Corrosion behaviour of Ni-P-SiO2 electroless composite coating

Su-Yan TIAN[a], Jun MA[b*], Rong-Jian YING[c] Shan-Liang MU[d]

School of Chemistry and Chemical Engineering, Linyi University, 276000, China

email: [a]tianyan198289@163.com, [b]majun716@163.com, [c]yingrongjian@lyu.edu.cn,   [d]chem@lyu.edu.cn

*Jun MA

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Abstract. In this paper, the protective electroless Ni-P/SiO$_2$ on iron substrate were successfully prepared. The prepared Ni-P/SiO$_2$ electroless composite coating were characterized for morphology, microstructure. The anticorrosion properties of the Ni-P/SiO$_2$ coating in 10wt.% HCl solution were evaluated by immersion tests, SEM and EDS at ambiance temperature. The results revealed that the SiO$_2$ concentration in the bath and heat treatment can influence the corrosion protection performance of electroless deposited Ni-P/SiO$_2$ coatings. The corrosion resistance of Ni-P/SiO^2 coating increases initially and decreases afterwards with the sustained increasing of immersion time in HCl solution. The Ni-P/SiO$_2$ electroless composite coating can afford better corrosion protection for magnesium alloy substrate compared with Ni-P coating

Introduction

It is well known that the corrosion problem of refining equipments in chemical industry becomes more and more serious, especially the heat-exchangers[1,2]. Generally different carbon steels are chosen to produce the heat-exchangers due to their low price. However, the corrosion rates of these heat-exchangers are very fast because of their severe application environment with acid or alkaline. Thus, choosing reliable materials and protective methods have attracted more and more attention.

Autocatalytic electroless plating technology has been invented to improve the corrosion resistance of chemical industry. High phosphorus chemical plating Ni-P coating has extensive application in the field of chemical industry due to Its high hardness, good mechanical properties and excellent corrosion resistance [3-6]. However, the P content over 8 wt.% shows the amorphous state structure of Ni-P coating [7]. The amorphous Ni-P coating has no defects such as dislocations and grain boundary. And it is easy to form a uniform passive film on the coating surface, which can improve the corrosion resistance of coating effectively. A major disadvantage of this coating at present is that its surface has many microporous, which are easy to become the corrosion source and lead to the damage of equipments finally [8].

In recent years, electroless composite plating method has attracted a lot of interesting [9-12]. Due to their excellent performance, the nano-particulates are used as reinforcing phase. The incorporation of nanoparticular within Ni-P electroless composite plating greatly improved their performance. Using as reinforcing phase, SiO$_2$ nano-particulates attracted tremendous interests in research community. In this paper, Ni-P/SiO$_2$ composite coating was prepared. The corrosion resistance of Ni-P-SiO$_2$ coating was evaluated.

Materials and methods

Sample preparation.

The iron alloys substrate contained (wt.%) 93.54% Fe, 0.34% Mn, 3.64% C and 2.47% O. In order to make substrate same surface roughness and ready for coating process, the substrate materials were polished up to grit silicon carbide paper. Iron alloys samples of dimensions 30mm×15mm×2mm were suspended on nylon wire and ultrasonically degreased in acetone, subsequently cleaned in an alkaline solution containing 45 g·L^{-1} NaOH and 8 g·L^{-1} Na$_3$PO$_4$·3H$_2$O at 60 °C for 15 min, then etched in a solution of 6wt.% HCl solution for a duration of 30 s. The sample

were rinsed using distilled water after different steps of the pretreatment process. Following the pretreatment stage, the sample were immersed in electroless bath.

The composition and operation conditions of electroless plating Ni-P was as follows: Nickel sulfate hexahydrate 26.7g·L^{-1}, Sodium hypophosphite 20 g·L^{-1}, Sodium acetate 17 g·L^{-1}, Lactic acid 12.09 g·L^{-1}, Propionic acid 4.95 g·L^{-1}, Surfactants 1 mg·L^{-1}, and Potassium iodide 1 mg·L^{-1}. The initial pH value of plating bath was adjusted ammonia solutions to 5-6. The temperature of the plating bath was controlled within 80 °C using a ditally controlled thermostat. In order to produce a composite coating, the pre-made concentrated plating bath containing 2 g·L^{-1} solid SiO$_2$ particles (0.4-0.6μm in size) was carefully added dropwise to the above mentioned electroless palting bath over 1 h and uniformly dispersed in the bath using ultrasonic.

Corrosion experiment.

The corrosion behavior was characterized by immersion tests at ambiance temperature in 3 mol·L-1 HCl solution. The samples for the corrosion evaluation were washed with distilled water and dried with warm flowing air. Corrosion macro-morphology was examined using scanning electron microscopy at different time after immersion.

Characterization of Composite Coating.

The composite coating was characterized by Scanning Electron Microscopy (SEM, JSM-5610LV) and Electron Diffraction Spectrum (EDS, Inca energy) techniques.

Results and discussion

The element of iron alloy substrate and Ni-P/SiO$_2$ coating was analyzed by EDS. Analytical spectra and chemical composition of substrate and composite coating were obtained. The results are shown in Fig.1. The results show that the content of phosphorus in Ni-P/SiO$_2$ coating is about 8 weight percent. The composite coating can be classified as medium phosphorus electroless nickel. The contents of O and Si in Ni-P/SiO$_2$ coating are about 7 and 6 respectively. The results can be used to predict existence of SiO2 in the Ni-P/SiO$_2$ coating.

Element	Weight%
O	7.06
P	7.85
Si	6.18
Ni	78.91
Totals	100.00

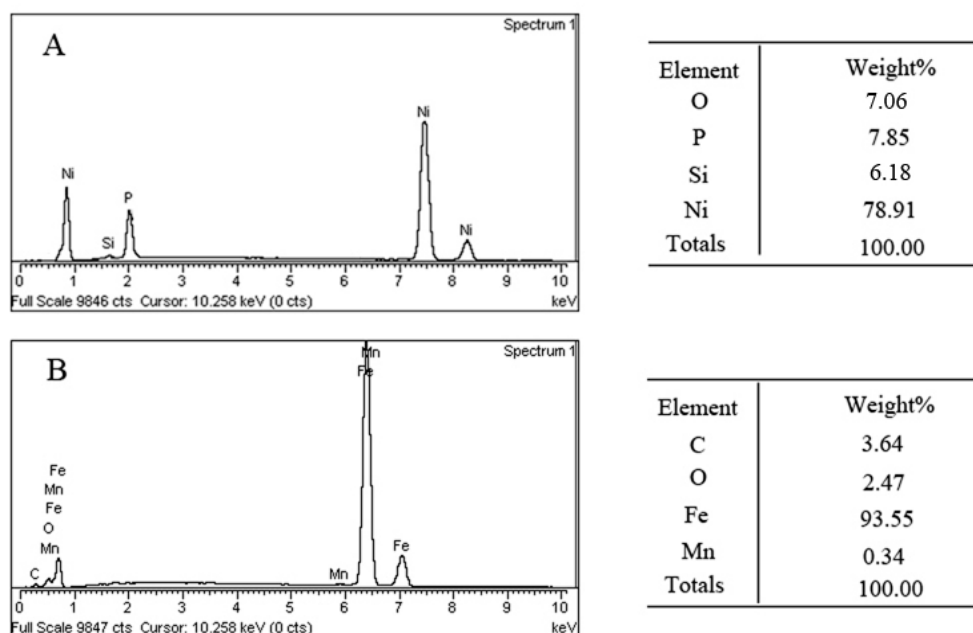| Element	Weight%
C	3.64
O	2.47
Fe	93.55
Mn	0.34
Totals	100.00

Fig.1 EDS spectra and chemical composition of the iron substrate and Ni-P/SiO$_2$ electroless deposited coating (A iron substrate, B Ni-P-SiO$_2$)

Fig.2 shows SEM micrographs of electroless deposited Ni-P and Ni-P/SiO$_2$ composite coating on iron alloys substrate. It can be seen that the surface of Ni-P coating shows a typical spherical nodular structure with good uniformity and dense coverage. The Ni-P/SiO$_2$ composite coating exhibits coarse nodular structure due to the codeposition of SiO$_2$ particle. It can also be observed that the number of these nodules in the Ni-P/SiO$_2$ coating was more than that in the Ni-P coating, indicating that the Ni-P/SiO2 composite coating was more compact than the electroless Ni-P

coating. In the process of electroless composite plating, the addition of SiO_2 particles can increase the catalytic active sites of the matrix surface and act as the nucleation center. The deposition of nickel phosphorus alloy will wrap the SiO_2 particle. The SiO_2 particles adsorption randomly on the sample surface, and some parts of the nodule boundaries are covered by the SiO_2 powders just adsorbed at the boundaries. Thus, the incorporation of SiO_2 particles in Ni-P coating leading to the more nodules and more apparent roughness of Ni-P/SiO_2 coating than those Ni-P coating.
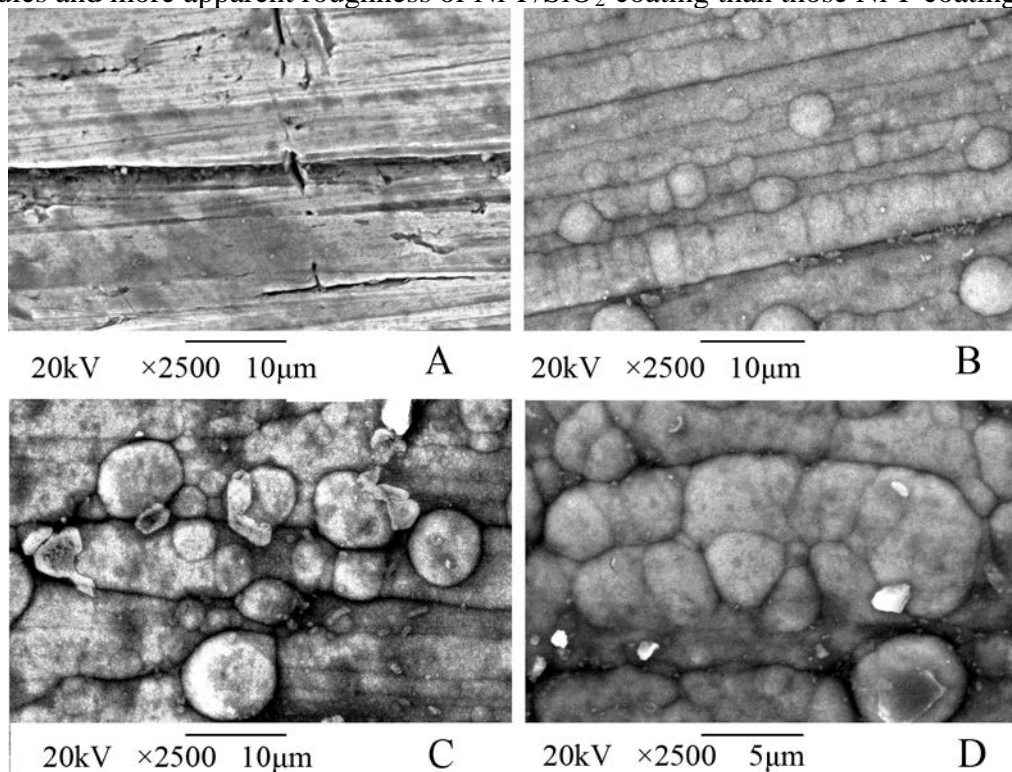

Fig.2 SEM micrographs of substrate and electroless deposited coating (A iron substrate, B Ni-P coating, C and D Ni-P/SiO_2 coating)

Fig.3 shows the SEM images of the substrate and coating. A transformation of morphology was observed. In Fig.3, SEM morphology A and B were iron substrate before and after immersion in HCl solutions. After immersed in HCl solution, the iron substrate was corroded rapidly, and the surface of substrate was not smooth and regular. SEM morphology C and D were Ni-P coating before and after immersion in HCl solutions. During the corrosion process, Ni-P coating was destroyed, allowing easy access of H+ and Cl- ions to penetrate the coating and interact with the iron alloy substrate.

Compared with iron substrate and Ni-P coating, the smoother surface shown by the Ni-P/SiO_2 indicated the protective behavior of the Ni-P-SiO_2 coating against corrosion. SEM images of the electroless Ni-P/SiO_2 coating before and after immersion in HCl solutions. The Ni-P/SiO_2 composite coating before immersion in the HCl solution showed that the incorporated particles are evenly distributed in the composite coating and are firmly bonded to the substrate with Ni content of 79%. The micrographs of the Ni-P/SiO_2 coating upon immersion in 10wt.% HCl solution showed that the composite coating was less compact and loosely bonded to the substrate, compared to the coatings before the corrosion process.
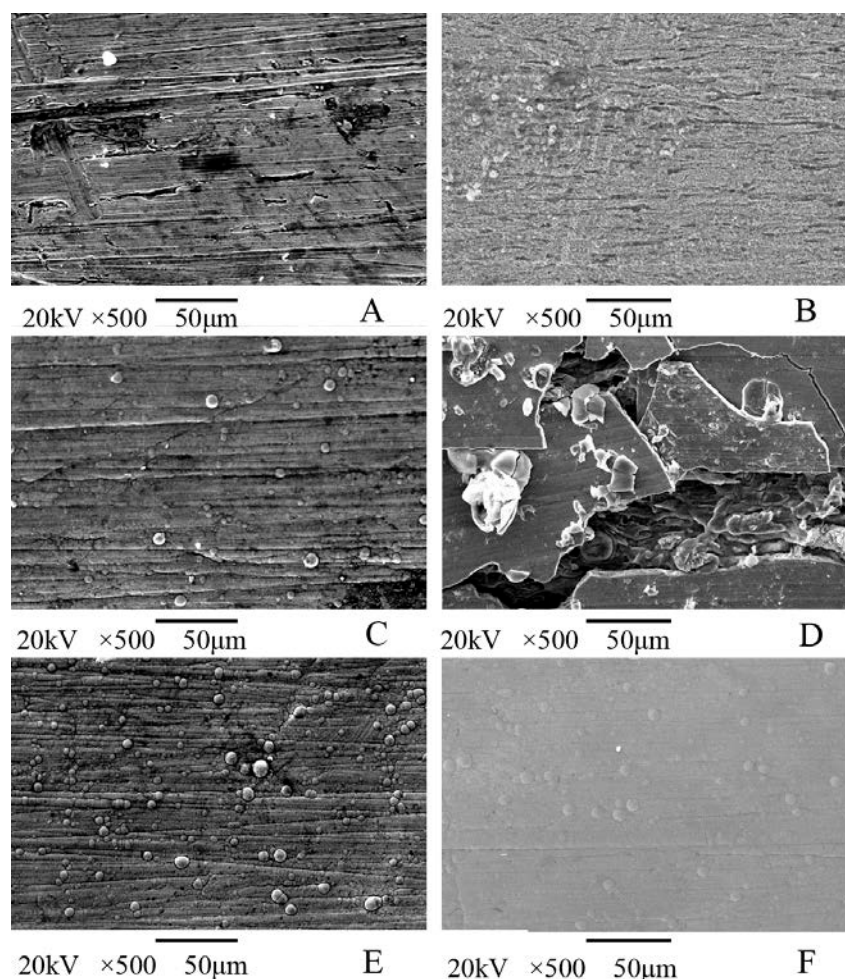
Fig.3 SEM micrographs of substrate and electroless deposited coating in 10wt.% HCl solution.
(A and B iron substrate, C and D Ni-P coating, E and F Ni-P/SiO$_2$ coating)
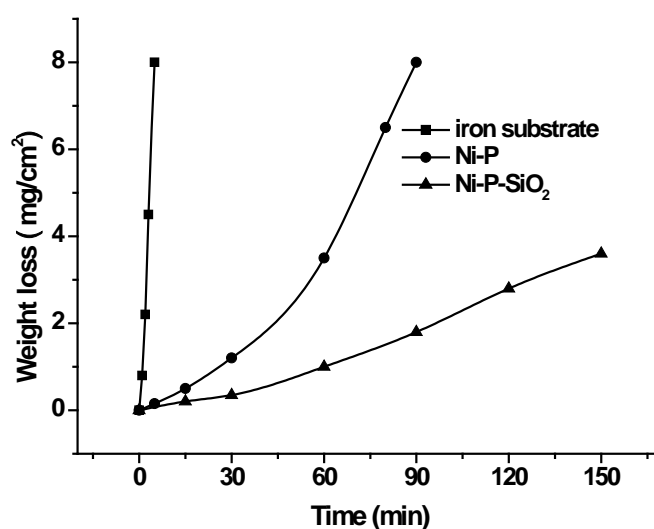

Fig.4 Corrosion quantity in the 10wt.% HCl solutions with time

The corrosion of Ni-P/SiO$_2$ composite coating in 10wt.% HCl solution at different time were shown in Fig.4. From the corrosion behaviors of iron substrate, Ni-P and Ni-P/SiO$_2$ coating in HCl solution, it was observed that the corrosion rates were different for the sample. The corrosion rates order was iron substrate > Ni-P > Ni-P/SiO$_2$. The Ni-P/SiO$_2$ composite coating had the best corrosion resistance in HCl solution. The decreased corrosion rate that was obtained from the weight loss seem to indicate that the corrosion resistance is related to increase of the SiO$_2$ particle in the coating.

Conclusion

Using SiO_2 nano-particulates as reinforcing phase, Ni-P/SiO_2 composite coating was prepared. The micrographs and composition of Ni-P/SiO_2 were analyzed by SEM and EDS. The corrosion performance of coating was also evaluated. Compared with iron substrate and Ni-P coating, the Ni-P/SiO_2 composite coating exhibits coarse nodular structure due to the codeposition of SiO_2 particle. However, the corrosion resistance of Ni-P/SiO_2 is better than Ni-P coating..

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