

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, Al₂O₃ 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 Luce⁹ and Hadley¹⁰ 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

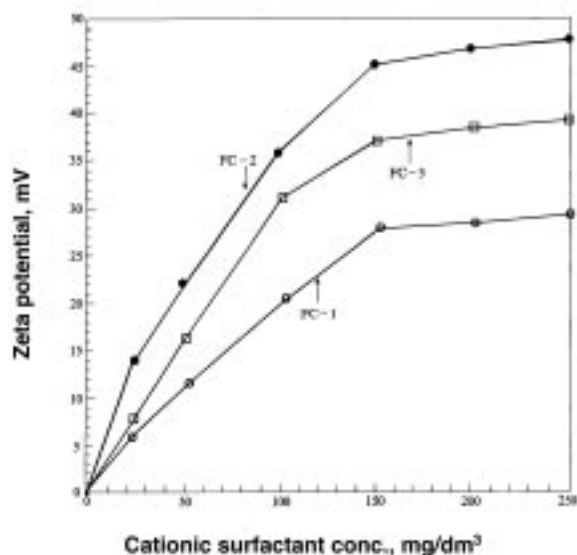


Fig. 1—Effects of cationic surfactants on Zeta potential.

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.

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 Helmholtz-Smoluchowski 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 ·6H ₂ O	28 g/dm ³	Lactic Acid (≥80%)	20 mL/dm ³
NaH ₂ PO ₄ ·H ₂ O	30 g/dm ³	pH	4.6
CH ₃ COONa·3H ₂ O	35 g/dm ³	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-CF ₂ -CF ₂ -O-R ⁺ I ⁻
FC-3	cationic	perfluoro polyoxypropylene ammonium iodide R-(CF ₂ -CF ₂ -O) ₂ -R ⁺ I ⁻
N-1	non-ionic	alkylphenol ether
N-2	non-ionic	dodecylphenol polyoxyethylene ether
N-3	non-ionic	nonyl phenyl polyoxyethylene ether

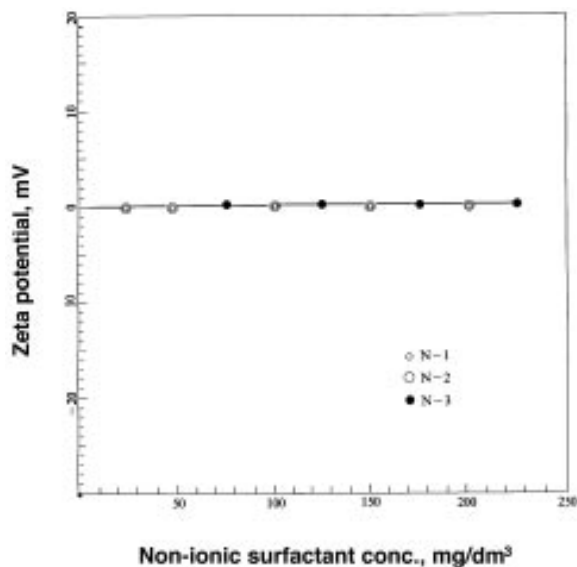


Fig. 2—Effects of non-ionic surfactants on Zeta potential.

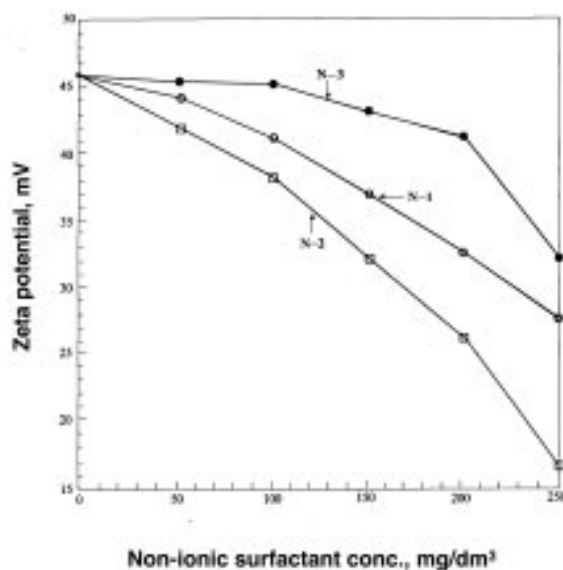


Fig. 3—Effects of non-ionic surfactant concentration mix FC-2, 150 mg/dm³, on Zeta potential.

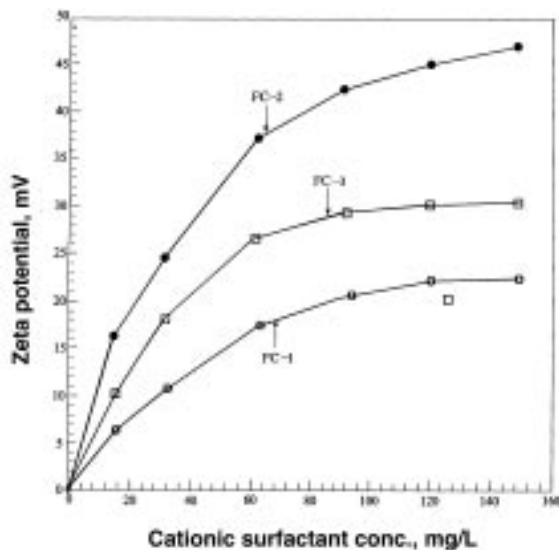


Fig. 4—Effects of cationic surfactant concentration mix N-3, 100 mg/dm³, on Zeta potential.

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 mV¹¹. 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.

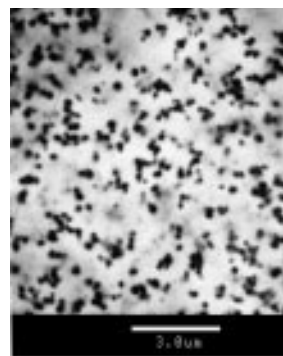


Fig. 5—SEM micrograph of Ni-P-PTFE composite coating; FC-2 cationic surfactant, 150 mg/dm³, plus N-1 surfactant.

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

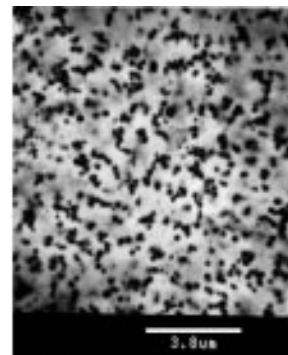


Fig. 6—SEM micrograph of Ni-P-PTFE composite coating; FC-2 cationic surfactant, 150 mg/dm³, plus N-2 surfactant.

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.

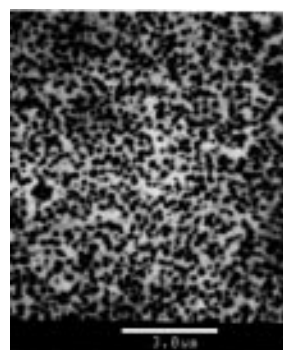


Fig. 7—SEM micrograph of Ni-P-PTFE composite coating; FC-2 cationic surfactant, 150 mg/dm³, plus N-3 surfactant.

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.

Editor's note: Manuscript received, July 1996.

References

1. W. Metzger et al., *Trans. Inst. Met. Fin.*, **54** (4), 173 (1976).
2. F. N. Hubbel, *Plat. and Surf. Fin.*, **65**, 58 (Dec. 1978).
3. Cowan, U.S. patent 3,401,619 (1983).
4. J.T. Kim, U.S. patent 4,716,059 (1987).
5. S.S. Tulsi, *Finishing*, **11** (11), 14 (1983).
6. S.S. Tulsi, *Trans. Inst. Met. Fin.*, **61** (1), 147 (1983).
7. P.R. Ebdon, *Plat. and Surf. Fin.*, **75**, 65 (Sept. 1988).
8. E. Schmeling, *Metalloberfläche*, **39** (4), 131 (1985).
9. W. Luce, *Galvanotechnik*, **78** (11), 3193 (1987).
10. J.S. Hadley, *Metal Fin.*, **85**, 51 (Dec. 1987).
11. H. Matsuda et al. *Trans. Inst. Met. Fin.*, **72**(2), 55 (1994).



Hu

Dai

Li

Wang

About the Authors

Prof. Xinguo Hu is a specialist in electrodeposition at the Center of Electroplating and Research, Harbin Institute of Technology, Box 414, Harbin 150001, P.R. China. His research interests are electroless and composite plating. He has published many papers and holds the Japan patent for chromium-based composite plating.

Changsong Dai is an assistant research fellow in the Center for Electroplating and research at HIT, from which he holds an MS degree. He is mainly engaged in research and application of electroless plating.

Jun Li is a doctoral candidate in the Dept. of Applied Chemistry of Harbin Institute of Technology (HIT), from which he received BS and MS degrees. He has worked with ternary electroless alloys for three years. His research project is electroforming Ni-PSZ (Partially Stabilized Zirconia) gradient composite coating.

Dianlong Wang is a project manager at the Center for Electroplating and Research, HIT. He is the principal investigator for electroless LP alloy and mechanisms. He holds an MS in electrochemical engineering from HIT.

High Definition Electroforming Course

"Hands-on"
Lab
Classes

\$875

member

\$985

non-member

Class size is
limited to
16 people.
Register early!

Website:
[http://
www.
aesf.org](http://www.aesf.org)

People from all walks of life and from many different cultures have embraced the 5.25-in. optical media storage device—a.k.a. *compact disc*—like never before. The potential growth to be experienced in the optical media formats in both the near-term and the next several years promises to be very exciting. New formats and media will be rapidly introduced by the end of the decade. In response to this, the plating and surface finishing community must be prepared to play an integral part in this interesting and fascinating challenge.

Two-day Course Helps Finishers Take Advantage of This Trend

AESF's two-day course covers basic plating and electroforming technology as it applies to video disc, holographic and compact disc stamper manufacturing. AESF Illustrated Lectures will be supplemented by instruction in the practical laboratory skills necessary to analyze, control and maintain typical chemical solutions used in electroforming. Additional information will be presented on cleanroom utilization and ultra-pure water technology.

Major facets of the course include chemistry; cleaning, rinsing and recovery; use of the Hull cell; analytical procedures (titration, pH meter, stalagmometer, tensiometer, and analytical balance); electrochemistry; nickel plating; electroforming (mandrel type & materials, metallization, filtration, solution composition, and racking/auxiliary anodes/thieves); analysis and testing (thickness, deposit analysis—deposit stress, composition, surface defects); and analytical procedures.

The laboratory classes will be held at the Reynolds Tech facility in East Syracuse, NY. The other sessions will be held at the Embassy Suites Hotel. Register early. Class size will be limited to 16 students.

Schedule for Course:

Apr. 10-11 Registration & Hotel deadline: March 26

July 10-11 Registration & Hotel deadline: June 26

Embassy Suites Hotel

315/446-3200

6646 Old Collamer Rd.

E. Syracuse, NY 13057; \$99 king room

(Must identify with AESF room block for this rate.)

Course Hours: 8 a.m. to 5 p.m.

A E S F
Phone: 407/281-6441
FAX: 407/281-6446
E - Mail:
aesf@worldnet.att.net