Zeta Potential & Codeposition of PTFE Particles Suspended in Electroless Nickel Solution

By X. Hu, C. Dai, J. Li and D. Wang

The relation between the Zeta potential and codeposition of PTFE particles was investigated by studying the effects of various kinds of surfactants on dispersion and the Zeta potential of the treated PTFE particles. The results show that the Zeta potential of PTFE particles is more positive, the PTFE particles are easier to codeposit with Ni-P and the PTFE content in coatings is greater. In this experimental process, the PTFE content is about 25 volume percent on average.

Many kinds of solid particles can be codeposited with electroless Ni-P alloy,[1-5] most of which are ceramic-like, such as SiC, WC, Al_2O_3 and diamond, etc. The composite coatings deposited in this way possess high hardness and excellent wear resistance. In recent years, Tulsi,[6] Ebdon,[7] Schmeling,[8] Luce[9] and Hadley[10] have reported that polymer particles, such as PTFE, can be codeposited in electroless nickel solutions. The Ni-P/PTFE composite films are non-adhesive, self-lubricating, have low coefficient of friction, and good corrosion resistance; therefore, they have extensive applications in many industrial areas.

PTFE particles are strongly hydrophobic and difficult to disperse in an acid electroless plating bath, so must be treated with a special active surfactant. To date, there are no reports about the mechanism of codeposition with Ni-P alloy in an electroless bath.

Experimental Procedure

Carbon steel plates with dimensions of 15 x 25 x 2 mm were used as specimens. Table 1 lists the composition of the electroless Ni-P bath and the operating conditions, in which thiourea and its derivatives act as stabilizers. The surfactants used to disperse the PTFE particles are listed in Table 2. During all experiments, the average diameter of PTFE particles was 0.2 µm; concentration in the bath was 5.0 g/dm³.

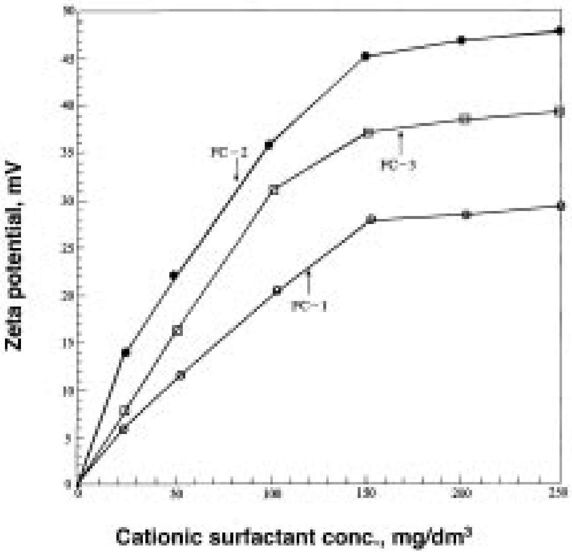

Fig. 1—Effects of cationic surfactants on Zeta potential.

The electrostatic charge of the PTFE particles in solution is determined with a streaming potential analyzer. The values of Zeta potential can be calculated using the following Helmholz-Smudchowski equation:

$$\xi = \frac{4\pi\eta}{DE} u$$

where ξ is the zeta potential, E is the potential gradient, η is the viscosity of the solution, u is the velocity of electrophoresis and D is the dielectric coefficient.

The content of PTFE particles in the composite coatings is determined by SEM analysis of the surfaces of composite coatings. PTFE content is then calculated by means of the following equation:

$$\text{PTFE (vol \%)} = \frac{4/3\pi R^3 N^{3/2}}{S^{3/2}} \times 100$$

where R is the radius of PTFE particles, S is the area of the coating, and N is the number of particles in area S.

Results and Discussion

Three kinds of FC-type cationic surfactant were applied separately to disperse PTFE particles. Figure 1 shows the Zeta potential of the treated PTFE particles in the plating bath. First, Zeta potential increases linearly with increasing concentration of the surfactant. As the concentration increases above 150 mg/dm³, the Zeta potential of the particle becomes stable, which may result from saturated adsorption

Table 1
Composition & Operating Conditions

$NiSO_4 \cdot 6H_2O$	28 g/dm³	Lactic Acid (≥80%) 20 mL/dm³
$NaH_2PO_2 \cdot H_2O$	30 g/dm³	pH 4.6
$CH_3COONa \cdot 3H_2O$	35 g/dm³	Temp 85 °C

Table 2
Surfactants Used for Dispersion

Sample	Ion Type	Composition
FC-1	cationic	perfluoro alkyl ammonium salt
FC-2	cationic	perfluoro polyoxypropylene ammonium iodide $R\text{-}CF\text{-}CF_2O\text{-}R'I$
FC-3	cationic	perfluoro polyoxypropylene ammonium iodide $R\text{-}(CF\text{-}CF_2O)_2\text{-}R'I$
N-1	non-ionic	alkylphenol ether
N-2	non-ionic	dodecylphenol polyoxyethylene ether
N-3	non-ionic	nonyl phenyl polyoxyethylene ether

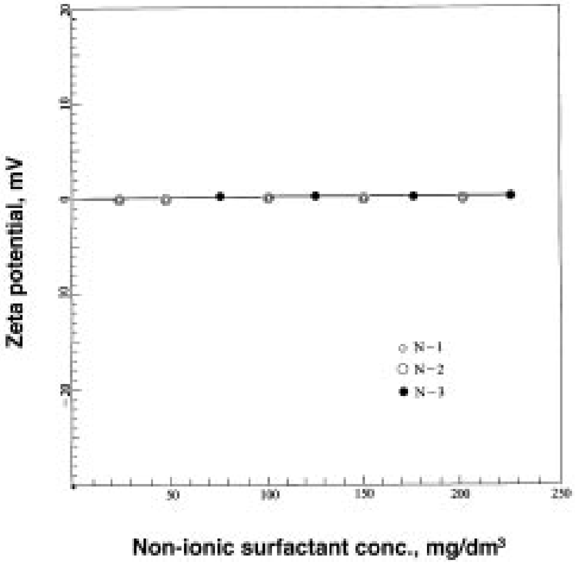

Fig. 2—Effects of non-ionic surfactants on Zeta potential.

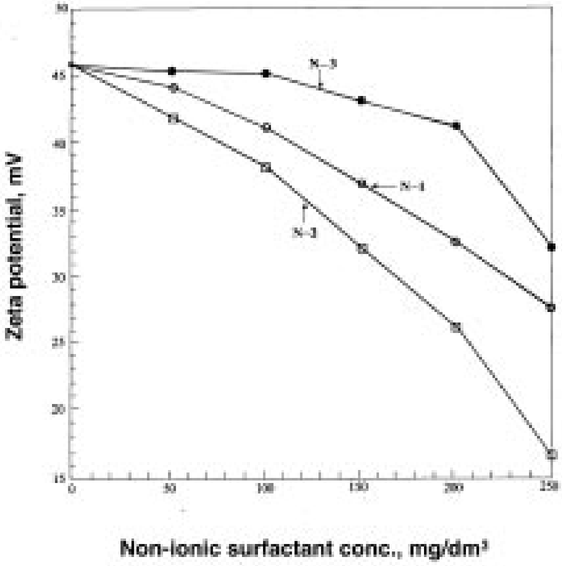

Fig. 3—Effects of non-ionic surfactant concentration mix FC-2, 150 mg/dm³, on Zeta potential.

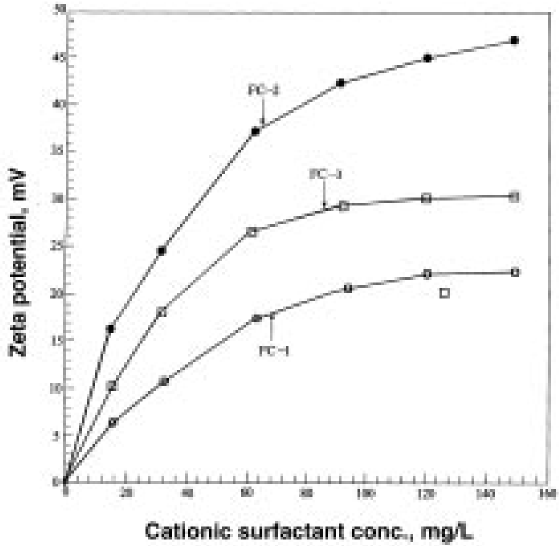

Fig. 4—Effects of cationic surfactant concentration mix N-3, 100 mg/dm³, on Zeta potential.

of cationic surfactant on the surface of the PTFE particles. On the other hand, the Zeta potential of PTFE particles activated by FC-2 surfactants appears more positive than with FC-type; the Zeta potential reaches 48 mV. when the concentration of FC-2 in the bath is about 250 mg/dm³, but in relevant reports, the Zeta potential is only 10 to 15 mV[11]. This indicates that FC-2 is more easily adsorbed on the PTFE particles, which can be proved as well by the quantity and distribution of the particles in the coatings. SEM observations indicate that codeposition of PTFE occurs in three types of the bath, and when the particles are activated by FC-2 surfactant, the PTFE content is greatest (38 vol percent). The PTFE particles can be uniformly distributed as well.

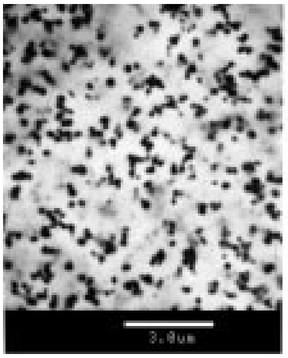

Fig. 5—SEM micrograph of Ni-P-PTFE composite coating; FC-2 cationic surfactant, 150 mg/dm³, plus N-1 surfactant.

Figure 2 shows that Zeta potential is almost unchanged and that almost no PTFE particles are codeposited when a non-ionic surfactant is used, the reason being that a non-ionic surfactant cannot provide a positive charge for adsorption on the surface of particles.

When the quantity of FC-2 that provides the best adsorption remains constant in the bath, some different non-ionic surfactants are added into the solution separately. Figure 3 indicates that the Zeta potential of the particles will be reduced. At this point, the cationic FC-2 surfactant on the particles can be replaced by a non-ionic one (N-1, N-2, N-3) in some degree, but replacement ability for N-3 surfactant is the weakest, which makes Zeta potential reduction the slowest. On the other hand, the Zeta potential of PTFE particles is measured when a certain quantity of N-3 surfactant (100 mg/dm³) was applied together with FC-type cationic surfactant (Fig. 4). The results are similar to those of Fig. 1—the Zeta potential moves to a positive value and becomes stable with the increase in concentration of FC. The FC-2 cationic surfactant is the most effective.

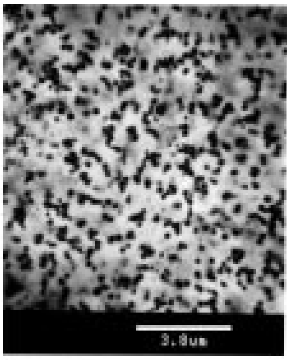

Fig. 6—SEM micrograph of Ni-P-PTFE composite coating; FC-2 cationic surfactant, 150 mg/dm³, plus N-2 surfactant.

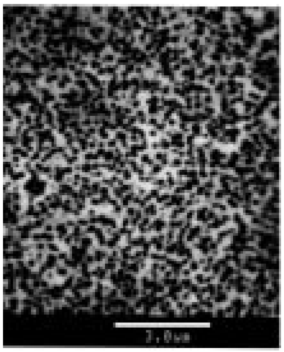

Fig. 7—SEM micrograph of Ni-P-PTFE composite coating; FC-2 cationic surfactant, 150 mg/dm³, plus N-3 surfactant.

A mixed surfactant system with 150 mg/dm³ FC-2 and 10 mg/dm³ N-1, N-2 or N-3, was applied to disperse the PTFE particles. Under the same operating conditions, electroless Ni-P/PTFE composite deposits can be obtained on carbon steel; Figs. 5, 6 and 7 are the corresponding SEM morphologies. It is obvious that PTFE in the deposits of Fig. 7 is the most homogeneous, which corresponds to the high Zeta potential of the particles, that is to say, the high Zeta potential of the particles is beneficial for codeposition of PTFE particles.

Findings

1. In an electroless nickel plating bath, the Zeta potential of the PTFE particles dispersed by FC-type cationic/non-ionic surfactant is from 35 to 46 mV; the PTFE particles with the more positive Zeta potential are the most beneficial for codeposition in electroless nickel solutions.
2. When FC-2 cationic surfactant, mixed with N-3 non-ionic surfactant, was applied to disperse the particles, the PTFE particles in the plating bath do not easily agglomerate and the particles in the coating are well-dispersed and homogeneous.
3. The average content of PTFE in the composite coatings is about 25 ±2 vol percent). The coatings are amorphous.
4. Deposition of PTFE together with Ni-P alloy is controlled by the mechanism of electrophoretic deposition.

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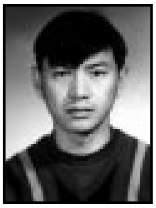
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