Effects of Properties on S45C Carbon Steel by Electroless Ni-P Adding Al₂O₃ Powder of Composite Deposition and Various Heat Treatments

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Abstract. This research studies the effects on the surface microstructure and mechanical properties of S45C carbon steel via electroless Ni-P, by adding αAl₂O₃ powder via composite deposition and various heat treatments. The plating specimens were treated with pH5 and pH8 baths heated to 350°C and 300°C, respectively, and soaked for 1 hr. Meanwhile, two different particle sizes of Al₂O₃ powder were added to the electroless Ni-P plating: 0.3 μm of αAl₂O₃ and 0.05 μm of γAl₂O₃ powder, respectively. The experimental results show that, after 1 hr of heat treatment at 300°C, the optimal hardness for the specimens using the pH8 of Ni-P with αAl₂O₃ and γAl₂O₃ added by composite deposition are HV₀.₀₅ 1237 and HV₀.₀₅ 1145, respectively. All of the specimens underwent the main precipitate phase of Ni₃P after heat treatment.

1. Introduction
Electroless Ni-P deposits have been used extensively in many industries due to their wear and corrosion resistance [1,2]. The properties and structures of the Ni-P coatings depend on its phosphorus content. After suitable heat treatment, the Ni-P coating could be strengthened with the crystallization of nickel and nickel phosphide [4,5]. S45C carbon steel (S45C) has been widely used in industrial applications, such as crankshafts, gears, main spindles of machine tools, connecting rods, etc., because of its distinguished mechanical property [6,7]. Several surface hardening for S45C have been carried out and discussed [8]. Moreover, composite coatings constitute is a new class of materials which are mostly used for mechanical and tribological applications [9,10]. The aim of this study was to evaluate the surface microstructure, wear resistance and phase transformation via various heat treatments of electroless Ni-P adding αAl₂O₃ and γAl₂O₃ composite depositions in regard to S45C carbon steel.

2. Experimental Procedures
In this study, JIS S45C carbon steel was used as a substrate, the specimen size is Ø36 × D5 mm; chemical compositions are listed in Table 1. Furthermore, the parent of S45C is oil quenched at 850°C, tempered at 400°C, and the tempering process is repeated twice to reach a hardness of HV₀.₀₅ 421. In addition, the plating bath is divided into an acid and alkaline bath (pH5 and pH8); sulfuric acid and ammonia were used to adjust the pH value. The bath compositions, concentration and operational conditions are listed in Table 2. As reported in our previous study, the optimal pH values of electroless Ni-P plating for S45C carbon steel were pH5 and pH8 when soaked for 1 hour at the optimal heat treatment temperatures of 350°C and 300°C, respectively. In order to further improve the surface...
hardness and wear of the samples, electroless Ni-P plating, with Al₂O₃ powder added by composite deposition, with different particle sizes of α-Al₂O₃ and γ-Al₂O₃ powders, was prepared. After the electroless plating process, the pH5 and pH8 baths specimens were heat treated at 350°C and 300°C, respectively, and soaked for 1 hr. The vacuum was kept at a 10⁻¹ atmosphere and the heating rate was 10°C min⁻¹.

Hardness of the specimens was measured by Vickers indenter (HV) with loading of 50 g, which complied with the ASTM E384-08a standard method. The wear resistance of specimens was evaluated in a ball-on-disk test. The parameters are: specimen size is Ø36 × D5 mm, diameter of Cr ball is 6 mm, axial load is 4.9 N, disc rotation is 100 rpm, sliding speed is 0.031 ms⁻¹, and total rotation is 3000 revolutions. The coefficient of friction was obtained from POD-FM406 software and the wear depth was measured by α-step equipment (ET-4000A).

### Table 1 Chemical composition of the S45C carbon steel (mass %)

| C   | Si | Mn   | S   | P   | Fe    |
|-----|----|------|-----|-----|-------|
| 0.46| 0.21| 0.72 | ≤0.04 | ≤0.03 | Bal.   |

### Table 2 Bath composition and operating conditions of S45C carbon steel by electroless Ni-P adding Al₂O₃ composite deposition

| Process      | Bath composition | Concentration (g/L) | Condition |
|--------------|------------------|---------------------|-----------|
| Acid bath    | NiSO₄ · 6H₂O      | 30                  | 84±1°C    |
|              | NaH₂PO₂ · H₂O    | 15                  | 1 hour    |
|              | Na₂C₄H₄O₄ · 6H₂O | 12                  | pH 5      |
| Alkaline bath| NiSO₄ · 6H₂O      | 30                  | 84±1°C    |
|              | NaH₂PO₂ · H₂O    | 10                  | 1 hour    |
|              | NaC₆H₅O₇ · 2H₂O | 40                  | pH 8      |

### 3. Results and Discussion

Fig. 1 shows the cross-section morphology of pH5 and pH8 on electroless Ni-P with the addition of 0.3 μm of α-Al₂O₃ and 0.05 μm of γ-Al₂O₃ via composite deposition, respectively. It could be clearly seen that the coating containing the Al₂O₃ particles, despite the effect of a slight agglomeration phenomenon, showed a good overall dispersion on the samples. Table 3 shows the composition analysis of the cross-section of the pH5 and pH8 electroless Ni-P composite depositions. Obviously, the γ-Al₂O₃ content was less than that of α-Al₂O₃, which could have been the reason why the smaller particles easily underwent the agglomeration phenomenon. Another possible factor was that the effect of the mixing made it easier for the smaller and lighter particles of the γ-Al₂O₃ powder to form a suspension, but harder for their co-deposition with Ni-P plating. Consequently, the γ-Al₂O₃ was not as effective in adsorbing the Ni-P coating, and thus its content was lower. Further comparison with our previous study showed that the thickness of electroless Ni-P with the addition of the Al₂O₃-powder coating was slightly less than without it, as the nickel-phosphorus in the plating process must co-precipitate with the Al₂O₃ powders in order for the result to be a thinner coating.

Fig. 2 shows the cross-section morphology of pH5 and pH8 on electroless Ni-P with α-Al₂O₃ and γ-Al₂O₃ added by composite depositions after heat treatment, respectively. Figs. 4c and 4d represent the cross-section of Ni-P with the addition of 0.05 μm of γ-Al₂O₃ by composite deposition; clearly, the agglomeration phenomenon was more severe than when α-Al₂O₃ powder was added (as seen in Figs. 2a and 2b). It seems reasonable to conclude that the relatively large surface energy of the fine γ-Al₂O₃ powders resulted in the larger attraction; thus, aggregates were easily produced as the overall adsorptive capacity of α-Al₂O₃ was greater than that of γ-Al₂O₃. In addition, the extra-fine γ-Al₂O₃ powder was easily affected by the stirring in the plating bath, which accounted for it not being adsorbed during the composite deposition, and then immediately being removed by the stirring bath.
Table 4 shows the surface hardness of pH5 and pH8 on electroless Ni-P with added αAl₂O₃ and γAl₂O₃ by composite deposition both without and with different heat treatments. In this study, the particle size (αAl₂O₃ or γAl₂O₃) did not obviously affect the surface hardness of the electroless Ni-P composite depositions; however, the pH value and heat treatment temperature significantly affected the surface hardness. The pH8 of Ni-P with added αAl₂O₃ or γAl₂O₃ powder had a greater hardness than those of the pH5 of Ni-P composite deposition. The greatest hardness was HV₀.₀₅ 927, which appeared in the pH8 of Ni-P with added αAl₂O₃ by composite deposition. At the same pH value, the αAl₂O₃ powder had better dispersion than that of γAl₂O₃, which resulted in a greater hardness. Previous literature [6] also indicated that a bigger particle size results in better dispersion and greater hardness after the electroless plating treatment, which also agrees with our findings.

In this study, all the specimens of Ni-P with added αAl₂O₃ and γAl₂O₃ by composite deposition had greater hardness after heat treatment. The main reason could be ascribed to the phase transformation of the Ni-P depositions. As a result, the surface hardness of the Ni-P composite depositions obviously increased after heat treatment. Furthermore, the greatest hardness was HV₀.₀₅ 1237, which appeared in the pH8 of the Ni-P with added αAl₂O₃ by composite deposition after a 300°C heat treatment. The hardness of the pH8 of Ni-P with γAl₂O₃ added by composite deposition was HV₀.₀₅ 1145 after a 300°C heat treatment. It was confirmed that the adding of either αAl₂O₃ or γAl₂O₃ powder to the electroless Ni-P deposition significantly increased the surface hardness of the Ni-P plating on S45C carbon steel after suitable heat treatment. These results suggest that both the better dispersion of Al₂O₃ and the phase transformation of the Ni-P deposition play important roles in improving the surface hardness of Ni-P plating on S45C carbon steel.

**Figure 1** The cross-section morphology of pH5 and pH8 on electroless Ni-P adding αAl₂O₃ and γAl₂O₃ composite depositions (a) pH5 αAl₂O₃, (b) pH8 αAl₂O₃, (c) pH5 γAl₂O₃, (d) pH8 γAl₂O₃.
Table 3 The composition analysis of the cross-section of pH5 and pH8 on electroless Ni-P adding Al₂O₃ composite depositions (mass %)

| Powder  | pH value | Ni   | P    | Al   | O    |
|---------|----------|------|------|------|------|
| αAl₂O₃  | 5        | 90.48| 5.57 | 1.83 | 2.12 |
|         | 8        | 90.59| 5.02 | 2.15 | 2.24 |
| γAl₂O₃  | 5        | 91.09| 5.53 | 1.57 | 1.81 |
|         | 8        | 91.70| 5.28 | 1.29 | 1.73 |

Figure 2 The cross-section morphology of pH5 and pH8 on electroless Ni-P with added αAl₂O₃ and γAl₂O₃ composite depositions after different heat treatment (a) pH5 αAl₂O₃ and 350°C, (b) pH8 αAl₂O₃ and 300°C, (c) pH5 γAl₂O₃ and 350°C, (d) pH8 γAl₂O₃ and 300°C.

Table 4 Comparison of the surface hardness of pH5 and pH8 on electroless Ni-P with added αAl₂O₃ and γAl₂O₃ composite depositions with non heat-treated and different heat treatments (HV₀.₀₅)

| Materials Condition                           | Hardness(HV₀.₀₅) |
|----------------------------------------------|-----------------|
| pH5(αAl₂O₃)                                  | 739             |
| pH5(αAl₂O₃) after 350°C heat treatment       | 1095            |
| pH8(αAl₂O₃)                                  | 927             |
| pH8(αAl₂O₃) after 300°C heat treatment       | 1237            |
| pH5(γAl₂O₃)                                  | 730             |
| pH5(γAl₂O₃) after 350°C heat treatment       | 1045            |
| pH8(γAl₂O₃)                                  | 889             |
| pH8(γAl₂O₃) after 300°C heat treatment       | 1145            |
The wear test was used to evaluate the wear resistance of Ni-P with Al$_2$O$_3$ added by composite deposition. Fig. 3a shows the coefficient of friction of pH5 and of pH8 on electroless Ni-P with $\alpha$Al$_2$O$_3$ added by composite deposition without heat treatment, or after different heat treatments. The lowest coefficients of friction were 0.411 and 0.437, which appeared in the pH5 and pH8 of Ni-P with $\alpha$Al$_2$O$_3$ added by composite deposition without heat treatment, respectively. Fig. 3a also shows that, after heat treatment, the average coefficient of friction (~0.5) of Ni-P with $\alpha$Al$_2$O$_3$ added by composite deposition is higher than without heat treatment. Because the composite depositions from the original amorphous or microcrystalline structure transferred to the crystalline structure of the Ni$_3$P phase precipitation, it was more dense than amorphous. Moreover, the effect of precipitation hardening of the Ni$_3$P phase and the added Al$_2$O$_3$ powder led to greater friction between the chrome steel ball and the contact surface of the sample during the sliding test. Thus, the coefficient of friction was higher after heat treatment; this result also agrees with the previous study [10-13]. Fig. 3b shows the coefficient of friction of pH5 and of pH8 on electroless Ni-P with $\gamma$Al$_2$O$_3$ added by composite depositions without heat treatment or after different heat treatments, with a similar trend as in Fig. 3a. The coefficient of friction for the pH5 of Ni-P with added $\gamma$Al$_2$O$_3$ was minor (0.422) without heat treatment. Significantly, the effect of the lubricant explained the lower coefficient of friction.

![Figure 3](image_url)

**Figure 3** Comparison of the coefficient of friction of pH5 and pH8 on electroless Ni-P with added Al$_2$O$_3$ composition depositions when non heat-treated or after different heat treatments (a) $\alpha$Al$_2$O$_3$ and (b) $\gamma$Al$_2$O$_3$. 
4. Conclusions
In this study, the hardness of the electroless Ni-P deposition was increased by adding Al₂O₃ powders. Without heat treatment, the maximum hardness was HV₀.₀₅ 927, which appeared in the pH8 of electroless Ni-P with α-Al₂O₃ added by composite deposition. The greatest hardness was HV₀.₀₅ 1237, which appeared in the pH8 of electroless Ni-P with α-Al₂O₃ added by composite deposition after 1 hr of heat treatment at 300°C. The lowest coefficient of friction (0.411) appeared in the pH5 of electroless Ni-P with α-Al₂O₃ added by composite deposition without heat treatment because of the effect of the lubricant. In addition, the coefficient of friction of Ni-P with Al₂O₃ added by composite deposition was higher after heat treatment. From the wear morphology point of view, both showed obvious abrasive wear but also better wear resistance.

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