

Studies on electroless nickel–PTFE composite coatings

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Electroless deposition of nickel based composites produces outstanding tribiological behaviour. These composite coatings are formed by addition to the electroless nickel solution of the material to be codeposited, in powder form, and by maintaining it in suspension during the deposition process so that it is incorporated into the deposit. The most commonly used hard dispersed compounds are SiC, diamond powder, alumina, TiC, BN, chromium carbide or WC. Recently, electroless nickel containing PTFE as a composite material has been used because it is uniform, highly adherent, hard wearing, dry lubricating, non-galling, has a lower coefficient of friction and good corrosion resistance properties. The present paper studies the effect of PTFE in an electroless Ni–acid bath on the rate of deposition, incorporation of PTFE and phosphorous content in the deposit, wear and corrosion resistance.

Keywords: Electroless composites, Chemical deposition, Nickel–phosphorous–PTFE composites, Composite coating

Introduction

An electrodeposited composite plating is a uniform dispersion of small discrete particulate matter deliberately codeposited within a metallic coating.^{1–3} Electroless nickel phosphorous coatings have many properties that are superior to those of electrodeposited nickel.⁴ Because of the phosphorous content, electroless nickel is harder and has better corrosion resistance.⁵ Electroless nickel composites combine the unique properties of conventional electroless nickel deposits such as uniformity of deposition over complex geometries, high hardness and good corrosion resistance with that of abrasive materials possessing high temperature resistance and other tribiological properties.

It is interesting to note that in electroless deposition it is possible to achieve a high percentage of incorporation even at low concentrations of particles in the bath, in contrast to electroplating, where a large concentration of particles must be present to get a high percentage of incorporation. In recent years, composite materials have gained importance in engineering industries, especially for high technology applications such as aero engines, modern gas turbine engines, automobiles, etc.⁶ In electroless composites, the matrix is not pure nickel, but it can be either Ni–P or Ni–B, depending upon the nature of the reducing agents used in the bath. The most commonly used hard dispersed compounds are SiC, diamond powder, alumina, TiC, BN and WC.^{1–9} The latest development in electroless codeposition is the incorporation of polytetrafluoroethylene (PTFE) with

nickel. PTFE particles are added to the solution in the form of a water dispersion.^{10,11}

The properties of electroless Ni–PTFE coatings such as wear resistance, corrosion resistance, friction coefficient, microhardness and all other properties are excellent.^{12–18} The production, properties and applications of composite electroless Ni/PTFE coatings are good.^{19,20} Uniform dispersibility of PTFE particles is obtained in electroless nickel composite plating.^{21,22} Duncan¹³ deposited coatings which contain 10–30 vol.-%, 0.3–0.4 μm diameter particles of PTFE with 5–10 wt.-%P. The coefficient of friction is typically 0.1–0.2 for non-lubricated conditions. It was also found from microhardness tests and wear tests that the hardness of composite coatings with 14–16%PTFE was typically 250–400 HV, while the hardness of those with 26%PTFE had only 275 HV. After heat treatment at $>300^\circ\text{C}$ hardness values were increased to 625–700 HV and 400 HV, respectively. Hadley and Harland¹⁷ described a coating containing up to 25 wt.-%PTFE uniformly distributed in chemical Ni–P containing 8.4–6 Ni–7P–8.4PTFE (wt.-%) and with a specific gravity 6.5. They also found that hardness depends on heat treatment. Nishira *et al.*²³ found that suspension of PTFE particles in an electroless Ni–P bath was affected by non-ionic and cationic surfactants. Matsuda *et al.*²⁴ found that PTFE particles were codeposited in electroless Ni–P plated film. This codeposition depends on surfactant type, i.e. zeta potential of particle surface in the plating solution and content of particles in films.

PTFE has been used as a versatile material to protect parts from corrosion and wear.²⁵ Daniels and Harne²⁶ found that the Ni–PTFE coating increases service life and product quality in plastic manufacture.²⁶ Zhengshan *et al.*²⁷ reported the morphology and structure of Ni–P–PTFE coatings. This imparts considerable non-galling, dry lubricant properties to the

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deposit and a low coefficient of friction. With the small particle size, there is no associated problem of roughness, and it is possible to filter the solution in the normal way. Tulsi^{28,29} obtained a Ni-PTFE coating based on the addition of 6.5–11 g dm⁻³ PTFE (60% active) of particle size up to 1 µm at a temperature of 88–92°C and pH 4.7–5.2 with gentle agitation. The PTFE codeposited was 25–30 vol.-%. The coated plate contained a specific wear rate and coefficient of friction. It was used for various rubber and plastic moulds, butterfly valves, for oil and gas industry fasteners, aluminium air cylinders and carburettor choke shafts. Pearce³⁰ outlined the problem in obtaining coatings with Ni-PTFE. He achieved 25–30%PTFE in the deposit with a deposition rate of 12 µm h⁻¹ at 92–95°C. The 12.5 µm coatings are smooth, dull grey, while thicker coatings develop orange peel. Coatings can be precipitated and hardened at 350°C for 1 h. Roberto³¹ described a composite coating typically containing 85Ni–6.6P–8.4PTFE (wt-%). He also found that these types of coatings are used for hydraulic clutch components, tools, seat belt components, gear mechanics and automotive fuel system parts.^{32,33}

Przybylska and Raczynska³⁴ were able to get nickel plating with a PTFE content of coating between 2.5 and 11 wt-%, yielding different dispersion coatings. Coating containing 75Ni–7.9P–6.8 PTFE (wt-%) has good antiadhesive and tribological properties. Zhao *et al.*³⁵ developed a graded Ni–P–PTFE coating technique which significantly improves the coating adhesion. Lui and Zhao³⁶ studied the effects of surfactants on the PTFE particle size in an electroless Ni–P system and found that the maximum PTFE content in the coatings depends mainly on the ratio between the concentration of the surfactant and the concentration of PTFE particles in the plating solution. Huang *et al.*^{37,38} studied the synergistic effects of SiC and PTFE particles in the electroless nickel–phosphorous system on corrosion, wear and antisticking properties of the coatings. Rossi *et al.*³⁹ evaluated the corrosion behaviour of electroless nickel/PTFE, phosphate/MoS₂ and bronze/PTFE coatings applied to improve the wear resistance of carbon steel. The present authors studied the effect of bath temperature, concentration of PTFE and pH on the rate of deposition and incorporation of PTFE in the deposit. Deposit characteristics such as hardness, wear resistance, corrosion resistance and topographic studies using SEM were obtained with and without heat treatment.

Experimental

Electrode preparation

Mild steel and stainless steel panels were used as electrodes. The electrodes were cut to a suitable size and mechanically polished. The polished specimens were degreased with trichloroethylene and etched with dilute hydrochloric acid. Stainless steel panels were used only for phosphorous analysis.

Bath development

Various formulations reported in the literature were selected and studied for their rate of deposition at different temperatures. Among the various solutions, the following bath based on trisodium citrate, sodium

hypophosphite and nickel sulphate was selected for further studies:

- (i) nickel sulphate 30 g L⁻¹
- (ii) trisodium citrate 50 g L⁻¹
- (iii) sodium hypophosphite 25 g L⁻¹
- (iv) Teflon dispersion (60% active).

The composition of the bath ingredients was varied to achieve the optimum composition to give a relatively high rate of deposition at 90°C.

Bath preparation and purification

Chemicals were weighed and dissolved in distilled water (about 75% of the total volume required). The solution was filtered through a G.4 crucible and made to the required volume using distilled water. PTFE was added as a dispersion in water (60% active). The pH of the solution was adjusted electrometrically using ammonia.

Bath maintenance and control

The temperature of the bath was maintained using a relay system which maintained the temperature within $\pm 2^\circ\text{C}$. The pH of the solution was continuously monitored using a pH meter, and suitable additions of sulphuric acid or ammonia were made, depending on the pH of the bath. Bath ingredients, mainly nickel sulphate and sodium hypophosphite, were suitably replenished, depending on the nickel that was deposited from the solution. The electroless bath container was replaced periodically, and the tank was cleaned with nitric acid. The bath was periodically filtered through a G.4 crucible to remove any nickel metal, which gets reduced in the solution. The solution was agitated by means of a magnetic stirrer to keep the particles in suspension as well as to maintain a uniform temperature.

Effect of bath variables on the rate of deposition

Effect of temperature

Mild steel panels 10 × 10 mm were taken, degreased with trichloroethylene, etched in dilute hydrochloric acid, alkaline cleaned, washed with water, dried and weighed. Then these panels were EN/PTFE composite plated at different temperatures, namely 60°C, 70°C and 90°C, for 2 h at pH 5.5. An agitator was used to keep the PTFE dispersed in the bath. After 2 h the panels were taken out, washed, dried and weighed. From the difference in weights, the weight of nickel/PTFE deposited was calculated. From the weight of the deposit, the thickness of the deposit could be calculated.

Effect of plating time

The pretreated and weighed panels were plated with EN/PTFE composite at pH 5.5 for different durations, namely 1 h, 2 h, 3 h, 4 h and 5 h. After the specified time, the panels were removed, washed with water, dried and weighed. From the difference in weights, the thickness of the deposit was calculated for different plating times.

Effect of concentration of PTFE

The mild steel panels were plated with EN/PTFE composite in baths with concentrations of PTFE 5 g L⁻¹ to 20 g L⁻¹, and the thickness of the deposit was calculated.

Determination of hardness

The cleaned mild steel panels were plated with EN/PTFE and the hardness was measured using the Vicker’s hardness method. The diagonal of the diamond shaped indentation made by applying a known load through a diamond indenter for a definite time was measured using a microscope fitted with a calibrator eyepiece. The Vicker’s hardness was calculated from the length of the diagonal.

Determination of abrasion resistance using Taber abraser

The EN/PTFE plated specimen was weighed, then placed under a pair of weighted abrading wheels (each 500 g) of closely controlled composition in such a manner as to cause side slip between the abrading wheels and the surface of the test specimen. The wheels rotated on the specimen for 1000 revolutions, after which the panel was weighed again. The difference in weights was the wear index (Taber index) or rate of wear. The experiments were repeated twice, and the average value was taken. The same experiment was carried out using a specimen which was plated with electroless nickel only, and the abrasion resistance properties of both the specimens, with and without PTFE, were compared.

Effect of heat treatment on hardness

Two similar panels were taken. One was plated with nickel alone and the other with nickel/PTFE composite. Both were heat treated at 400°C for 1 h and then tested for abrasion resistance using the Taber abraser.

Analysis of nickel and phosphorous in deposit

Stainless steel panels were deposited with EN/PTFE deposit in various conditions. The panel was etched in concentrated hydrochloric acid for 1–2 min and activated in palladium chloride solution. Then it was plated with EN/PTFE composite. The deposit was removed from the panel, weighed, dissolved in 20 ml of 40% nitric acid and increased to 100 ml in a standard measuring flask. Nickel content in the solution was analysed volumetrically by the EDTA method and phosphorous by the ammonium phosphomolybdate method.

Corrosion measurements by potentiostatic polarisation

Two mild steel samples were cut to 75 × 15 mm, mechanically polished, degreased with trichloroethylene and etched in 20% sulphuric acid at 60°C or 2 min. One specimen plated with nickel alone and the other with EN/PTFE composite for 2 h at 90°C and pH 5.5. Polarisation measurements were carried out potentiostatically by exposing a 1 cm² area of each plated specimen (both with and without PTFE) using a

Table 1 Influence of temperature of bath on rate of deposition at pH 5.5

Temperature, °C	Rate of deposition, µm h ⁻¹
60	3.7
70	5.0
80	8.0
90	10.5

potentiostat. Platinum was used as an auxilliary electrode and a saturated calomel electrode as the reference electrode. The electrolyte used in the study was 3% sodium chloride. Both anodic and cathodic polarisations were carried out. A graph was drawn with current density against potential. Using the Tafel extrapolation method, the corrosion current and corrosion potentials were determined. The corrosion rate in millilitres per year was calculated.

Results and discussions

Effect of temperature

The effect of temperature on the rate of deposition is shown in Table 1. The rate of deposition increases with temperature. An increase in solution temperature increases the flow of the solution towards the electrode by convection. Because the electroless plating of metals invariably involves a reaction proceeding at a rate limited by diffusion, increasing the temperature of the solution favours more nickel ion movement towards the electrodes, which leads to a high rate of deposition. The volume percentage of PTFE codeposited was also found to increase with rising temperature.

Effect of deposition time

Table 2 shows the change in thickness of the deposit with increase in deposition time. It was found that, as the deposition time increases, the thickness of the deposit also increases.

Effect of concentration of PTFE in bath

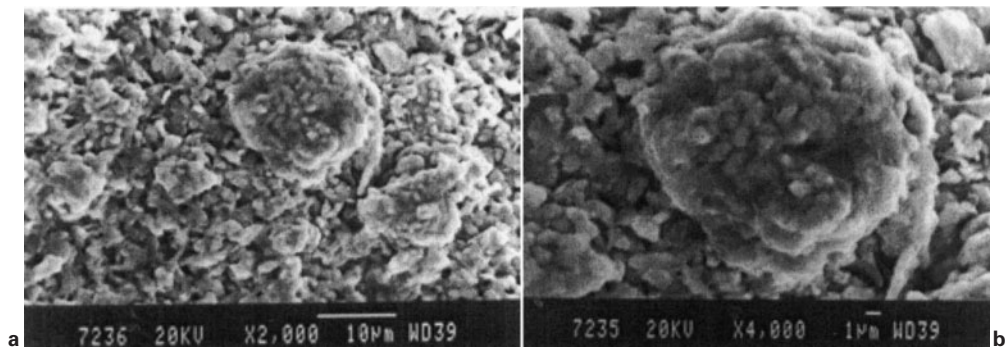
The PTFE content in the bath was varied from 5 g L⁻¹ to 20 g L⁻¹, and the nickel and phosphorous content in the deposits was analysed. The analysis showed that the hypophosphite added to reduce Ni²⁺ produced a phosphorous content of 8%. The amount of nickel in the deposit was found to decrease as the PTFE concentration increased. This confirms that there is an increase in the volume percentage of PTFE with an increase in its concentration. The volume percentage of PTFE attained a constant value from 15 g L⁻¹ onwards. The effect of concentration of PTFE is given in Table 3.

Table 2 Effect of plating time on thickness of deposit at bath temperature 90°C and pH 5.5

Thickness of deposit, µm	Time of deposition, h
10.5	1
17.9	2
25.9	3
30.8	4
5	38.1

Table 3 Effect of concentration of PTFE in bath

Concentration of PTFE, g L ⁻¹	PTFE in EN/PTFE deposit, vol.-%
5	18.0
7	20.8
9	22.6
11	24.0
13	24.8
15	24.9
17	25.0
19	25.0



a × 2000; b × 5000

1 SEM photographs of Ni–P–PTFE composite coating

Effect of PTFE incorporation and heat treatment on hardness and abrasion resistance of deposit

The hardnesses of the electroless nickel-plated and plated composite panels were compared. These tests confirmed that the addition of Teflon particles to electroless nickel reduces the hardness, because it reduces the effective load bearing area of the coating. The two panels were subjected to heat treatment at 400°C for 1 h. Heat treatment produced an increase in hardness for both EN and EN/PTFE composite coatings. However, the hardness of the EN/PTFE deposit was found to be less than that of the EN deposit. PTFE particles get sintered by the heat treatment process, which leaves a PTFE rich film on the surface of the coating, because PTFE is forced to the top by the elevated temperature. The results are listed in Table 4. There was an improvement in the wear resistance of the EN/ PTFE composite deposit compared with the wear resistance of an electroless nickel deposit. PTFE acts as a dry lubricant and hence increases the wear resistance. A 1 h treatment at 400°C produced a better performance. Typical average values for wear rate before and after heat treatment are given in Table 5.

The corrosion behaviour of both electroless nickel and EN/PTFE composite deposits was compared using Tafel polarisation curves. Electroless nickel phosphorous deposits are highly corrosion resistant in hostile environments. EN/PTFE codeposits were reported to behave similarly.¹⁶ Table 6 shows the results. It is sometimes advisable to deposit dual layers of a PTFE free low or high phosphorous layer followed by the EN/PTFE composite to improve base metal protection. Figure 1 shows the photomicrographs of EN/PTFE composite coatings before heat treatment. It is evident from the figure that the PTFE particles are incorporated in the Ni–P matrix.

Applications of electroless nickel–PTFE composite coatings

EN/PTFE composites are used mainly as lubricated coatings. EN/PTFE protects components from solvents

Table 4 Effect of heat treatment on hardness

Substrate	Hardness, HV	
	As plated	After heat treatment
Electroless nickel alone	550	857
EN/PTFE composite	238	701

at various temperatures where normal lubricants cannot be employed. The coating is typically used for valves, aluminium cylinders and pistons, carburettor components, pump rotors and mould cores. EN/PTFE features a self-lubricating and low friction surface, good wear and corrosion resistance, and uniform thickness of coating

Conclusions

1. A suitable bath formulation for electroless nickel/ PTFE composite coating on mild steel was calculated, with a rate of deposition 10.5 µm h⁻¹ at 90°C at pH 5.5. The composition of the bath was:
 - (i) nickel sulphate 30 g L⁻¹
 - (ii) trisodium citrate 50 g L⁻¹
 - (iii) sodium hypophosphite 25 g L⁻¹
 - (iv) Teflon dispersion(60% active).
2. The volume percentage of PTFE codeposited was found to increase with increasing temperature and with increasing concentration of PTFE in the solution.
3. Incorporation of 18–25%PTFE in electroless nickel deposits was found to decrease wear, which can be further decreased by heat treatment at 400°C.
4. The hardness was found to be decreased by codeposition of PTFE which can be improved by heat treatment at 400°C.
5. The incorporation of PTFE does not affect the corrosion behaviour of electroless nickel.

Table 5 Effect of heat treatment on abrasion resistance of electroless nickel and PTFE composite coating

Wheel	Weight applied	Taber wear index, weight loss in mg for 1000 revolutions		
			As plated	After heat treatment
CS10	1 kg	EN	10.43	7.6
		EN/PTFE	7.46	5.5

Table 6 Corrosion data in 3% sodium chloride at pH:5.5

Substrate	<i>I</i> _{corr} , µA cm ⁻²	Corrosion rate, mL year ⁻¹
Electroless nickel alone	25.7	10.918
EN/PTFE	25.18	10.670

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