Effect of heat treatment on the microstructure and mechanical properties of electroless nickel-phosphorus coatings

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Abstract. Electroless deposition have been considered as one of the most important nickel-based coating synthesization methods because of their coatings uniformity, high wear resistance, excellent corrosion and electrical properties. In this paper, nickel-phosphorus coatings were synthesized by electroless method on medium carbon steel substrates. The effect of heat treatment on the microstructure and mechanical properties of nickel-phosphorus coatings were investigated in detail. Structural analyses suggest that the coatings remain amorphous structure if the annealing temperature is below 400 °C. The crystalline Ni and Ni3P were formed in the coatings when the annealing temperature reach 400 °C and the grains grown significantly with increasing the heat treatment temperature from 500 °C to 800 °C. The mechanical properties of the nickel-phosphorus coatings display a significant change with the different heat treatment temperature. It was found that the highest microhardness value and the best wear resistance property has been obtained under heat treatment temperature of 400 °C. The possible mechanism of the relationship between microstructure and mechanical properties was also explored.

1. Introduction

Nickel-phosphorus alloy (Ni-P) films, which are characterized by excellent corrosion protective and, accordingly, good solderability, wear resistance, high electrical conductivity, high hardness, low friction coefficient and electrocatalytic activity, have attracted considerable attention in recent years. Compared to Ni films, Ni-P films present a smooth, bright, and shiny look [1-3]. Due to the above advantages, Ni-P films have been used extensively in the electronics, automobile, microelectronics, aerospace, machinery, valve and gas pipeline industries.

Of the preparation methods of Ni-P films, electroless deposition is very attractive because this process can deposit the Ni-P films on any irregularly shaped surface and on many kinds of substrates, such as brass, steel, glass, silicon, and ceramics [4]. To date, numerous papers on the properties of Ni-P films prepared via electroless deposition have been reported. Wang et al. reported that the indentation behavior of electroless Ni-P films is significantly affected by film thickness [5]. Hsu et al. reported the mechanical and fatigue properties of electroless Ni-P coating on brass substrates [6]. The
effect of bath condition on the microstructure, composition and functional properties of electroless Ni-P films have also been studied extensively [7, 8].

Despite the above interest, the studies about the properties of electroless Ni-P coatings after heat treatment are still deficient. In this article, Ni-P films were synthesized on medium carbon steel substrates by electroless plating process. The microstructures and mechanical properties of the Ni-P films after heat treatment were investigated in detail, and the relation between the microstructure and the properties of the Ni-P films was also discussed.

2. Experimental details
Ni-P alloy (Ni 91.91 wt%, P 8.09 wt%) coatings were deposited on medium carbon steel substrates using an electroless deposition method. Prior to deposition, the medium carbon steel substrates were polished mechanically, degreased using acetone, rinsed with deionized water, activated by acid pickling (18% HCl for 8 second), and then rinsed with deionized water fleetly. Deposition was then conducted using an electroless nickel solution containing 36.8 g/L NiSO$_4$·6H$_2$O, 3.2 g/L NiCl$_2$·6H$_2$O, 37.3 g /L NaH$_2$PO$_2$·H$_2$O and other additives (complexing agent, pH value buffers, surfactant and stabilizer) as basic bath for electroless plating Ni–P coatings. The plating bath temperature and pH value were 92 °C and 4.8. The heat treatment of the as-plated Ni-P coatings were carried out in the air atmosphere furnace and heating at 200, 300, 400, 500, 600, 700, and 800 °C for 1 hour, which were named as Ni-P$_{200}$, 300, 400, 500, 600, 700, and 800, respectively.

The surface morphologies of the Ni–P alloys were examined by metallurgical microscope (Nikon H550L). The structural qualities of the coatings were investigated by X-ray diffraction (XRD) (Rigaku D/max 2550) using Cu Kα radiation. Microhardness was measured using a Vicker’s diamond indenter under a 100 g load for dwell time of 15 s. The wear tests for Ni-P coatings were carried out using a 35mm diameter GCr15 steel rotating cirque (MMS-2A wear tester) under the applied normal load of 400 N at a spin velocity of 200r/min.

3. Results and Discussion
The optical micrographs of Ni-P coatings are shown in figure 1. It can be seen that the as-plated Ni-P alloys coating disclosed a smooth surface morphology. From the comparison of figure 1, it was observed that the surface microstructure of Ni-P coatings after heat treated temperature below 500 °C almost unchanged. Figure 1(a-d) show that the surface morphology exhibited a slight change and become a little rough after 500 °C heat treatment. However, a number of fine grains appeared on the optical micrograph of the Ni-P coating when the heat treatment temperature reached 500 °C. Figure 1(e-h) show the grains grown significantly with increasing the annealing temperature from 500 °C to 800 °C.
Figure 1. The micrographs of Ni-P coatings before and after heat treatment at different temperature: (a) as plated, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, (f) 600 °C, (g) 700 °C, and (h) 800 °C.

Figure 2 shows the XRD pattern for the Ni-P coatings before and after heat treatment. From the observation of figure 2, the pattern for as-plated Ni-P coating presents a broad diffraction peak, indicating the coating is X-ray amorphous. The broad peaks also appear in the XRD patterns for Ni-P_200 and Ni-P_300 coatings, which indicates the coatings still remain amorphous structure. There were several diffraction peaks appear in the XRD patterns for Ni-P coatings when the heat treatment temperature reach 400 °C, which can be indexed to the crystalline Ni and Ni₃P [9]. The XRD patterns indicate that the structure of Ni-P coatings was transformed from amorphous to crystal when the annealing temperature approaches 400 °C.

Figure 2. XRD pattern of Ni-P coatings: (a) as plated and after heat treatment at temperature 200–400 °C, (b) after heat treatment at temperature 500–800 °C.

To provide more details for the effect of heat treatment on the Ni-P coatings’ structures, the crystallite size of the coatings was calculated from XRD patterns using Scherrer’s equation:

\[
D = \frac{0.9 \lambda}{B \cos \theta}
\]  

where \(D\) is the main crystallite size, \(\lambda\) is the incident Cu Kα radiation wavelength (0.154 nm), \(\theta\) is the Bragg diffraction aspect and \(B\) is the full width at half maximum (FWHM) of the maximum intensity diffraction peak.

The maximum intensity peak was obtained for Ni (111) plane. As the heat treatment temperature increased further, the position of the diffraction peaks remained unchanged, and the full width at half maximum (FWHM) value of these peaks changed obviously. The corresponding calculated crystallite sizes of the samples were given in Table 1. It can be found that the calculated mean grain size shows an increase with the increasing of heat treatment temperature at lower temperature but deviates at higher heat treatment temperature.

| Sample    | Ni-P_400 | Ni-P_500 | Ni-P_600 | Ni-P_700 | Ni-P_800 |
|-----------|----------|----------|----------|----------|----------|
| Crystallite size | 22.0 nm  | 31.8 nm  | 39.0 nm  | 35.7 nm  | 33.1 nm  |
Figure 3. Microhardness of coatings after heat treatment at different temperature.

Figure 3 shows the microhardness values of the coatings as plated and after heat treatment at different temperature. The microhardness value of the coating is increased with increasing heat treatment temperature at lower temperature and reaches a maximum value at 400 °C. This increasing can be attributed to fine Ni crystallites and hard Ni$_3$P particles precipitated during the crystallization from the amorphous phase [10]. However, the microhardness value of the coatings decreases when the heat treatment temperature increased further, which may due to large grain growth [11].

Figure 4. The micrograph of wear scar for Ni-P coatings before and after heat treatment at different temperature: (a) as plated, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, (f) 600 °C, (g) 700 °C, and (h) 800 °C.

The wear track morphology of the Ni-P coatings are shown in figure 4. Longitudinal grooves along the sliding direction can be discerned on the surface morphology for all the samples. These grooves were developed due to microploughing and micro cutting effect by the GCr15 steel counter surface. Apart from grooves, some torn patches are observed on the surface of the as-plated, Ni-P$_{200}$, Ni-P$_{600}$, Ni-P$_{700}$, and Ni-P$_{800}$ coatings. These torn patches can be indicative that the severe adhesive transfer occurred between coatings and counter surface during sliding [12]. Considering relatively low microhardness value, adhesive wear mechanism in these coatings may be attributed to their ductile nature, which contributes to serious plastic deformation. By contrast, rare torn patches can be discerned on the surface of Ni-P$_{300}$, Ni-P$_{400}$, and Ni-P$_{500}$ coatings. The cumulative volume loss results of wear test for all the samples are summarized in Table 2. Ni-P$_{300}$, Ni-P$_{400}$, and Ni-P$_{500}$ coatings possess lower wear rates, which corresponds with the wear track morphology. The
lowest wear rate observed in Ni-P 400 coating is probably due to the transition of wear mechanism from severe adhesive wear to mild adhesive wear. This transition of wear mechanism may be attributed to lower mutual solubility between interacting surfaces as a result of high coating’s hardness value.

Table 2. Cumulative volume loss ($\Delta V$) results of wear test.

| Sample       | As-plated | Ni-P 200 | Ni-P 300 | Ni-P 400 | Ni-P 500 | Ni-P 600 | Ni-P 700 | Ni-P 800 |
|--------------|-----------|----------|----------|----------|----------|----------|----------|----------|
| $\Delta V$ (mm$^3$) | 0.01013 | 0.00873 | 0.00759  | 0.00376  | 0.00603  | 0.00939  | 0.00976  | 0.01198  |

4. Conclusions
In summary, Ni-P coatings were deposited on medium carbon steel substrates by electroless plating process. The effect of heat treatment on the microstructure and mechanical properties of the Ni-P coatings were investigated in detail. The coating after heat treatment at 400 °C possess a maximum hardness and lowest wear rate, which may be due to the formation of fine Ni crystallites and hard Ni3P particles precipitation. These results may provide a promising approach for meeting the growing requirement of wear resistant applications.

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