

Characterizations of Cr-P-PTFE composite coatings electroplated from trivalent chromium-based bath

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Chromium plating is a common surface treatment technique extensively applied in industry due its excellent properties which include substantial hardness, abrasion resistance, corrosion resistance, surface color, and luster. In this study, the effect of PTFE on corrosion behavior of Cr-P plating, low carbon steel substrates are electroplated in Cr(III) baths without and with PTFE. Trivalent chromium carbon plating was electroplated from trivalent chromium sulfate-based baths with different PTFE dispersion contents. The study focused on the microstructure, PTFE content, roughness, and corrosion resistance of the Cr-P-PTFE composite plating. Scanning electron microscopy and atomic force microscopy images showed a smoother plating and a decrease in the surface roughness of the electrodeposited. The results demonstrate that PTFE eliminates the cracks within plating by reducing internal stress. Therefore, the corrosion resistance of Cr-P-PTFE composite platings were better than that of Cr-P alloy platings.

Key words: PTFE, Composite plating, Morphology, Roughness.

Introduction

Recently, various functionalities have been demanded as a result of high-functionalization and high-speed industrialization. Therefore, surface treatment technologies such as composite plating have attracted attention. [1-3]. However, chromium platings are deposited from hazardous hexavalent chromium baths. In view of the very high toxicity of Cr(VI) compounds, the development of an alternative process for hexavalent chromium plating is urgently needed. Compared with hexavalent chromium platings, the trivalent chromium platings have numerous environmental, health, and technical advantages [4]. A suitable candidate is the trivalent chromium (Cr(III)) electroplating process owing to the low toxicity of the electrolyte. Therefore, trivalent chromium electrodeposition has attracted significant attention in recent years. However, this process has several demerits such as the low deposition rate [5-7]. The most common trivalent chromium plating solutions typically contain a Cr(III) salt such as CrCl₃ or Cr₂(SO₄)₃ [8]. However, it is not easy to obtain deposits from trivalent chromium baths. In order to promote the reduction reaction of Cr ions, a complex agent must be added [9-12]. The carbon existing in

these complex agents in the bath will get incorporated in the plating accompanying the reduced chromium metal. As a result, a Cr-C plating is formed [13]. However, cracks were frequently observed in the Cr-C deposits, resulting in the deterioration of mechanical and electrochemical properties, especially the corrosion resistance of the deposits [14-15]. The formation of cracks could be ascribed to stress relief [16]. Composite platings produced by the co-deposition of particles such as carbides or oxides have been used to improve the corrosion resistance and hardness of the platings. These composite platings are widely used in the mechanical, chemical, and electronic industries because of their corrosion and wear resistance, hardness, lubricity, uniformity of deposition regardless of geometries, solderability and bondability and nonmagnetic properties. The mechanical and tribological properties of these deposits can be further improved by the incorporation of hard particles (SiC, B₄C, Al₂O₃, and diamond) and dry lubricants (PTFE, MoS₂, and graphite), resulting in a plating with self-lubricating and excellent anti-sticking characteristics. PTFE particles readily coagulate and precipitate in the plating solution since PTFE is a water-repellent material. Due to this agglomerate formation, it is difficult to obtain a uniform dispersion of PTFE particles in a plating bath. This will not only reduce the PTFE content in the platings, but also increase the surface roughness as larger PTFE particles are

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incorporated. To achieve optimum properties of composite platings, the PTFE particles must be uniformly distributed throughout the Cr-P matrix. Areas where lower amounts of PTFE are incorporated do not have the same physical and mechanical properties as areas where the PTFE content is uniform and higher. This influences the mechanical and tribological (friction, lubrication, bearing, and hydrodynamic) properties of the plating. The purpose of this study is to elucidate the effect of the Cr-P-PTFE plating rate and PTFE content in the platings. Furthermore, a method for improving the lubrication of the Cr-P-PTFE composite plating is described.

Experimental

Preparation of Cr-P-PTFE composite platings

Mild steel specimens (65 mm × 50 mm × 1 mm) were used for the formation of Ni-P and composite platings containing micro-sized aluminum oxide particles by electroless plating. Specimens were ultrasonically cleaned in acetone, and cathodically cleaned in a 10% sodium hydroxide solution at 155 mA/cm² for 5 min. Then, the specimens were thoroughly rinsed with deionized water and immersed in a 50 vol.% sulfuric acid solution for deoxidization for 30 s. After rinsing with deionized water, the specimens were immersed immediately in the plating solution. Then, the specimens were thoroughly rinsed with deionized water again and immersed in 50 vol.% sulfuric acid solution for deoxidization for 30 s. The PTFE particles suspended in the Cr-P bath diffused to the surface of the specimen under the action of stirring and Coulomb's force. They then absorbed physically and chemically on the surface. The PTFE particles are buried in the growing Cr-P plating to form the Cr-P-PTFE composite plating. Operating parameters and procedure for preparing the Cr-P-PTFE platings are

Table 1. The composition and procedure condition of Cr-P-PTFE composite electrolyte.

Composition	Concentration (mol)	pH	Temp (°C)	Time (min)	Current density (A/dm ²)
Chromium (III) Sulfate	0.3				
Formic Acid	1.8				
Ammonium chloride	0.5				
Ammonium bromide	1.0				
Potassium chloride	1.0	2 ± 0.1	30 ± 1	30	20
Boric Acid	0.6				
Sodium hypophosphite	0.15 ~ 0.5				
Additive	2.0				
Polytetrafluoroethylene (PTFE)	1.0, 3.0, 5.0, 10 mL				

very similar to those for normal Cr plating. The optimal chemical compositions of Cr-P-PTFE composite platings and operating conditions are illustrated in table. 1. A 60% PTFE emulsion from Aldrich with a particle size of ~30 μm and a cationic surfactant were used. Both the PTFE emulsion and the surfactant were diluted with demineralized water and stirred for 1 h before use.

PTFE content in the Cr-P-PTFE composite platings

In this investigation, the PTFE content is therefore determined by measuring the plating thickness h . Assuming that the porosity is negligible in the calculation of the total plating volume, the following two equations are obtained:

$$\rho_{Cr-P} \cdot V_{Cr-P} + \rho_{PTFE} \cdot V_{PTFE} = V \cdot \rho \quad (1)$$

$$V_{Cr-P} + V_{PTFE} = V \quad (2)$$

where ρ_{Cr-P} , ρ_{PTFE} , and ρ are the densities of the Cr-P plating, PTFE, and Cr-P-PTFE composite plating, respectively. V_{Cr-P} , V_{PTFE} , and V are the corresponding volumes of Cr-P, PTFE, and Cr-P-PTFE plating, respectively. ρ_{Cr-P} varies slightly with the phosphorus content in the Cr-P plating. In general, the phosphorus content is approximately 7-9 wt.%, and the corresponding density of the Cr-P plating is approximately 6.3 g/cm³. The density of PTFE is approximately 2.2 g/cm³. By combining Eqs. (1) and (2), the PTFE content V_{PTFE}/V is then determined by:

$$\frac{V_{PTFE}}{V} = \frac{\rho_{Cr-P} - \rho}{\rho_{Cr-P} - \rho_{PTFE}} \quad (3)$$

To determine the plating density ρ , Cr-P-PTFE was coated onto the mild steel substrates with 1 mm thickness. Each specimen was weighted before and after plating. The relationship between h (μm) and the plating density, ρ (g/cm³) is given by the following equation:

$$h = \frac{h_{Fe}}{2} \cdot \left(\frac{w_a - w_b}{w_b} \right) \cdot \left(\frac{\rho_{Fe}}{\rho} \right) \quad (4)$$

By combining Eqs. (3) and (4), the PTFE content V_{PTFE}/V is then determined by:

$$\frac{V_{PTFE}}{V} = \frac{1}{\rho_{Cr-P} - \rho_{PTFE}} \cdot \left(\rho_{Cr-P} - \rho_{Fe} \cdot \frac{h_{Fe}}{2h} \cdot \frac{w_a - w_b}{w_b} \right) \quad (5)$$

Characterization of Cr-P-PTFE composite platings

The Cr-P-PTFE composite plating samples were sectioned in the direction perpendicular to the metal interfaces and then mounted on epoxy resin. The surface and cross-sectional morphologies of the conversion plating layers were observed using a scanning electron microscope (SEM) (Model S-4300 HITACHI, Tokyo, Japan) coupled with energy dispersive X-ray

spectrometry (EDS). The surface 3D morphology and roughness of the Ni-P-Al₂O₃ platings were observed by atomic force microscopy (AFM). The chemical nature of the Cr-P-PTFE composite-coated Fe samples was evaluated by X-ray photoelectron spectroscopy (XPS) (ESCA⁺, Omicron Nanotechnology, Germany). A high-transmission SPHERA small-spot hemispherical analyzer and XM 1000 high-power monochromator were used to achieve the highest resolution. Analysis was performed on a circular area with 3 mm diameter in ultrahigh vacuum environment (10^{-10} mbar). The photoelectrons were excited by Al K α (1486.6 eV) radiation. The survey spectrum was acquired at a pass energy of 50 eV and all possible elements that could present were identified from it. The corrosion resistance of the plating layers was determined using a 10% HCl solution via potentiodynamic polarization and electrochemical impedance techniques. Tests were carried out in a three-electrode cell (where the working electrode was the plating layer) using a Bio-Logic Potentiostat/Galvanostat equipped with the software EC-Lab version 10.2. The potentiodynamic scan was carried out in the range of -250 mV to +250 mV versus the open-circuit potential using a scan rate of 1 mV s⁻¹ at a constant temperature of 25 °C.

Results and Discussion

The effects of the PTFE dispersion on the surfaces of Cr-P-PTFE composite platings are illustrated in Fig. 1. Increases the amount of incorporation in the coating depending on the PTFE content. Whereas, it was confirmed that the amount of incorporation was decreased in 10 mL/L PTFE. As can be seen, the addition of PTFE results in the homogeneous dispersion of particles in the Cr-P matrix is shown in Fig. 2. The SEM micrographs of the surfaces of the as-deposited Cr-C platings produced with different PTFE contents in the Cr-P bath show a ball like structure, which was caused main Cr-P matrix are consist of amorphous.

The cross-sectional microstructure of the Cr-P-PTFE-

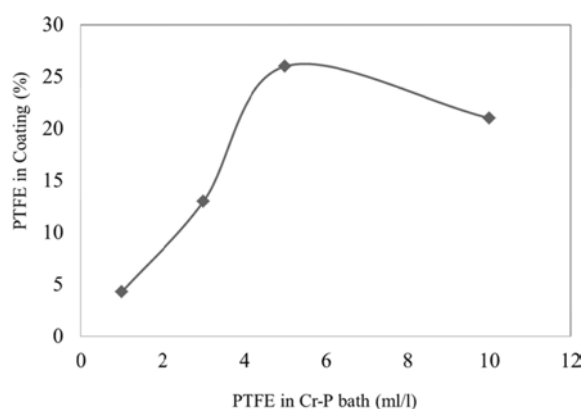


Fig. 1. Effect of PTFE dispersion content on Cr-P-PTFE composite platings.

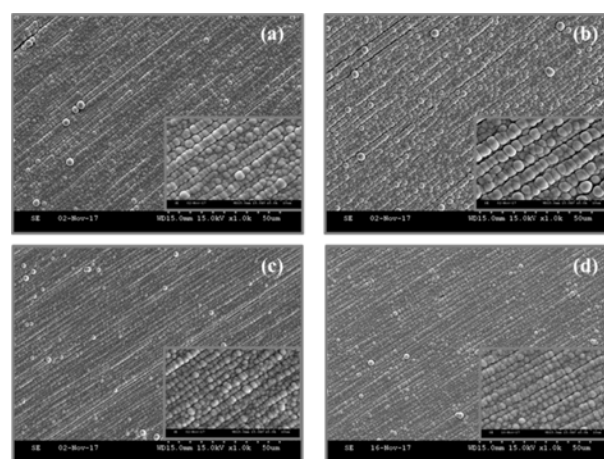


Fig. 2. Morphologies of Cr-P-PTFE composite plating layers with different PTFE concentrations; (a) 1.0 mL/L, (b) 3.0 mL/L, (c) 5.0 mL/L, and 10 mL/L.

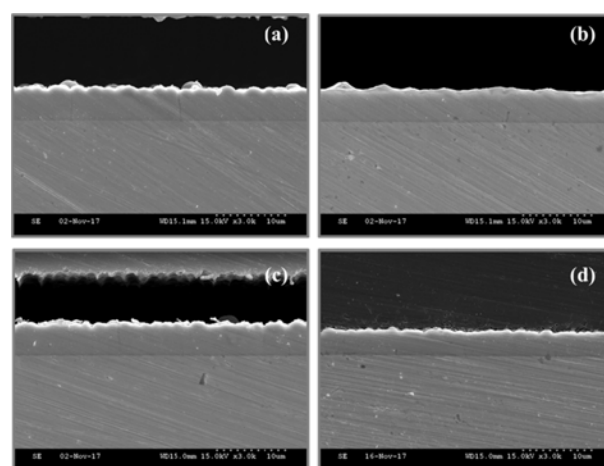


Fig. 3. Cross section of Cr-P-PTFE composite plating layers with different PTFE concentrations; (a) 1.0 mL/L, (b) 3.0 mL/L, (c) 5.0 mL/L, and 10 mL/L.

coated specimens plated with Cr-P baths with different PTFE contents is shown in Fig. 3. The thickness of the platings is almost uniform and cracks were hardly observed within the deposits. As shown in Fig. 3, the volumetric PTFE content in the plating increases with the PTFE concentration in the solution up to a maximum value that is approximately 5 mL/L. For higher PTFE concentrations, a significant reduction is observed. The reason for this is that PTFE particles were found to agglomerate and settle out during the plating process, once the PTFE concentration in the solution exceeded a certain value. This indicates that was not sufficient to disperse the PTFE particles and hence maintain them in suspension.

If too much surfactant is added and the solution becomes super-saturated, then the rest of the surfactant will accumulate near the depositing surface and hence suppress the diffusion of PTFE particles and Cr-P

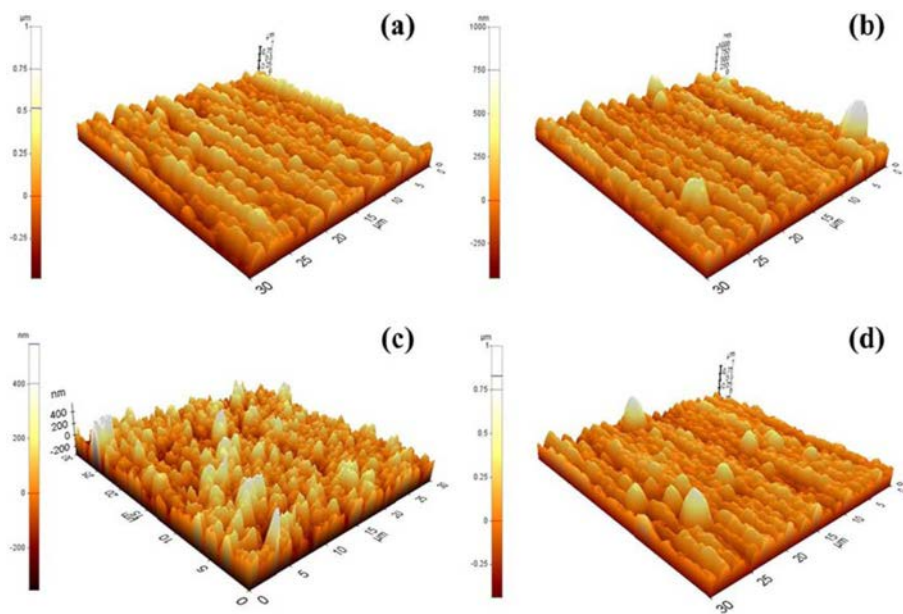


Fig. 4. Typical three-dimensional AFM images of Cr-P-PTFE composite plating layers with different PTFE concentrations; (a) 1.0 mL/L, (b) 3.0 mL/L, (c) 5.0 mL/L, and 10 mL/L.

Table. 2. Roughness parameters including Ra and Rt obtained from AFM images.

Conditions (g/L)	Ra (μm)	Rt (μm)
Non-additive	0.154	0.718
1.0	0.105	0.771
3.0	0.107	1.012
5.0	0.148	1.167
10	0.159	1.334

matrix towards the interface. It is, therefore, critical to determine the optimum ratio between the concentration of PTFE particles and Cr-P bath. AFM micrographs of Cr-P-PTFE composite platings are shown in Fig. 4.

The crystal structure size and surface roughness decrease with increasing PTFE content. The surface roughness was expressed using an average deviation parameter (Ra). This value gives the average height of irregularities in a direction perpendicular to the surface. The surface roughness values including Ra (arithmetic average of absolute values) and Rt (maximum height of the profile) were calculated from 3D AFM images (Table. 2) according to Eqs. (6) and (7).

$$Ra=\frac{1}{n}\sum_{k=1}^n|y_k| \tag{6}$$

$$Rt=R_p-R_v \tag{7}$$

The values of the surface roughness of Cr-P-PTFE (1-10 mL/L) composite platings are found to be 0.116 μm, 0.107 μm, 0.083 μm, and 0.094 μm, respectively. This observation confirms that the surface roughness decreases with increasing amount of the PTFE particles. This is because PTFE particles remain

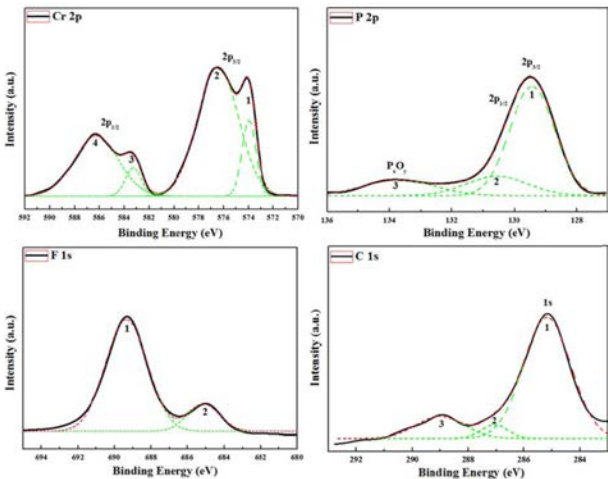


Fig. 5. XPS analysis of Cr-P-PTFE composite plating. High resolution of Cr 2p, P 2p, F 1s and C 1s.

insoluble in the Cr-P matrix.

XPS analysis of the Cr-P-PTFE composite plating shows that the plating contains chromium, phosphorus, fluorine, and carbon, as shown in Fig. 5. The Cr2p band spectrum shows only two chemical states of chromium in the plating. The Cr2p_{3/2} peak can be resolved into two peaks corresponding to 573.9 and 576.4 eV that represent Cr(s) and Cr (III), respectively. The binding energies of Cr2p_{1/2} bond corresponding to 583.2 and 586.2 eV also represent the metallic state Cr(s) and Cr(III) in the plating. No Cr(VI) was detected in the Cr-P platings. This is an indication that the oxidation of Cr(III) to Cr(VI) at the anode is not a significant problem. The binding energies of the P2p_{1/2} and P2p_{3/2} peaks are around 129.4 and 133.6 eV. The peaks at about 689.3 and 285.1 eV correspond to

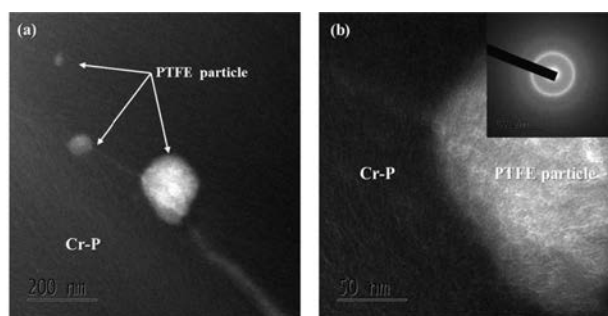


Fig. 6. (a) High-resolution transmission electron micrograph and (b) the Electron diffraction pattern of the Cr-P-PTFE composite plating.

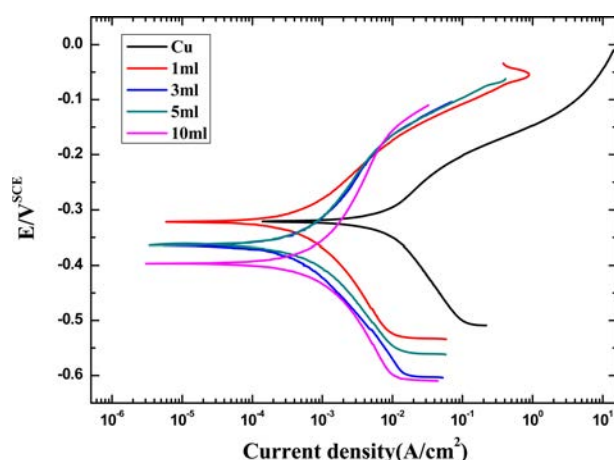


Fig. 7. Potentiodynamic polarization curves of Cr-P composite plating different contents of PTFE.

fluorine and carbon, respectively. The spectrum data were curve-fitted with Gaussian peak decomposition using a computer.

High-resolution transmission electrode microscopy (HR-TEM) was also performed. The HR-TEM micrograph and selected area diffraction pattern (SADP) of deposited Cr-P-PTFE films are shown in Fig. 6. The HR-TEM images show multi/polycrystalline structures, and the PTFE particle was estimated. The electron diffraction pattern showed three relatively sharp rings and a broad ring, indicating a crystalline structure.

Fig. 7 shows potentiodynamic polarization curves for the Fe substrate and Cr-P alloy platings deposited from the trivalent chromium baths with different PTFE contents. The cathode polarization curve is related to the evolution of hydrogen gas (H_2), while the anodic polarization curve is the most important feature associated with corrosion resistance.

In general, Fe substrates have a poor corrosion resistance against chlorine ions and must be protected by applying some platings. In our previous studies, results indicated that the trivalent Cr-C platings have excellent corrosion resistance and can protect substrates from corrosion in conditions such as in a 10% HCl solution [10]. The corrosion potential (E_{corr})

Table 3. Tafel analysis for uncoated and plating after tested in 10% HCl aqueous solution at a scan rate of 1 mVs^{-1}

Specimen	E_{corr} (mV)	β_a (mV/ decade)	β_c (mV/ decade)	i_{corr} (A/cm ²)
Bare metal (Fe)	-0.439	722	284	7.86×10^3
PTFE 1 mL/L	-0.363	175	142	6.59×10^3
PTFE 3 mL/L	-0.364	168	168	6.06×10^3
PTFE 5 mL/L	-0.321	101	148	4.77×10^3
PTFE 10 mL/L	-0.396	359	262	16.50×10^3

and corrosion current density (i_{corr}) of the carbon steel and Cr-P-PTFE composite platings were determined by extrapolating the linear sections of the anodic and cathodic Tafel lines. The corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and Corrosion current density (i_{corr}) of the carbon steel and coated samples obtained from polarization curves are listed in Table 3. The anodic and cathodic Tafel slope (β_a , β_c) decrease from 284 and 722 mV for uncoated carbon steel to 101 and 148 mV for Cr-P-PTFE 5 mL/L, indicating that the addition of PTFE prevents the chloride penetration to the metal surface and subsequently decrease the corrosion rate, see Table 3. Addition of PTFE dispersion content on (1-5 mL/L) decrease the i_{corr} respectively. The combined effect of PTFE significantly enhanced the corrosion resistance of the Cr-P platings in 10 wt.% HCl. This indicates that the mechanism of activity and passivation is similar in essence for all electrodeposits.

Conclusions

Trivalent chromium carbon platings were electroplated from trivalent chromium sulfate-based baths with different PTFE dispersion contents. The results for the Cr-P-PTFE composite platings showed the following:

1. The effect of PTFE on corrosion behavior of Cr-P composite plating, low carbon steel substrates are electroplated in Cr(III) baths without and with PTFE.
2. The introduction of PTFE eliminates the cracks within Cr plating, as a result of the reduction of internal stress.
3. Therefore, the corrosion resistance of Cr-P-PTFE composite plating is better than that of Cr-P plating.

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