is concerned.

Impedance measurements permitted a more detailed characterization of the corrosion behavior of Ni-P-UFD and Ni-P-CNTs alloys. It were performed at three different potential (vs. SCE): (a) −0.4 V; (b) −0.2 V and (c) 0.2 V. Taking into account the charge transfer resistance values (R_{t}) with the loops, the dissolution process is more intense for Ni-P than for the Ni-P-UFD and

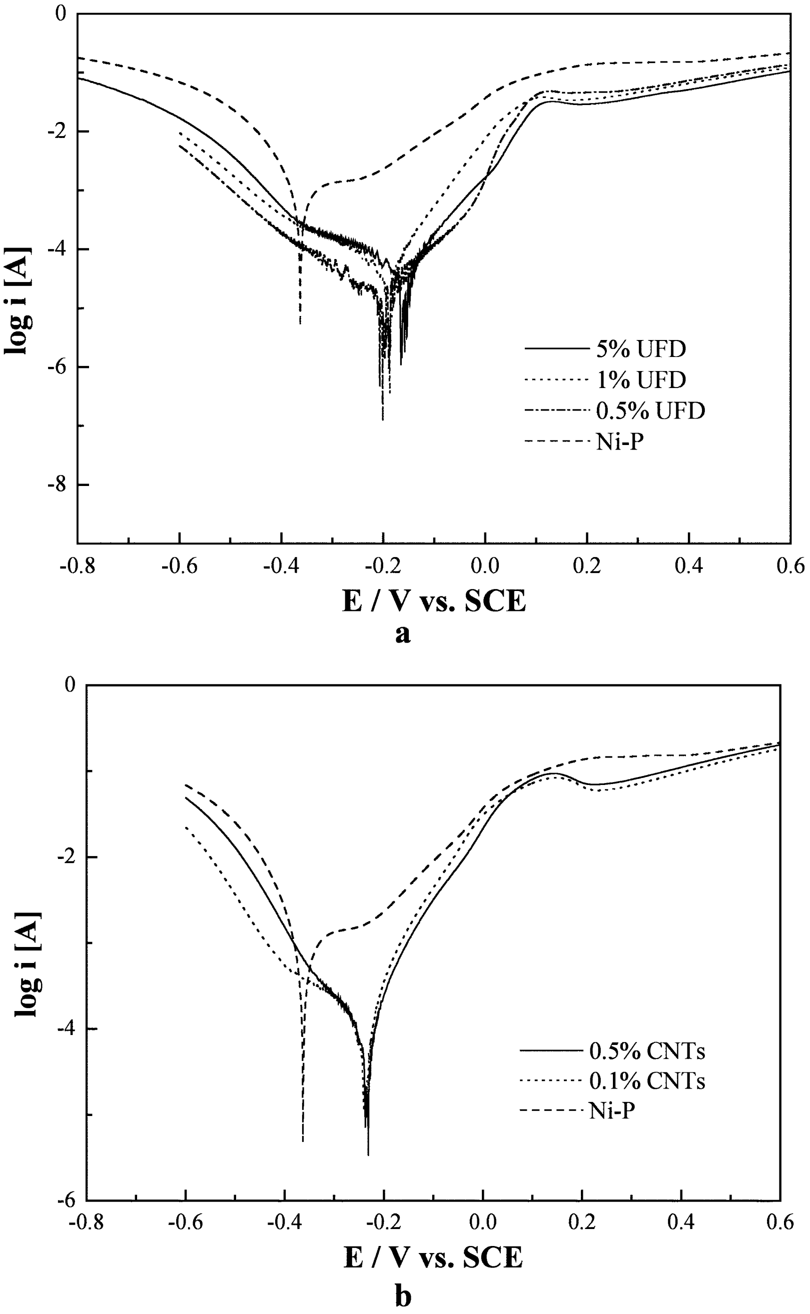

Figure 3 Anodic polar curves of (a) UFD-incorporated Ni-P alloy and (b) CNTs-incorporated Ni-P alloy in 0.5 M H_2SO_4 electrolyte.

Ni-P-CNTs amorphous alloys. And the similar shape of the impedance curve at all the potentials is observed, suggesting the same kinetics of dissolution-passivation process. It can be noted from Fig. 3 an obvious tendency of increasing the total impedance with increasing UFD content especially at −0.2 V, however, it is not too different for 0.5 wt% and 1% UFD content at the other two potentials. This result could be associated with a more efficient passivation process as a consequence of high UFD content in the alloy. In Fig. 4, 0.5% CNTs incorporation always leads to the highest R_t value presenting the better corrosion resistance performance. With the potential increasing, the corrosion resistance role of 0.1% CNTs content disappears gradually. The impedance diagrams at −0.2 V, the middle of the plateau, suggested a better resistance of the passive film. It further confirms the incorporation of UFD and CNTs is advantageous of forming passive film. At the more positive potential, there is a significant decrease on impedance values for all samples, indicating the passive film is no longer of protective nature. This also confirms the crucial role of the structural state of the alloy in agreement with other authors [24–26].

4. Conclusion

This result shows that the C content in alloy deposits increase with the amount of UFD in the electroplating solution and decreases with that of CNTs. Polarization curves in NaCl and H_2SO_4 solutions indicates that the presence of UFD and CNTs in the alloy deposits provides better corrosion resistance performance. The corrosion resistance of Ni-P coatings increases with an increase in the UFD content, whereas contrary result for the CNTs incorporated alloy. Such an effect of the carbon concentration on the anodic dissolution of Ni-P

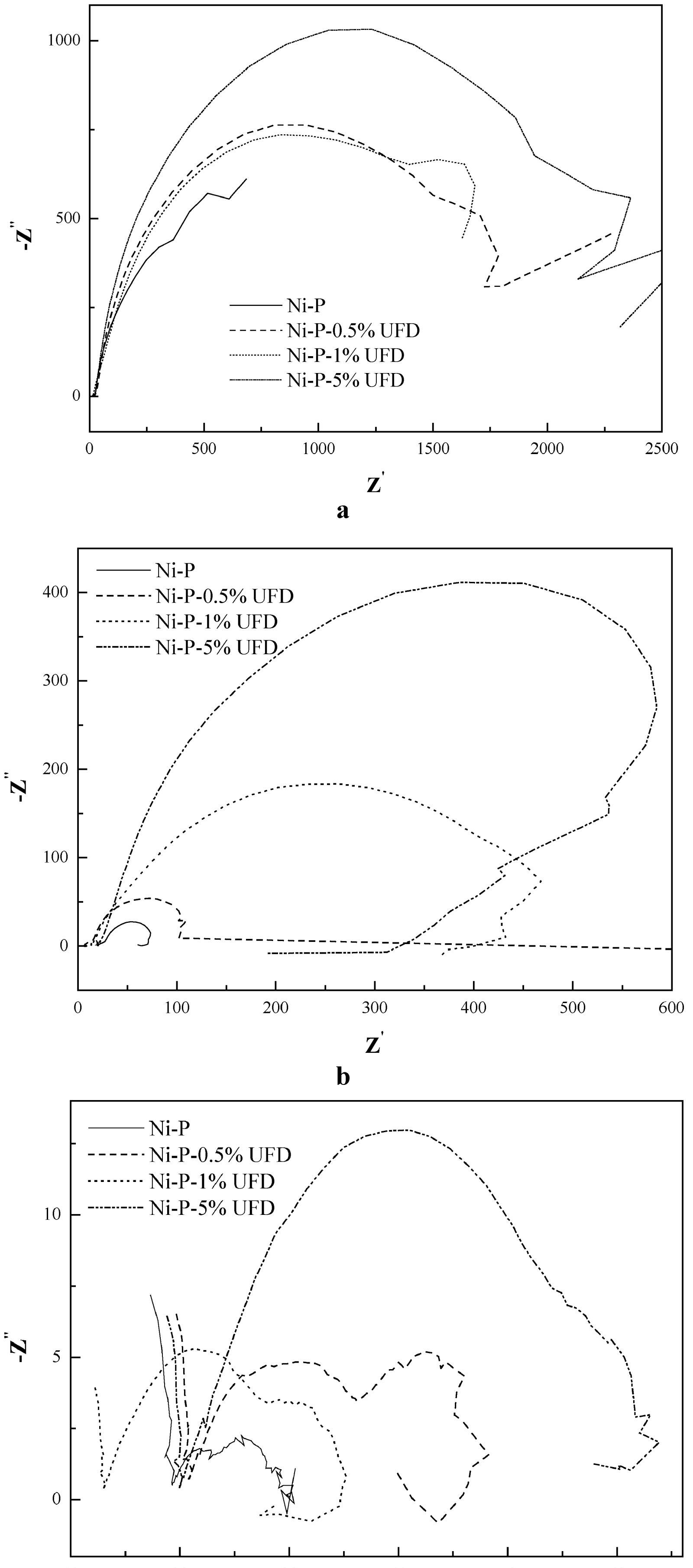

Figure 4 Niquist plane impedance spectra of UFD incorporated Ni-P alloy at different potentials (a) −0.4 V; (b) −0.2 V and (c) 0.2 V electrolyte: 0.1 M NaCl solution.

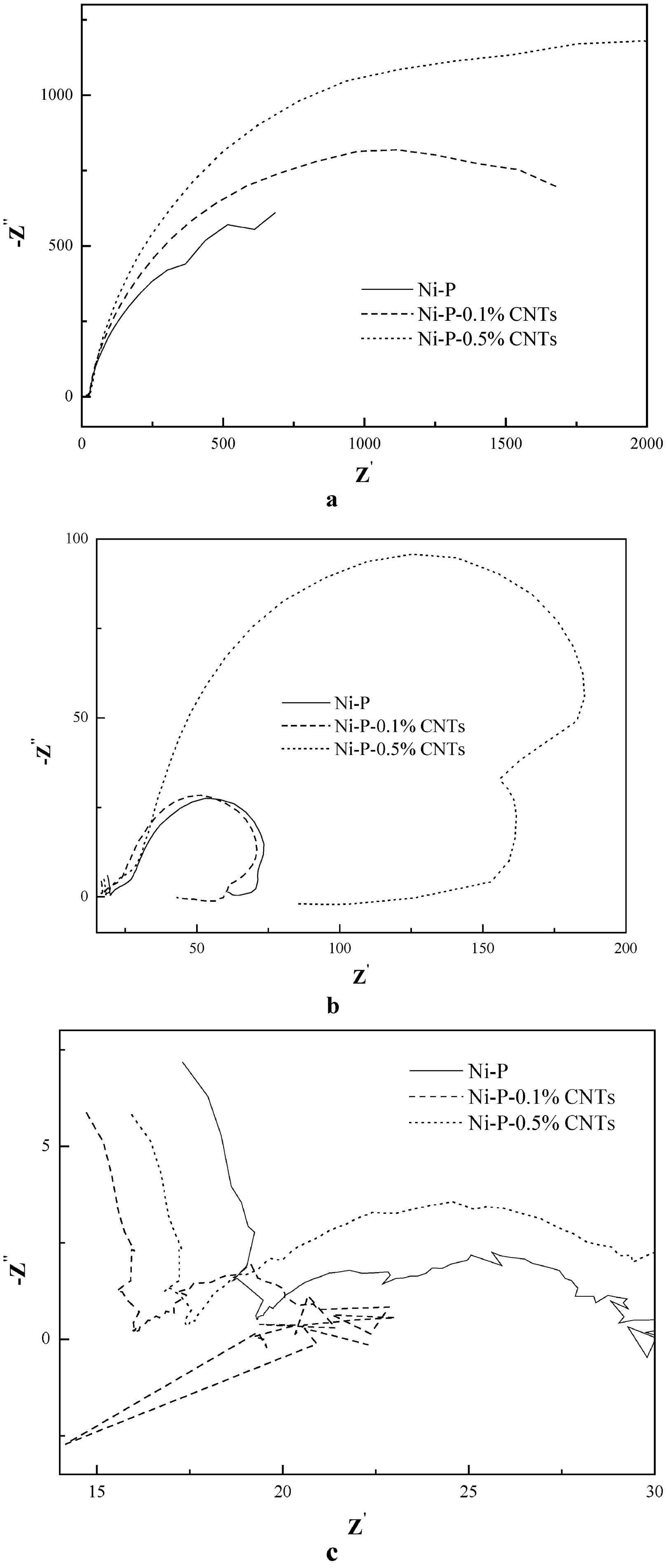

Figure 5 Niquist plane impedance spectra of CNTs incorporated Ni-P alloy at different potentials (a) −0.4 V; (b) −0.2 V and (c) 0.2 V electrolyte: 0.1 M NaCl solution.

coatings can be explained by the property of the incorporated particles. Electrochemical impedance data reveal the passive film is formed when the UFD and CNTs are incorporated and therefore promotes the corrosion resistance.

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