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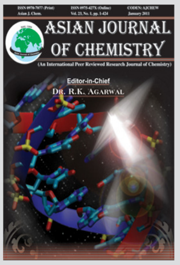

# Preparation and Properties of Electroless Deposited Ni-Zn-P-$TiO_2$ Nano-composite Coating†

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In this paper, Ni-Zn-P-$TiO_2$ nano-composite coatings were prepared by electroless depositing. The electroless deposited Ni-Zn-P-$TiO_2$ nano-composite coatings were characterized by scanning electron microscopy, energy dispersive analysis and X-ray diffractometer. The effect of $TiO_2$ bath concentration on deposition behaviour was investigated. The erosion property was tested with 0.05 M HCl. The results show that the $TiO_2$ bath concentration has great influence on deposition rate and $TiO_2$ content in composite coatings. The mass losses of coatings are increasing with corrosive medium flow rate increasing and erosion angle decreasing. Electroless deposited Ni-Zn-P-$TiO_2$ nano-composite coatings have better anti erosion property than Ni-Zn-P alloy coatings.

**Key Words: Electroless deposition, Ni-Zn-P-$TiO_2$ nano-composite coating, Erosion.**

## INTRODUCTION

Electrodeposited zinc-nickel alloys are often used as sacrificial anode coatings to protect steel materials from corrosion. It was shown that, inclusion of phosphorus in Ni-Zn alloys can modify the microstructure of the coatings and improve their corrosion resistance. Schlesinger[1,2] have reported the effect of process parameters on deposition rate and composition of the coatings deposited from the electroless plating bath which utilizes ammonia as buffer agent and sodium citrate as complexing agent. Valova[3] has reported the effect of zinc on structure and composition of electroless deposited Ni-Zn-P alloys.

To add insoluble particles in electroless plating bath and make them co-deposited with electroless deposited alloys, we can obtain composite coatings which have excellent properties. As the nano-particles have quantum size effect, small size effect, surface and interface effects, they have special physical and chemical properties[4]. Nano-composite coatings have specific functions such as hardenability, good wear resistance and good corrosion resistance[5,6]. The incorporated nano particles are mostly non-metallic particles like SiC, ZnO, BN, CNT, $Al_2O_3$ or $Fe_2O_3$[7-12].

Titania was selected as the composite by virtue of its properties like semiconductivity, high hardness and good corrosion resistance. It has been found to have enormous applications when applied as catalytic support, reinforcement and inert filler[13]. In this paper, electroless deposited Ni-Zn-P-$TiO_2$ nano-composite coatings were prepared. The structure and properties of the composite coatings were investigated.

## EXPERIMENTAL

Ni-Zn-P-$TiO_2$ nano-composite coatings were electroless deposited from the bath of the following composition: $NiSO_4 \cdot 6H_2O$ (30 g $dm^{-3}$), $ZnSO_4 \cdot 7H_2O$ (5 g $dm^{-3}$), $NaH_2PO_2 \cdot H_2O$ (25 g $dm^{-3}$), bath stabilizer (0.002 mg $dm^{-3}$) appropriate amount of complexing agent, nano $TiO_2$ 0.8-1.4 g $dm^{-3}$. The bath temperature was 80-90 ºC and the pH of the bath is adjusted to 7.0-9.0. The solution was prepared with distilled water and analytical grade reagents. The bath was stirred using magnetic stirrer. $TiO_2$ nano-particles were dispersed by ultrasonic device in order to make them dispersed completely. The composite coating was deposited on low carbon content steel. The dimension of the sample is 15 mm × 25 mm × 3 mm. The samples were mechanically polished and chemically etched in dilute hydrochloride acid before the experiments. The deposition rate was calculated from sample weight gains and surface areas. The surface morphology and composition of the composite coatings were analyzed with JSM-6490LV scanning electron microscope (SEM) and INCA energy X-ray energy dispersive spectroscopy (EDS). Phase analysis was performed by Y-2000 X-ray diffractometer.

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The set up of erosion tester was shown in Fig. 1. The flowing media was 0.05 M hydrochloride. The mass loss of the coatings was calculated from the weight of the sample before and after the erosion. The samples were observed by SEM.

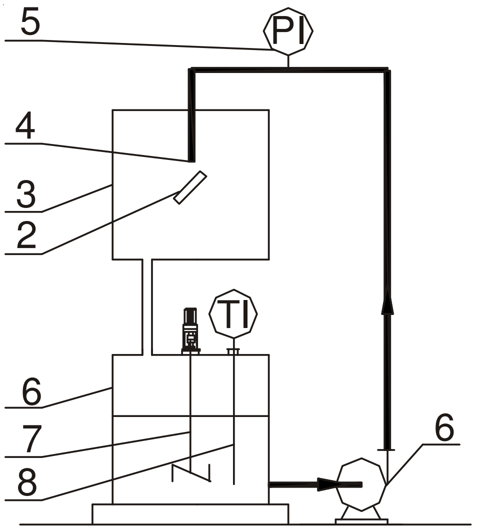
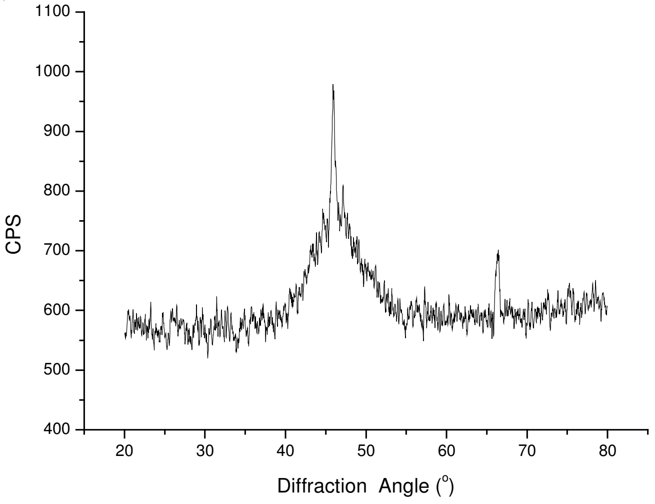


Fig. 1. Sketcher of erosion tester (1 = storage container; 2 = sample; 3 = sample chamber; 4 = noddle; 5 = pressure meter; 6 = pump; 7 = blender; 8 = thermometer)

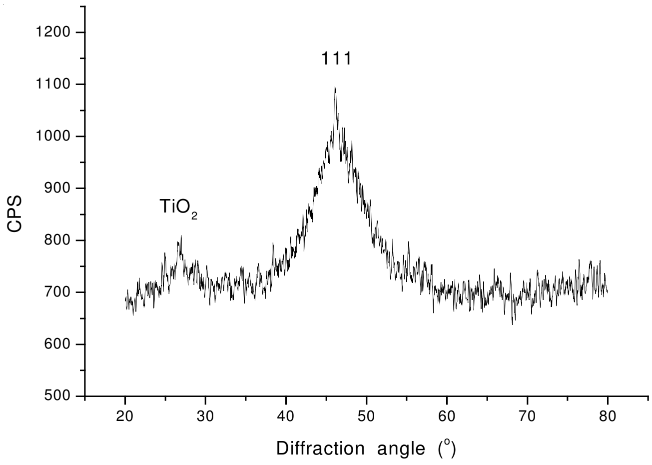
## RESULTS AND DISCUSSION

The XRD patterns of electroless deposited Ni-Zn-P alloy and Ni-Zn-P-$TiO_2$ composite coating were shown in Fig. 2. There are "broad" peak *ca.* 44° diffraction angle and a sharp peak of nickel. These show that amorphous phase and solid solution phase co-exist in electroless deposited Ni-Zn-P alloy and Ni-Zn-P-$TiO_2$ composite coating. A sharp diffraction peak of anatase $TiO_2$ at 25° is shown in Fig. 2(b). This indicates that $TiO_2$ nano particles were successfully deposited in Ni-Zn-P alloy matrix during electroless depositing process.

Fig. 3 is a scanning electron microscope photograph of the electroless deposited Ni-Zn-P-$TiO_2$ composite coating. Many cellular exist on the surface of composite coating are seen. Some of the co-deposited $TiO_2$ nano-particles are embedded in the Ni-Zn-P alloy matrix and some are encapsulated in the Ni-Zn-P cellular but exposed to the coating surface. It can be seen from the picture that there is partial reunion of nano-$TiO_2$, but the overall distribution is relatively uniform. This conforms that nano $TiO_2$ particles are co-deposited with Ni, Zn and P on the substrate in the electroless plating process. Inclusion of $TiO_2$ nano-particles increases interfaces in the layer and will have great effect on the properties of the composite coating.



(a)



(b)

Fig. 2. XRD picture of the deposite (a) XRD partten of Ni-Zn-P alloy coating; (b) XRD partten of Ni-Zn-P-$TiO_2$ nano-composite coating

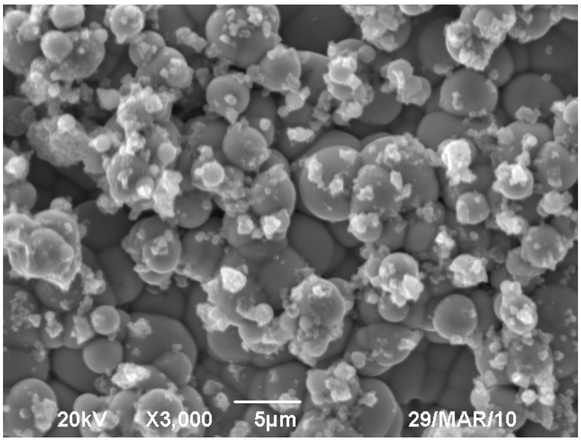


Fig. 3. SEM of Ni-Zn-P-$TiO_2$ nano-composite coating

Fig. 4 shows EDS result of the composite coating obtained from the bath, which the content of nano $TiO_2$ particles is 1 g/L. The weight percent of the elements are 76.75 % Ni, 6.55 % Zn,10.24 % P and 6.45 % Ti. The conversion can be drawn that the weight percentage of nano-$TiO_2$ in the composite coating reaches 10.76 %.

Figs. 5 and 6 show the effect of $TiO_2$ nano-particles concentration in the bath on deposition rate and $TiO_2$ content in the composite deposition. The deposition rate increases with increasing concentration of nano-$TiO_2$ particles in the bath and attains an optimum value with the addition of 1 g/L nano-$TiO_2$ particles in electroless plating bath. With further additions, a decreasing trend of deposition rate was observed. The content of $TiO_2$ in the composite deposition increases with increasing concentration of nano-$TiO_2$ particles in the bath. The absorbing

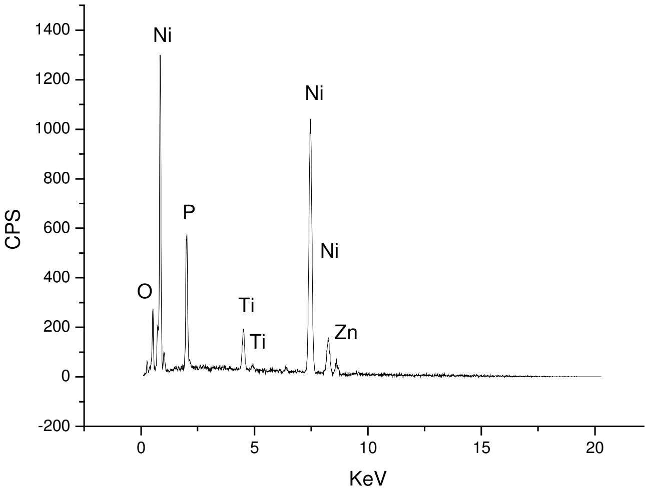


Fig. 4. EDS of Ni-Zn-P-$TiO_2$ nano-composite coating

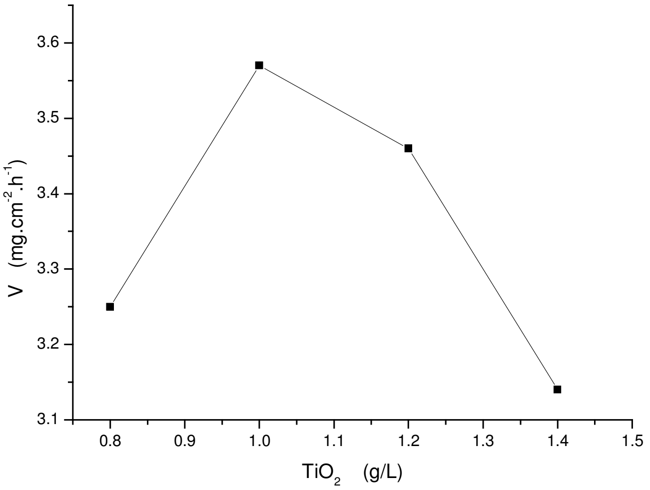


Fig. 5. Effect of $TiO_2$ concentration on deposition rate

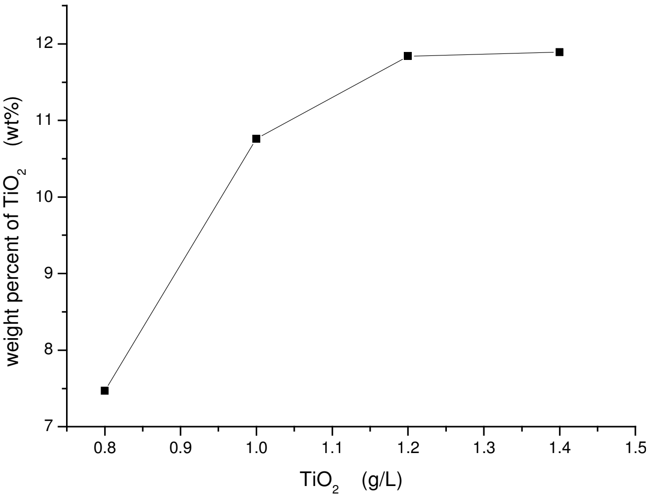


Fig. 6. Effect of $TiO_2$ concentration on deposition content

mechanism[14,15] being considered is the best one suggested so far. According to this mechanism, the amount of $TiO_2$ particle suspended in the bath increases with increasing the content of nano-$TiO_2$ particles in the bath. This will increase the probability of $TiO_2$ particles adsorbing to the substrate. The amount of $TiO_2$ particles co-deposited in the coating will increase too. So the deposition rate and $TiO_2$ content in the composite deposition increase. But if the concentration of $TiO_2$ particles in the bath is too high, the number of nano-$TiO_2$ particles adsorbed on the substrate surface increases too. This will reduce the area of the substrate which has catalytic activity. The deposition rate will decline. When nano-$TiO_2$ particles concentration in the bath suppresses certain value, the amount of $TiO_2$ particles adsorbed on the substrate changes little. So content of $TiO_2$ in the composite coating increased slowly when the concentration of nano-$TiO_2$ particles in the bath is more than 1 g/L.

Fig. 7 shows the effect of impact angle on mass loss of electroless deposited Ni-Zn-P alloys and electroless deposited Ni-Zn-P-$TiO_2$ composite coatings. The mass loss of Ni-Zn-P-$TiO_2$ composite coatings is less than that of Ni-Zn-P alloy coating at the same impact angle. Compare to electroless deposited Ni-Zn-P alloys, electroless deposited Ni-Zn-P-$TiO_2$ composite coatings have finer grain and higher hardness value because of inclusion of nano-$TiO_2$ particles. On the other hand, inclusion of nano-$TiO_2$ particles in the composite coatings will increase corrosion potential[16,17], so corrosion resistance of composite coating is improved. The mass loss of this two kind of coating increased with the impact angle decreasing. In the flowing corrosive media, with the impact angle decreases, the shear force and the impact area increased gradually. The passive film is more easily to damage. Then the coating dissolved in the corrosive medium more easily. So the mass loss of the coatings increased.

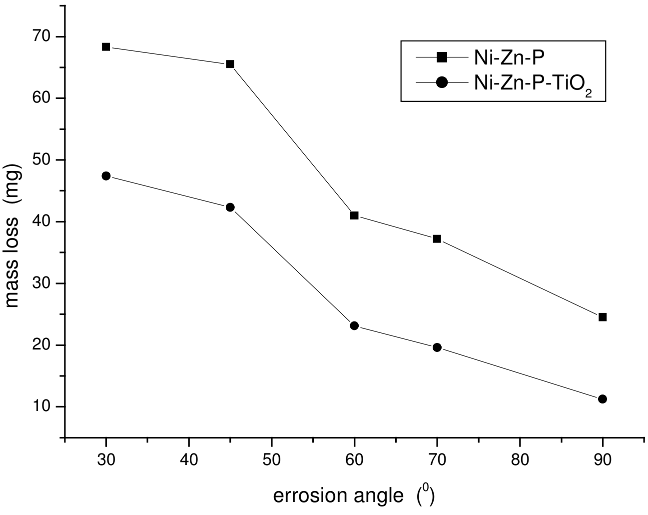


Fig. 7. Effect of erosion angle on mass loss of the coatings

Fig. 8 shows the effect of medium flow velocity on mass loss of the coatings. From the data it is find that the mass loss of the coatings increases with medium flow velocity increasing. The mass loss of Ni-Zn-P-$TiO_2$ composite coatings is less than that of Ni-Zn-P alloy coating at the same flow velocity. The greater the flow rate of corrosive medium, the greater kinetic energy deliveries to the coating. The effect of the mechanical wear and erosion becomes greater. So the mass loss of the coatings increases. Fig. 9 shows the surface morphology of the coating after erosion test. Some deformation and tiny pits caused by the impact of the corrosive medium can be seen from Fig. 9.

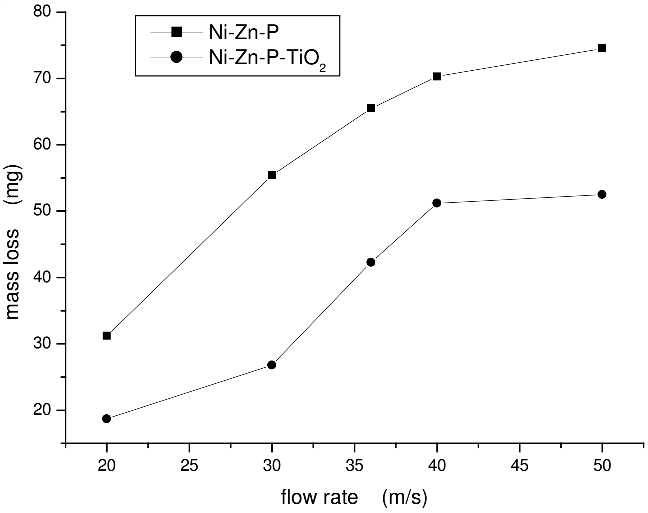
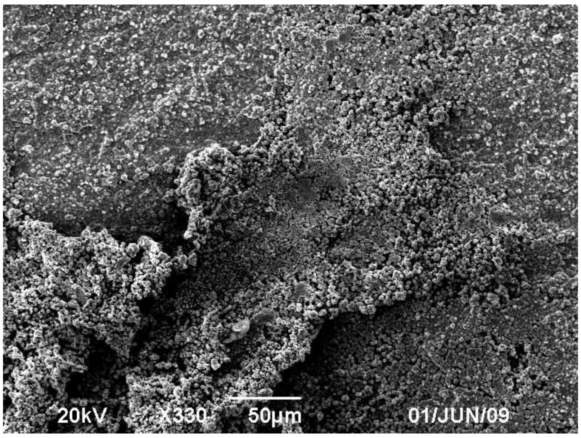
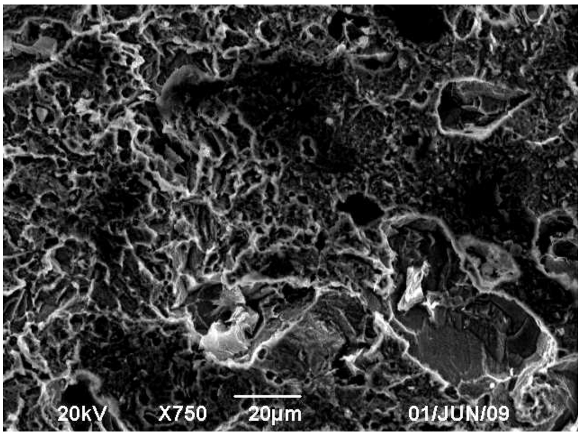


Fig. 8. Effect of corrosive medium rate on mass loss of the coating



(a) 330 ×



(b) 750 ×

Fig. 9. SEM of the coating surface after erosion test

## Conclusion

Chemical and phase analyses of the Ni-Zn-P-$TiO_2$ nanocomposite coating produced confirm the co-deposition of Ni-Zn-P and $TiO_2$ and the formation of a homogeneous material. Electroless deposited composite coatings exhibit an amorphous structure of Ni-Zn-P matrix in which nano $TiO_2$ is incorporated. Electroless deposited Ni-Zn-P-$TiO_2$ nano-composite coatings have better anti erosion property than Ni-Zn-P alloy coatings.

## ACKNOWLEDGEMENTS

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