

Study of PTFE Content & Anti-Corrosion Properties of Electroless Ni-P-PTFE Coatings

by Y. Liu & Q. Zhao*

The polytetrafluoroethylene (PTFE) content of electroless Ni-P-PTFE composite coatings has a significant effect on the surface properties of the coatings. In this paper the principal factors affecting PTFE content of electroless Ni-P-PTFE coatings were investigated, including pH, temperature, the concentrations of PTFE and surfactant in plating bath and substrate materials. The optimum parameters for maximum PTFE content in electroless Ni-P-PTFE coatings were obtained. The morphology and deposition rate of the coatings were also investigated. Corrosion rates of the Ni-P-PTFE coatings in 20% NaCl solution and 1N HCl solution were measured and compared with electroless Ni-P coatings and copper.

The first electroless nickel-phosphorus and polytetrafluoroethylene (PTFE) composite coatings were introduced about 20 years ago.¹ PTFE is chemically inert with a relatively high melting point (325°C; 617°F). Because of its extremely low surface energy (18.6 mN/m; 0.000106 lbf/in.), PTFE has excellent non-stick properties.² The resulting properties of electroless Ni-P-PTFE coatings, such as non-sticking,

anti-adhesive, good wear and good corrosion resistance have been used successfully in many industries.^{1,3} The PTFE content in the coating has been shown to have a significant influence on the properties of the coatings.^{4,5,6} However only a few papers have reported the effects of electroless plating conditions on the PTFE content in the Ni-P-PTFE coatings. Hu, *et al.*⁷ investigated the relation between the zeta potential and codeposition of PTFE particles by studying the effects of various kinds of surfactants on the dispersion and zeta potential of the treated PTFE particles. The results showed that the more positive the zeta potential of the PTFE particles, the easier for the PTFE particles to codeposit with Ni-P and the greater the PTFE content in the coatings. The PTFE content in the coatings averaged about 25 vol%.⁷ Ger and Huang⁸ investigated the role of surfactants in the codeposition of PTFE particles with Ni-P. Mastuda, *et al.*⁹ found that the PTFE content in the coatings depended on the type of surfactant. Zhao, *et al.*¹⁰ selected an optimum surfactant, leading to uniform distribution of nano-PTFE particles throughout the Ni-P matrix, using no additional mechanical or ultrasonic agitation.

The anti-corrosion performance of electroless Ni-P coatings has been investigated extensively.^{11,12} However there is no information on the corrosion resistance of electroless Ni-P-PTFE coatings. Only few papers relating to corrosion resistance of electroplated Ni-P-PTFE coatings have been reported in the very recent literature.^{13,14} Shoeib¹³ and Ibe, *et al.*¹⁴ demonstrated that the anti-corrosion properties of electroplated Ni-P-PTFE coatings were greatly enhanced, even in a strong alkaline solution.

The aim of this paper is to investigate the effects of pH, temperature, the concentrations of PTFE and surfactant in solution and the substrate materials on the PTFE content and corrosion resistance of electroless Ni-P-PTFE coatings.

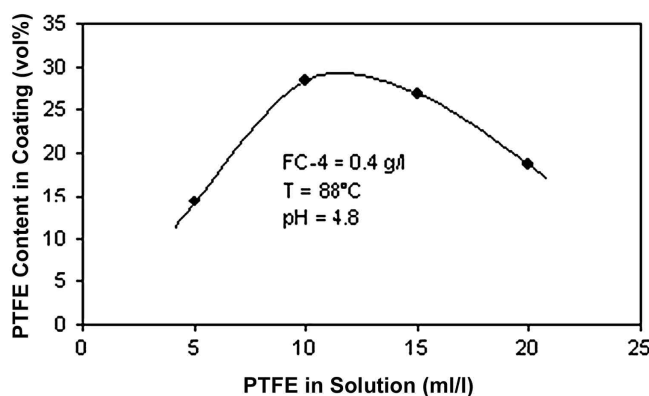


Fig. 1—Effect of PTFE concentration in solution on the PTFE content in the coating.

Nuts & Bolts: What This Paper Means to You

This work deals with electroless nickel-phosphorus composite coatings containing PTFE (polytetrafluoroethylene). The resulting non-stick, wear and corrosion resistance properties have application in many industries. This work was a detailed study into how process factors, including pH, temperature, PTFE and surfactant concentration and the substrate itself, influence the coating properties. The authors report the conditions for optimum performance.

Experimental Procedure

Operating Parameters

The electroless plating solution composition was as follows:

- 25 g/L (3.3 oz/gal) nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$)
- 30 g/L (4.0 oz/gal) sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)

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- 18 g/L (2.4 oz/gal) citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 6\text{H}_2\text{O}$)
- 18 g/L (2.4 oz/gal) sodium acetate (NaCH_3COO).

In order to codeposit PTFE nanoparticles with Ni-P, 0.2 to 0.8 g/L (0.03 to 0.11 oz/gal) of FC-4 fluorocarbon surfactant ($\text{C}_{20}\text{H}_{20}\text{F}_{23}\text{N}_2\text{O}_4\text{I}$) and 5 to 20 mL/L of 60% PTFE emulsion were added to the plating bath. The pH and temperature were held at 4.0 to 5.6 and 80 to 95°C (176 to 203°F), respectively. The coatings were produced on copper, stainless steel and carbon steel substrates.

The substrate dimensions were $15 \times 10 \times 0.35$ mm ($\sim 0.6 \times 0.4 \times 0.013$ in). The substrates were first cleaned with alkaline solution at 60 to 80°C (140 to 176°F) for 5 to 10 min. After rinsing with water, they were immersed into a dilute HCl solution for a few seconds. They were first coated with a thin Ni-P underlayer, and then with Ni-P-PTFE under various coating conditions.

Deposition Rate

The Ni-P-PTFE coating thickness, h , was measured with a digital micrometer and the coating rate γ ($\mu\text{m/hr}$), was calculated using following equation:

$$\gamma = \frac{h}{t} \quad (1)$$

where t is the coating time.

PTFE Content in the Coating

The PTFE nano-particles are distributed throughout the nickel-phosphorus matrix. By altering the bath composition and operating conditions, the PTFE content can be varied significantly. The PTFE content is usually determined either by titration (*i.e.*, determining the contents of Ni and P and subtracting) or by filtration (weighing the PTFE cake left on a filter). For both methods, the Ni-P-PTFE coating is dissolved in 50% nitric acid. Obviously this is time-consuming. In this investigation, the PTFE content was determined by measuring the coating thickness h . Assuming that porosity is negligible in the calculation of the total coating volume, the following two equations were used:

$$\rho_{\text{Ni-P}} \cdot V_{\text{Ni-P}} + \rho_{\text{PTFE}} \cdot V_{\text{PTFE}} = V \cdot \rho \quad (2)$$

$$V_{\text{Ni-P}} + V_{\text{PTFE}} = V \quad (3)$$

where $\rho_{\text{Ni-P}}$, ρ_{PTFE} and ρ are the densities of the electroless Ni-P coating, PTFE and Ni-P-PTFE coating respectively. $V_{\text{Ni-P}}$, V_{PTFE} and V are the corresponding volumes of Ni-P, PTFE and Ni-P-PTFE, respectively. $\rho_{\text{Ni-P}}$ varies slightly with the phosphorus content in the electroless Ni-P coating. In general, the phosphorus content is approximately 8 to 10 wt%, and the corresponding density of the Ni-P coating is about 7.9 g/cm^3 (0.285 lb/in^3). The density of PTFE is about 2.2 g/cm^3 (0.080 lb/in^3). By combining equations (2) and (3), the PTFE content, V_{PTFE}/V is:

$$\frac{V_{\text{PTFE}}}{V} = \frac{\rho_{\text{Ni-P}} - \rho}{\rho_{\text{Ni-P}} - \rho_{\text{PTFE}}} \quad (4)$$

To determine the coating density, ρ , Ni-P-PTFE was applied to 0.35-mm (13.8-mil) thick copper substrates. Each specimen (10×15 mm; 0.39×0.59 in) was weighed before and after coating, using an electronic scale with 10^{-5} g precision. The relation between Ni-P-PTFE coating thickness, h (μm) and coating density, ρ (g/cm^3) is given by the following equation:

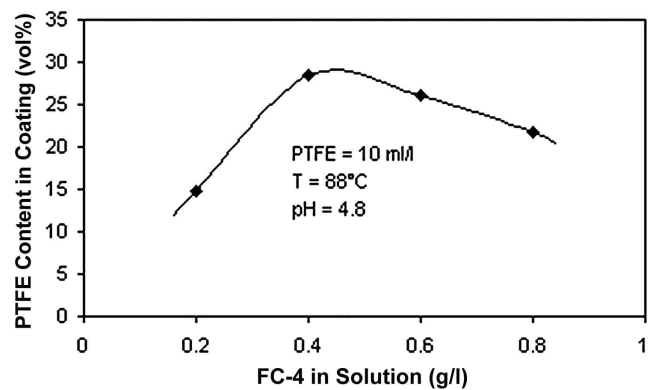


Fig. 2—Effect of FC-4 concentration on the PTFE content in the coating.

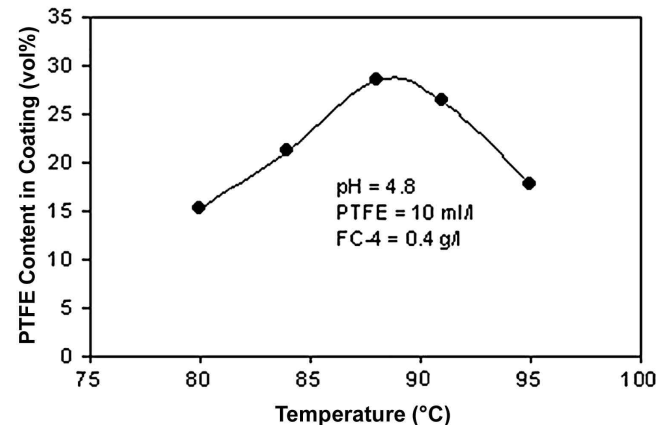


Fig. 3—Effect of plating solution temperature on the PTFE content in the coating.

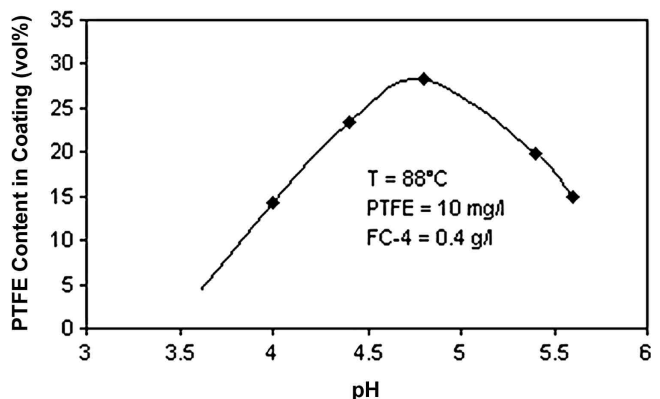


Fig. 4—Effect of solution pH on the PTFE content in the coating.

$$h = \frac{h_{\text{Cu}}}{2} \cdot \left(\frac{w_a - w_b}{w_b} \right) \cdot \left(\frac{\rho_{\text{Cu}}}{\rho} \right) \quad (5)$$

where h_{Cu} is the thickness of the copper substrate before coating [$350 \mu\text{m}$ (13.8 mils) in this investigation], w_b and w_a are the weights of the copper substrate before and after coating, respectively and ρ_{Cu} is the density of copper (8.9 g/cm^3 ; 0.322 lb/in^3). As both sides of the copper substrates are coated, the above equation must be divided by 2. By combining equations (4) and (5), the PTFE content, V_{PTFE}/V is:

$$\frac{V_{\text{PTFE}}}{V} \cdot \left(\frac{1}{\rho_{\text{Ni-P}} - \rho_{\text{PTFE}}} \right) \cdot (\rho_{\text{Ni-P}} - \rho_{\text{Cu}}) \cdot \frac{h_{\text{Cu}}}{2h} \cdot \frac{w_a - w_b}{w_b} \quad (6)$$

Results & Discussion

Effect of PTFE Concentration

Figure 1 shows that for a given surfactant concentration, 0.4 g/L (0.053 oz/gal), the volumetric PTFE content in the coatings increased with increasing PTFE concentration in the plating solution up to a maximum value, when the PTFE concentration was 10 mL/L and then decreased with further increases in PTFE concentration. The cationic surfactant was effective in suspending the PTFE particles in the plating solution. However, for any given surfactant concentration, the PTFE particles were found to agglomerate and settle-out during the plating process, once the PTFE concentration in the solution exceeded a certain value. This indicated that the given amount of cationic surfactant was not sufficient to disperse the PTFE particles and hence maintain them in suspension. For example, for the given cationic surfactant concentration of 0.4 g/L (0.053 oz/gal), agglomeration and settling occurred when the PTFE concentration in the solution exceeded 20 mL/L. This is why the PTFE content in coatings decreased when the PTFE concentration in the solution exceeded a certain value.

Effect of Surfactant Concentration

Figure 2 shows that, at a PTFE concentration 10 mL/L, the PTFE content in the coating increased with increasing cationic surfactant concentration in solution up to a maximum value, and then decreased when the surfactant concentration was over 0.4 g/L (0.053 oz/gal). The optimum ratio of PTFE to surfactant in solution for obtaining the maximum PTFE content was 10 mL/L:0.4 g/L (0.053 oz/gal). If the surfactant was too high, the plating solution could become supersaturated. As a result, some surfactant would accumulate near the depositing surface and suppress the diffusion of PTFE particles toward the interface. This is why the PTFE content began to decrease when the surfactant concentration exceeded a certain value.

Effect of Temperature

For given cationic surfactant and PTFE concentrations, the volumetric PTFE content in the coating increased with increasing solution

temperature up to a maximum value when the temperature reached 88°C (190°F), and then decreased, as shown in Fig. 3.

Effect of pH

As shown in Fig. 4, for given cationic surfactant and PTFE concentrations, the volumetric PTFE content in the coating increased with increasing pH in the solution up to a maximum value. When pH was above 4.8, the PTFE content decreased with increasing pH.

Effect of substrate material

The Ni-P-PTFE deposition rates on various substrate materials (copper, stainless steel and steel) showed no significant difference and were all approximately 6 to 7 $\mu\text{m/hr}$ (0.24 to 0.28 mil/hr), because all of the substrates were coated with a thin Ni-P underlayer. The maximum PTFE contents were all around 29 vol%.

Figures 5, 6 and 7 are SEM photos of the surfaces of the Ni-P-PTFE coatings on copper, stainless steel and steel substrates, respectively. The PTFE particles (black points) were uniformly distributed throughout the Ni-P matrix.

Corrosion rates

Figures 8 and 9 show the corrosion rates of copper, regular Ni-P-PTFE on copper, Ni-P on copper and graded Ni-P-PTFE on copper in 20% NaCl and 1N HCl solutions, respectively. The results demonstrate that although the regular Ni-P-PTFE coating can protect copper substrate from corrosion, its corrosion resistance is not as good as for Ni-P coatings. In order to improve the corrosion resistance of the Ni-P-PTFE coatings, a graded electroless Ni-P-PTFE coating technique was developed by gradually increasing the PTFE content from the substrate to the top surface. This not only improved the corrosion resistance of the Ni-P-PTFE. The coating adhesion was significantly improved as well. Figures 8 and 9 show that the corrosion resistance of the graded Ni-P-PTFE coatings was superior to that of the regular Ni-P-PTFE coatings and the Ni-P coatings.

Conclusions

The operating parameters, including pH, temperature, the concentrations

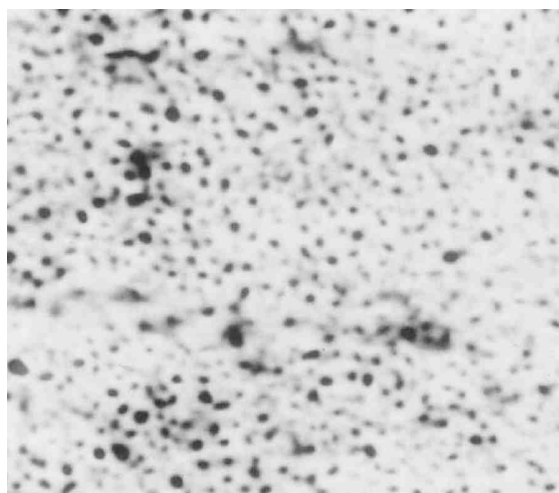


Fig. 5—Uniform distribution of PTFE particles in the coating on a copper substrate.

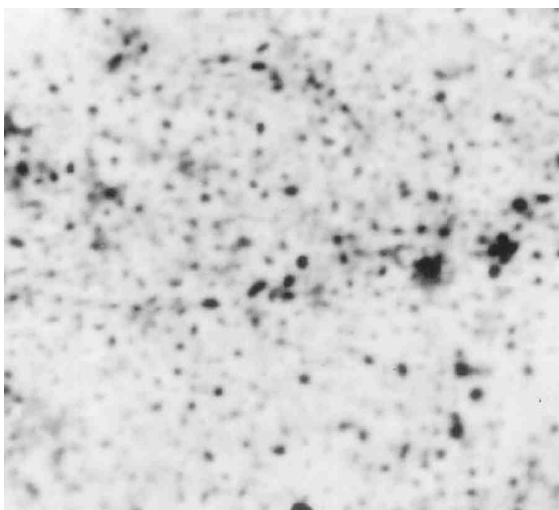


Fig. 6—Uniform distribution of PTFE particles in the coating on a stainless steel substrate.

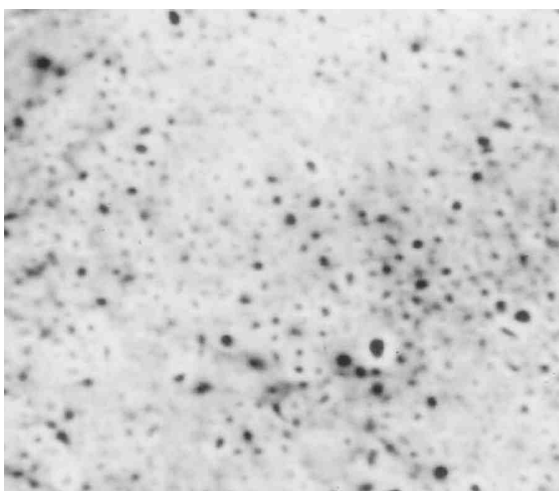


Fig. 7—Uniform distribution of PTFE particles in the coating on a steel substrate.

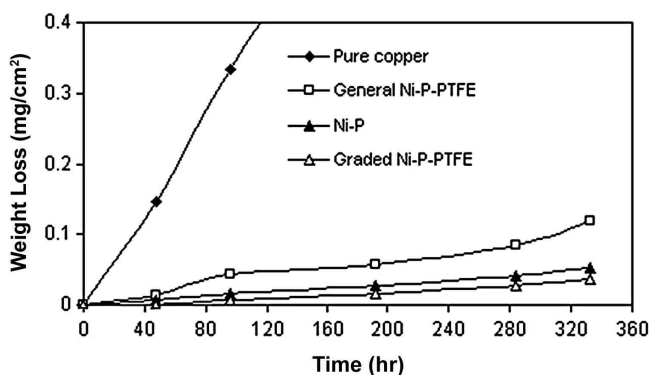


Fig. 8—Corrosion rate in 20% NaCl solution.

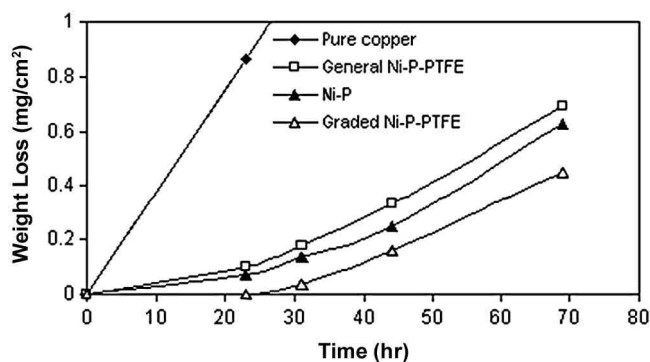


Fig. 9—Corrosion rate in 1N HCl solution.

of PTFE and surfactant in the plating bath solution have significant effects on the PTFE content in electroless Ni-P-PTFE coatings. The optimum parameters to maximize the PTFE content were pH 4.8; temperature, 88°C (190°F); PTFE concentration, 10 mL/L and surfactant concentration, 0.4 g/L. The corrosion resistance of the graded Ni-P-PTFE coating was superior to that of the regular Ni-P-PTFE and Ni-P coatings.

Acknowledgements

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