Process and Properties of Electroless Ni-P-PTFE Composite Coatings

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The process of electroless Ni-P-polytetrafluoroethylene (EN-PTFE) plating was investigated in this study. The microstructural analysis was conducted with scanning electron microscopy. Differential scanning calorimetry was used to study the phase transition of the coating during heat treatment. The mechanical and tribological properties were measured using a hardness tester and a ring-on-disk machine. The corrosion resistance of the coatings was evaluated by polarization measurements. It was found that the microhardness and corrosion resistance of EN-PTFE decreased with increasing PTFE content. PTFE had little effect on the phase transition of the coating and a low surface energy. The results of wear test show EN-PTFE composite coatings had a low coefficient of friction of 0.1 and good anti-wear properties.

Electroless nickel (EN) coatings are widely used in the chemical, mechanical and electronic industries because of their wear and corrosion resistance, and thus the EN plating process has been developed into an effective technique for surface treatment.¹ Moreover, in order to improve further the mechanical and tribological properties of EN coatings, numerous EN composite coatings have been developed. Ni-P-PTFE composite coatings are of major interest because of their non-stick, non-galling, low friction and non-flammability properties. Electroless EN-PTFE coatings have been applied in many industrial applications.²⁻⁴

PTFE particles are difficult to disperse in electroless plating baths because they are strongly hydrophobic. Matsuda⁵ and Hu⁶ studied the effect of surfactants on PTFE particle dispersion and proposed that the zeta potential of the particles was the dominant factor for the codeposition of PTFE with electroless nickel. Ger⁷ analyzed the mechanism of surfactants by mathematical modeling. Nishira⁸ discussed the effect of agitation type on the dispersion of the particles and showed that ultrasonic agitation was beneficial to the dispersion and deposition of particles. Additionally, Nishira⁹ and Yu¹⁰ investigated the tribological properties of Ni-P-PTFE. However, only a few details about the process and properties of EN-PTFE were presented. The effect of PTFE particles on the structure and properties of EN has not yet been established.

In this work, the process and properties of EN-PTFE coatings were systemically investigated. The effects of PTFE concentration on plating rate and content were studied. In addition, the hardness, corrosion resistance, surface energy and tribological properties were evaluated.

Nuts & Bolts: What This Paper Means to You

Electroless nickel with codeposited PTFE particles has been of interest in providing a coating with exceptional wear properties. Dispersing PTFE in solution is a challenge because the particles tend to shed water (hydrophobic). Here, the authors have shed light on what is needed to better incorporate PTFE into the deposit and also how the corrosion and wear properties are affected.

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Experimental

The composition and plating conditions of the EN and EN-PTFE baths contain follows:

Nickel sulfate (NiSO ₄ ·6H ₂ O)	25.0 g/L (3.4 oz/gal)
Sodium hypophosphite (NaH,PO, H,	O) 30.0 g/L (4.0 oz/gal)
Sodium acetate (CH ₃ COONa·3H ₂ O)	15.0 g/L (2.0 oz/gal)
Lactic acid (CH ₃ CHOHCO ₂ H)	33 mL/L (4.2 fl.oz/gal)
PTFE (EN-PTFE baths) 2.0 to 1	13.0 g/L (0.27 to 1.74 oz/gal)
Temperature	$88 \pm 2^{\circ}C (190.4 \pm 3.6^{\circ}F)$
pH	4.8

The surfactants used were as follows:

- 1. Hexadecyltrimethylammonium bromide (HTAB) cation surfactant
- 2. FC4 cation surfactant
- 3. FC134 cation surfactant

4. Mixed FC4 and FC10 surfactant (non-ionic surfactant).

EN and EN-PTFE coatings were deposited on $30 \times 30 \times 0.1$ mm (1.18 × 1.18 × 0.004 in.) copper sheet, $20 \times 30 \times 1$ mm (0.79 ×

1.18 \times 0.039 in.) and $\Phi30$ \times 5 mm mild carbon steel, respectively. The average PTFE particle size was 0.2 μ m (7.9 μ -in.). The weight percentage of PTFE in the coating was determined by dissolving the coating from the copper sheet in 50% nitric acid. After centrifuging and washing in distilled water, the PTFE was dried at 100°C (212°F) and weighed. The morphology of the coatings was analyzed by scanning electron microscopy (SEM). Differential scanning calorimetry (DSC) was used to study the phase transition of the coating during heat treatment. In this experiment, the DSC samples were prepared by stripping the coatings from copper substrates. A microhardness tester was used to measure the hardness of the coatings. The average value of five measurements was taken as the reported hardness value. The surface energy was analyzed using water droplet surface contact angle measurement. The tribological properties were evaluated by wear testing which was carried out at an air humidity of 50 ± 10 RH% and a temperature $25 \pm 1^{\circ}$ C (77 \pm 1.8°F) using a ring-on-disk machine under dry conditions (Fig. 1). The disk was made of carbon steel

on which was deposited a $30-\mu m$ (0.0012-in.) thick coating. The 10-mm (0.4-in.) diameter ring material was GCr15 high carbon chromium bearing steel (AISI 52100) with a hardness of H_{RC} 62-



63. The surface roughness of the disk and ring were $R_a < 0.3 \ \mu m$ and $R_a < 0.1 \ \mu m$, respectively. A normal load of 50 N (11.2 lbf) was used in the wear test and rotation speed is 50 rpm. The wear loss and normalized wear rate were calculated by the weight loss which was measured with an electronic balance with a 0.1 mg accuracy before and after wear testing.

Results and discussion

Process of electroless EN-PTFE plating

According to the DLVO theory,^{11-13,**} the surfactant influences the ion intensity, Hamaker constant and zeta potential of a colloid particle, but it acts mainly on the ion intensity because of its low concentration. Several kinds of surfactants were used individually to disperse PTFE particles. Additionally, a mixed surfactant containing the cationic surfactant FC4 and non-ionic FC10 was selected. As shown in Fig. 2, the FC surfactant was clearly better than the HTAB type. Simultaneously, non-ionic surfactant was indispensable. Although the non-ionic surfactant reduced the potential of the particle, the stability of the colloid was enhanced so the particle content in the coating was increased.



Figure 2—Metallographic cross-sections of Ni-P-PTFE coatings using different surfactants: (a) HTAB; (b) FC4; (c) FC134 + FC10; (d) FC4 + FC10.

Figure 3 shows the morphology of the composite coating as observed by SEM. It can be seen that the PTFE was uniformly distributed throughout the deposit. The solution with the combined FC4 and FC10 surfactant remained stable for eight MTO (metal turnovers) and exhibited a plating rate of 8 μ m/hr (0.0003 in/hr).

Figure 4 shows that the plating rate decreased with increased PTFE in solution. This could be explained by the surfactant occupying the active sites where nickel and phosphorus would normally be deposited. On the other hand, more and more particles may have hindered the diffusion of Ni⁺² and $H_2PO_2^-$, so the reduction of Ni and P decreased.

^{**} Named after the authors in references 12 and 13: Derjaguin, Landau,¹² Verwey and Overbeek.¹³



Figure 3-SEM image of PTFE in the coating.

The influence of the concentration of particles in solution on the percent PTFE codeposited is shown in Fig. 5. It can be seen that the PTFE content in the coating increased with increasing PTFE in solution until a maximum was reached at about 12 g/L (1.6 oz/gal). It would appear that, with the increased PTFE concentration, the ratio of particles to the working surface increased, and thus more particles were codeposited. However, when the PTFE concentration of Ni⁺² and H₂PO₂⁻. The adsorption and codeposition of PTFE came to equilibrium when the PTFE concentration reached 12 g/L (1.6 oz/gal). The content of PTFE in the coating then stabilized.

Properties of electroless EN-PTFE coatings

The effect of particles on the hardness of the coatings is shown in Fig. 6. As the weight percent of particles increased, the hardness of the coatings decreased linearly. The hardness of EN-PTFE (10 wt% PTFE) was only 300 VHN. The decrease of hardness can be related to the PTFE, which is a soft particle and easily deformed. Additionally, the effective loading area decreased because of



Figure 4-Effect of PTFE on the plating rate.



Figure 6-Effect of PTFE on the hardness of EN-PTFE.



Figure 5–Effect of PTFE concentration in solution on the PTFE content in the coating.



Figure 7-Polarization curves of EN and EN-PTFE.

the PTFE so that the hardness decreased rapidly. According to the results of Duncon,¹⁴ the effective loading area of EN-PTFE decreased by 25% when the percentage of PTFE was 15 vol%. Thus the hardness of EN-PTFE fell sharply when the coating contained more particles.

The polarization curves of EN-PTFE and EN coatings are shown in Fig. 7. In a 5% HCl medium, the corrosion resistance of EN-PTFE was worse than that of EN. The corrosion resistance of the coating with 8.4 wt% PTFE was worse than that of the coating with 3.6 wt% PTFE. Although PTFE has excellent corrosion resistance, the corrosion resistance of the coating became worse. This could be explained by the increase of interfacial area and porosity because of the introduction of PTFE particles. There were microstructural defects introduced, so the corrosion resistance of the composite coating deteriorated.

Figure 8 shows a typical DSC thermogram of an EN-PTFE coating. At a heating rate of 20 C°/min (36 F°/min), there was an exothermic peak at approximately 346°C (655°F) observed in the DSC curve associated with the phase transition from amorphous EN matrix to a mixed structure of polycrystalline Ni and Ni₃P. It

can be seen that the introduction of PTFE did not change the crystallization temperature.***

The contact angle, the friction coefficient and the wear rate of EN and EN composite coatings are listed in Table 1. To estimate the surface energy, the contact angle of a deionized water droplet was measured using a goniometer.**** The results demonstrated that EN-PTFE had a very low surface energy. This can be explained by the fact that the introduction of PTFE particles into the EN coating effectively increased the contact angle, and decreased the surface energy. A small change of contact angle over the course of three minutes showed that the surface of the coatings was compact.

Figure 9 shows the friction coefficients of the four coatings as a function of sliding distance. The uneven curve with the Ni-P was caused by spalling of the coating along the wear track. It was found

****OCA15 Video-Based Optical Contact Angle Measuring System, Future Digital Scientific Corp., Bethpage, NY 11714



Figure 8-DSC curve of EN-PTFE (6 wt%).



Figure 9-Friction coefficient with sliding distance of EN-PTFE and EN.

Table 1 Some properties of EN and EN-PTFE coatings

Coating	Average friction coefficient	Wear rate, 10 ⁻³ mg/N·m	Contact angle	
			Time = 0	Time = 3 min
Ni-P	0.24	3.53	95°	90°
Ni-P-PTFE	0.10	2.70	113°	109°

^{***} The crystallization temperature of EN is 345°C (653°F).

that the friction coefficient of EN increased and reached stability with sliding distance. On the other hand, the friction coefficient of EN-PTFE remained low and stable. This could be explained by the formation of a PTFE transfer film between the coating and the counterpart sample during sliding. The film had a low cutting intensity so that the chains of PTFE polymer were easily cut. Additionally, the EN-PTFE coating exhibited much improved antiwear properties over the EN coating under a load of 50 N (11.2 lbf) and a lower rotation speed 50 rpm. The wear rates of EN-PTFE and EN are also shown in Table 1.

Conclusions

- 1. Fluorocarbon-type (FC) surfactants perform better than hexadecyltrimethyl ammonium bromide (HTAB). A mixed surfactant rendered the particles homogenous in solution and uniformly distributed throughout the deposit. The solution with FC4 and FC10 remained stable for eight metal turnovers and exhibited an 8 μ m/hr (0.0003 in/hr) plating rate. The plating rate decreased with increasing PTFE in solution.
- 2. The as-deposited coatings had an amorphous EN structure incorporated with uniformly distributed PTFE. The DSC thermogram showed that the phase transition from the amorphous EN to a mixed structure of crystalline Ni and Ni₃P alloy occurred at about 346°C (655°F).
- 3. By comparison with EN, the hardness and corrosion resistance of EN-PTFE decreased. The introduction of PTFE had no obvious effect on the phase transition, whereas it did reduce the surface energy of EN-PTFE coating.
- 4. EN-PTFE showed a reduced friction coefficient and better antiwear properties when compared to EN. The friction coefficient of EN-PTFE reached 0.1 at a rotation speed of 50 rpm under a 50 N (11.2 lbf) load.

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