Electroless Co-P-PTFE Composite Coatings

By J. Tang, S. Zhou & Y. Xie

On the basis of its structures, surface properties and adhesion with iron, cobalt was selected as the matrix in a composite coating to support a load. PTFE was inserted into the matrix to assist lubrication. A composite coating of Co-P-PTFE was prepared by electroless plating. The composite consists of 9.0 percent PTFE, 5.1 percent P and 85.9 percent Co by weight. The properties and structures of Co-P-PTFE composite were studied by X-ray, SEM and ESCA, etc. The results show that the composite had high hardness and good adhesion to the matrix after plating. X-ray analysis showed that the composite was a hexagonal system and its crystal showed no change except that the lattice constant increased, evidently after it was treated with heat. The cobalt (100) face of the hexagonal system parallels the matrix surface and a solid solution was formed in the composite treated with heat. The composite has a strong tendency toward a certain direction. AES analysis indicated that the proportion of Co, P and F content is 13.9:3.1:83 on the surface of the composite. ESCA analysis proved further that fluorine exists in a form of PTFE on the surface of the composite, and phosphorus and cobalt exist in forms of simple phosphorus and Co^{+3}, respectively. Tribology tests showed that the Co-P-PTFE composite has good tribological properties. The composite wear is 45 percent lower by weight loss than the coating of Co-P and 79 percent lower than 45# steel in dry conditions and 60 percent lower by weight loss than the composite of Ni-P-PTFE in oil.

Many investigations have been made to decrease friction and wear between two bodies moving against each other. Generally, liquid lubricants are used for this purpose, but they are not satisfactory in many special situations, so other methods must be applied; for example, solid lubricants. The major solid lubricants are still graphite, molybdenum disulfide and PTFE. Unfortunately, they all have poor wear resistance. Accordingly, investigations in which solid lubricants and high-strength metal were mixed to produce composite coatings are very significant. Because most tribological parts consist of iron, the support layer ought to possess high strength, good sliding properties and low adhesion with iron.

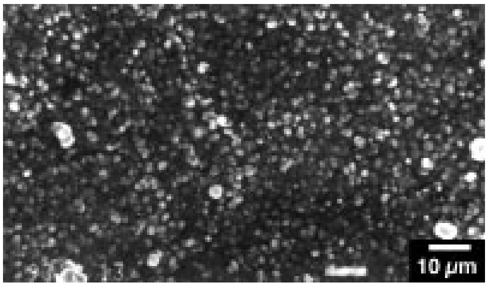

Fig. 2—Surface morphology of Co-P-PTFE composite coating.

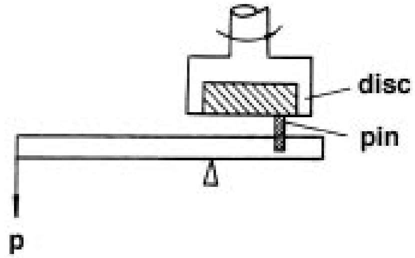

Fig. 1—Diagram of tribology tester.

Cobalt has these properties (see Table 1).[1] It was noted that a completely pure cobalt surface also exhibits low friction and wear in vacuum[2] and was therefore used as a support layer in composite coatings. PTFE has excellent chemical inertness and an extremely low friction coefficient.

If PTFE is added into the coating of Co-P, a self-lubricating coating with high strength and good slide properties may be obtained without heat treatment. PTFE is continuously exposed at the surface of the composite coating to decrease friction and wear during sliding. Composite coatings of Ni-P-PTFE have already been studied and commercial applications were introduced some years earlier,[3-6] as well as composite coatings of Cu-PTFE.[7,8] It has not been reported, however, that a composite coating of Co-P-PTFE has been obtained using electroless cobalt and PTFE. The coating of Co-P was obtained only in a basic electroless plating solution, but PTFE solutions dispersed by a cationic surfactant are not stable in basic solutions.[9] Even though difficult, the composite coating of Co-P-PTFE was obtained by electroless plating. The properties and structures of the composite coating were then studied.

Experimental Procedure

First, the samples of 45# steel with Φ 1.5 cm were polished with emery paper and degreased in acetone, then etched in a mixed solution of 4 percent H_2SO_4 and 3 percent HCl by

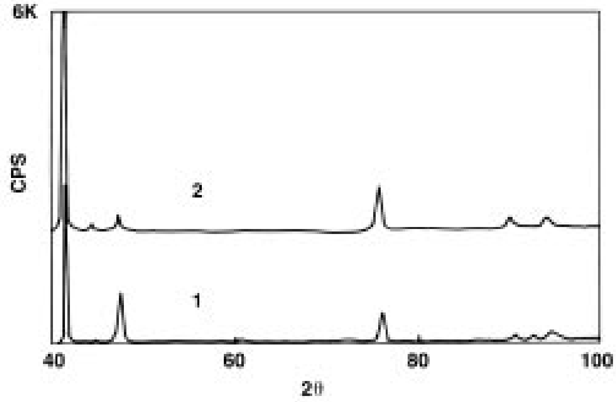

Fig. 3—X-ray diffraction spectra of Co-P-PTFE composite coating: (1) as plated; (2) after heat treatment.

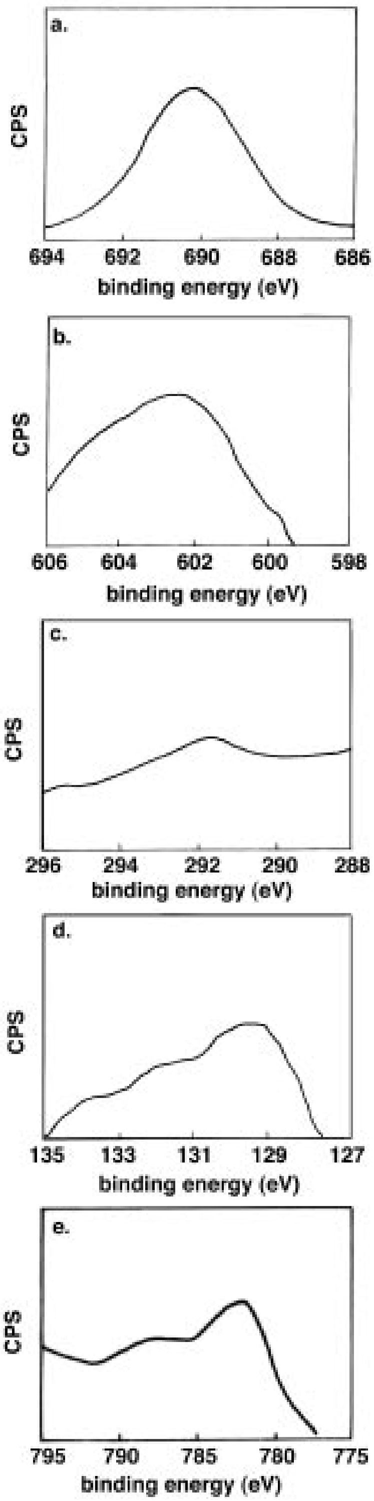

Fig. 4—Detailed ESCA spectra of Co-P-PTFE composite coating: (a) spectrum of fluorine; (b) Auger spectrum of fluorine; (c) spectrum of carbon; (d) spectrum of phosphorus; (e) spectrum of cobalt.

weight and activated in 3.6 percent HCl by weight. Finally, the samples were immersed in the electroless solution and plated for two hr. The composition and conditions of the electroless plating solution containing PTFE are listed in Table 2. The PTFE content of the composite was analyzed by weight method. The composite was treated at 300 °C for one hr. The microhardness of the composite was measured by a microhardness tester using a load of 100 g, with contact time of 15 sec. The structure of the coating was analyzed and determined by X-ray, SEM and XPS. Tribological performance of the composite was measured using a self-constructed tribology tester (Fig. 1) and the instrument of iron spectra. The contact configuration is point on a flat specimen in dry condition and flat on flat in an oiled condition. Loads are 10 N in dry and 312 N in oil. The samples were 10 µm thick composite on 45# steel. The counterpart was a Gr15 steel ball with Φ 5 mm in dry condition and a mild steel ring in oil condition. Relative velocity of the surfaces were 0.1 m/sec. The samples were weighed to the nearest 0.1 mg, before and after each increment to calculate weight loss.

Table 1
Properties of Metals & Their Adhesion Force with Iron[1]

Metal	Cohesion energy kcal/g-atom	Atomic size, Å 10^{-10} m	Adhesion force with iron* (dynes)
Fe	99.4	2.86	>400
Co	101.7	2.50	120
Ni	102.3	2.49	160
Cu	80.8	2.551	130
Ag	68.3	2.883	60
Au	87.6	2.877	50
Pd	134.8	2.796	100
Al	76.9	2.80	250
Pb	47.0	3.494	140

* load, 20 dynes; temp 20 °C; ambient atmosphere

Table 2
Components & Conditions of Composite Solution

Component	Content, g/L	Conditions
$CoCl_2$	20-27	pH 8-9
$(NH_4)_3 \cdot C_6H_5O_7 \cdot 2H_2O$	40	temp 90°C
$NaH_2PO_2 \cdot H_2O$	30	
Glycine	10	
Dispersing agent	0.04-0.20	
PTFE	6	

Results and Discussion

The Co-P-PTFE composite has high hardness and good adhesion with the matrix. Its microhardness is 669 as plated. Although it is lower than that of a Co-P coating, it is higher than that of Ni-P-PTFE composite.[10,11] The microhardness of the composite is 782 after heat treatment. The thickness of the composite is 5-10 µm and consists of 9 percent PTFE, 5.1 percent P and 85.9 percent Co by weight. Figure 2 illustrates the surface morphology of the Co-P-PTFE composite.

The surface of the Co-P-PTFE composite is an even spread of small spherical particles. The spectra of X-ray diffraction of the Co-P-PTFE composite are shown in Fig. 3, with the corresponding data listed in Table 3. The results indicate that the Co-P-PTFE composite has a hexagonal system as plated. Its crystal structure did not change except that the lattice constant increased, evidently after heat treatment. This shows that a solid solution was formed in the composite during heat treatment. The process by which the composite was formed, has a strong tendency to a certain direction and the cobalt (100) face of the hexagonal system parallels the matrix surface. AES analysis shows that the proportion of Co, P and F content is 13.9:3.1:83 on the surface of the composite.

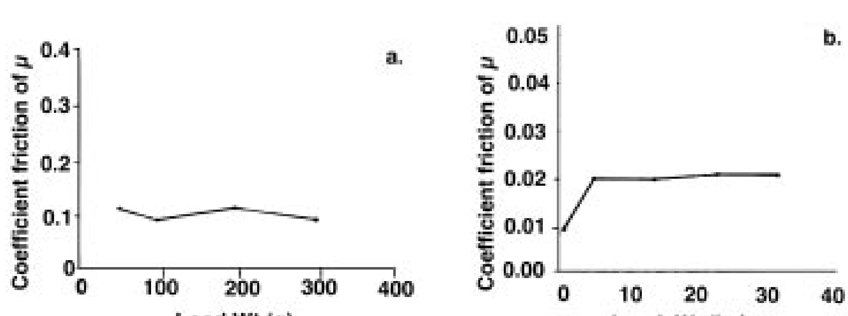

Fig. 5 (right)—Effect of load on coefficient of friction: (a) dry; (b) in oil.

Table 3
X-ray Diffraction Data for Co-P-PTFE Composite

Standard		Composite as plated		Composite after heat treatment	
d	I/I_0	d	I/I_0	d	I/I_0
1.908	100	1.912	33	1.918	6
1.252	80	1.251	19	1.257	15
1.066	80	1.065	6		
2.024	60	2.027	8	2.034	4
1.047	60	1.048	8	1.053	5
2.165	20	2.166	100	2.176	100
1.083	20	1.084	6	1.090	4

Table 4
Tribological Performance of Various Coatings

	Dry Condition Load: 10 N			Oil Condition Load: 312 N		
	45# steel	Co-P	Co-P PTFE	45# steel	Ni-P-PTFE	Co-P-PTFE
Coeff. of Friction μ	0.19	0.18	0.07	0.027	0.039	0.019
Wear Coeff. K (mg/N x 10^{-4})	5.7	2.2	1.2	0.071	0.221	0.089
Counterface area (mm^2 x 10^{-1})	5.0	8.24	2.16			

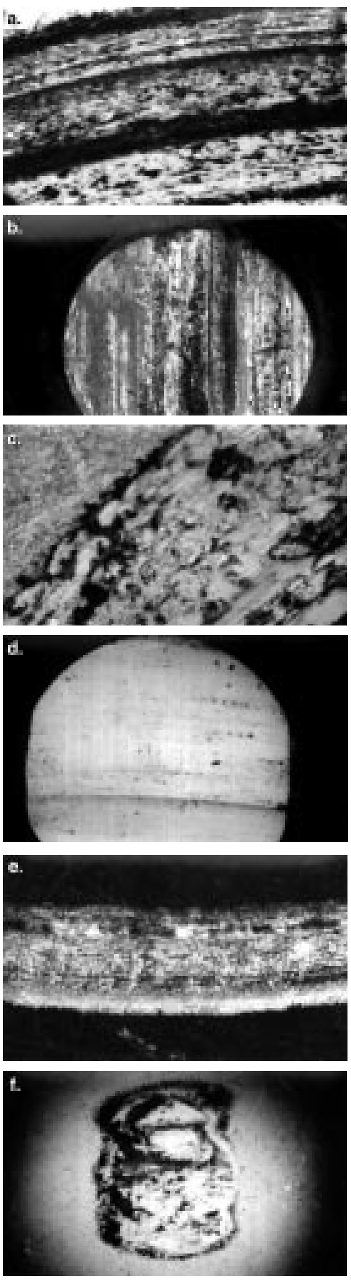

Fig. 6—Surface morphology of wear coatings, 300X: (a) 45# steel; (b) counterface of 45# steel; (c) Co-P coating; (d) counterface of Co-P coating; (e) Co-P-PTFE coating; (f) counterface of Co-P-PTFE coating.

ESCA spectra are shown in Fig. 4. The results reveal further that phosphorus and cobalt exist in forms of simple phosphorus and Co^{+3} on the surface of the composite, whereas fluorine and carbon exist in the form of PTFE. PTFE particles are rich on the surface of the composite.

The results of tribological tests are shown in Table 4 and Figs. 5, 6 and 7. Figure 5 shows that the load had little effect on the coefficient of friction of the composite in dry condition and oil. The coefficient did not change with increasing load under both conditions. Table 4 reveals that the Co-P-PTFE composite has better tribological performance than a Co-P coating or 45# steel in dry condition. Both the coefficient of friction and wear of the former are lower than that of the latter. The composite wear is 45 percent lower than that of the Co-P coating and 79 percent lower than for 45# steel. Figure 6 supports these results as well. In addition, the composite has better tribological performance than a Ni-P-PTFE composite coating or 45# steel in oil conditions. The coefficient of friction of the composite is low and the composite wear is lower by 60 percent than the wear for the Ni-P-PTFE composite coating, but slightly higher than for 45# steel.

Figure 7 shows that debris produced by the Co-P-PTFE composite coating in lubricant oil is smaller and less than that from 45# steel after the composite and 45# steel rub against mild steel. This indicates that the counterpart wear of the Co-P-PTFE composite is lower than that of the 45# steel. The Co-P-PTFE composite, therefore has better tribological properties than 45# steel in oil condition. Because PTFE plays the role of solid lubricant during dry or oil friction and because cobalt has a hexagonal crystal system, the Co-P-PTFE composite coating has excellent tribological properties.

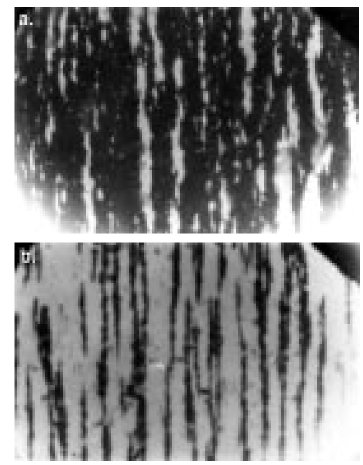

Fig. 7—Debris produced by samples rubbing against mild steel in lubricating oil: (a) 45# steel; (b) Co-P-PTFE composite coating.

Findings

A composite coating of Co-P-PTFE was prepared by electroless plating that had high hardness and a hexagonal crystal system. Its crystal showed no change except that the lattice constant increased, evidently because of heat treatment. The cobalt (100) face of the hexagonal system parallels the matrix surface and a solid solution was formed in the heat-treated composite. The composite has a strong tendency to a certain direction. PTFE is rich on the surface of the composite and phosphorus and cobalt exist in the forms of simple phosphorus and Co^{+3} on the surface of the composite. Tribology tests showed that the Co-P-PTFE composite has good tribological performance. The composite wear is 45 percent lower (by weight loss) than the coating of Co-P, and 79 percent lower than 45# steel in dry conditions and 60 percent lower than the composite in oil.

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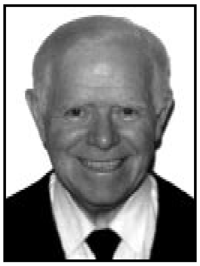

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