

Characterization of Cr-P-C/MoS₂ composite plating electro-deposited from trivalent chromium

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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 MoS₂ particles of the composite coating was investigated. To improve the lubrication of mold, Cr-P-C/MoS₂ composite plating was studied by varying the MoS₂ content. The current efficiency of the composite plating incorporated MoS₂ particles was increased at MoS₂ contents of 0.5 and 1.0 g/l due to the incorporation of fine particles. On the other hand, when the content of MoS₂ is 1.0 g/l or more, the current efficiency is lowered due to an increase in impact on the cathode surface. In order to evaluate the mechanical properties of Scratch test were conducted. Scratch test confirmed the lubricity and abrasion resistance characteristics revealed that the composite plating with added MoS₂ had relatively low surface roughness and uniform surface modification to improve its properties.

Key words: Cr-P-C/MoS₂, Composite plating, Electro-deposition, Abrasion resistance, Trivalent chromium.

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].

In particular, surface treatments for bearings, molds, tools, and other structural components are affected by corrosion resistance due to more periodic stresses, abrasion, friction, and lubrication than internal materials. Economic surface treatment is one of the most important elemental technologies and it contributes to reduce the damage caused by friction and abrasion and to improve durability and abrasion resistance [4].

At present, molds, tool steels, and other common platters are not chrome-colored, and chromium plating with a thickness of about 10 to 50 μm is resistant to abrasion and corrosion and is used for the purpose of imparting abrasion resistance to parts such as automobile parts, discrete parts, and shafts.

However, the main components of the chromium plating are those that are adversely affected by environmental hazards and workers' health due to mist and waste water generated during plating prior to the hexavalent chromium, and the harmful substances are designated and regulated globally Is a fact [5].

Recently, various studies have been carried out to improve the hardness, abrasion resistance and lubrication property of composite plating, which has recently attracted attention, and attention has been focused particularly recently molybdenum disulfide (MoS₂) have been developed for the application of materials for space, because they are characterized by abrasion resistance and lubricity in extreme environments such as high temperature, Has characteristics of affinity as a material used as a solid lubricant, distribution within a tissue, lubricity, and a friction coefficient. The friction coefficient and the frictional resistance of the object surface applied to various components such as bearings of bearings and load-sensitive components during rotation [6].

At present MoS₂ has been studied in terms of self-lubricating properties by adding MoS₂ solid lubricant in combination with plasma and sputtering deposition. However, there is little research on chromium composite plating for improving lubricity and abrasion resistance [7].

Therefore, in this study, the surface shape, quantitative analysis, and mechanical properties of the electrodeposited coating for the Cr-P-C/MoS₂ composite metal with MoS₂ particles, which is a solid lubricant, were analyzed for the lubricity and abrasion resistance.

Experimental

Cr-P-C/MoS₂ composite plating were electrodeposited onto 50 × 50 × 0.4 mm copper substrates by direct current plating. Prior to electrodeposition the copper

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substrates were mechanically polished down to 2000-grit SiC carbide paper, degreased sequentially with ethanol and distilled water, pickled in a 5 wt% hydrochloric acid aqueous solution for 3 min, then rinsed with distilled water. The electrolytes were electrodeposited from chromium sulfate based electrolytes. The Cr-P-C electrolyte consisted of $\text{Cr}_2(\text{SO}_4)_3$ as a source of Cr(III) ions, $\text{NaH}_2\text{PO}_2 \cdot 6\text{H}_2\text{O}$ as a source of phosphorus, H_3BO_3 as a buffer agent, and NH_4Cl as an electrolyte support. Cr-P-C/ MoS_2 composite electrolyte were electrodeposited from a Cr-P-C electrolyte dispersed in the range of 0.5, 1.0, 1.5 and 2.0 g/l of MoS_2 particle with an average diameter of 200 nm. Preparation of Cr-P-C/ MoS_2 composite electrolyte was agitated with the magnetic stirrer for 24 hrs and ultrasonic treatment for 60 min was used to prevent their sedimentation. All of the solutions were prepared using analytical grade chemicals and distilled water. The molybdenum (IV) sulfide powders were provided by Sigma-Aldrich (Korea) Chemical Co. Ltd.

Platinum was used as the anode for the electrolytes. The anode to cathode area ratios was approximately 2:1. The electrodeposition was carried out for 30 min with a stirring rate of 350 rpm at a temperature of 35 ± 2 °C. The composition of the electrolytes and the electrodeposition conditions are illustrated in Table 1.

The surface and cross-sectional morphologies of the electrodepositions were observed using field emission scanning electron microscopy (FE-SEM, Hitachi, S-4200,) and energy-dispersive X-ray spectroscopy (EDS). From this, the surface morphology was estimated.

The surface roughness was measured using an atomic force microscope (AFM, Park System, XE-150) in contact mode. The crystalline structure and constituent phase of the composite platings were measured using high-resolution X-ray diffraction (XRD, X'Pert-RRO

MRD, Phillips) with Cu $K\alpha$ radiation in a 2θ angle with scanning ranges from 20 to 80 °. To investigate the crystalline structure of the Cr-P-C/ MoS_2 composite layer, the bright field images and selected area diffraction pattern were analyzed using a high resolution transmission electron microscope (HR-TEM, JEM-2100F, JEOL) for the detection and identification of MoS_2 particles. The hardness values of composite platings were measured using nano-indentation (PICODENTOR HM500, Helmut Fischer); the mean values and standard deviations were quoted.

The surface roughness was examined using a 3D measuring laser microscope (OLS5000, Olympus). The electrochemical tests were carried out in 5.0 wt.% NaCl solution using a potentiostat (Bio-Logic SAS, model SP-150) to investigate the corrosion properties. Three electrode systems were applied: the working electrode exposed a surface area of approximately 1 cm^2 ; a saturated calomel electrode (SEC) (sat'd KCl) and a carbon rod were used as reference and auxiliary electrodes, respectively. Potentiodynamic polarization measurements were conducted after 5 min of immersion in a 5.0 wt.% NaCl solution at room temperature. To ensure the accuracy of the results, the measurements were repeated three times for each specimen. From the polarization curves, the corrosion behavior of the electrodeposited platings was compared and discussed.

Results and Discussion

The current efficiency of Cr-P-C/ MoS_2 composite plating was investigated in order to establish the optimum conditions for the MoS_2 contents. Fig. 1 shows the current efficiency at the electrodeposition of Cr-P-C/ MoS_2 composite platings. It is observed that the current efficiency increased from 0.5 and 1.0 g/l to 22 ~ 24%. On the other hand, The current efficiency decreased by about 6% when the content was above 1.5 g/l. The MoS_2 cohesion is formed in order to lower the surface energy during electrodeposition. In composite plating, the cohesion scale changes continuously during electrodeposition due to repeated particle collisions, dispersion, and aggregation [8].

In addition, particle cohesion is one of the factors that change the current efficiency and incorporation amount. As the cohesion scale increases due to the collision as the particle content increases, the particle incorporation decreases during plating time. Therefore, the current efficiency of the composite plating according to the MoS_2 content tended to increase with the MoS_2 content of 0.5 and 1.0 g/l. In case of above with the MoS_2 content of 1.0 g/l, the current efficiency tended to decrease due to the increase in collision effect on the cathode surface [9, 10].

As shown in Fig. 2, the surface morphology of Cr-P-C/ MoS_2 composite plating according to the MoS_2 contents. It was confirmed that Cr-P-C/ MoS_2 composite

Table 1. The composition and procedure condition of Cr-P-C/ MoS_2 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				
Molybdenum (IV) sulfide	0.5, 1.0, 1.5, 2.0 g/l				

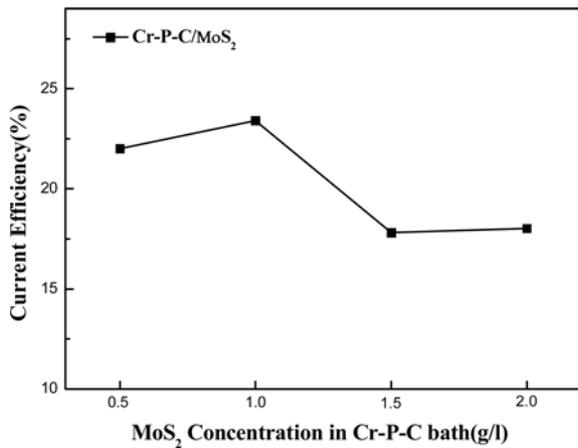


Fig. 1. Current efficiency of Cr-P-C/MoS₂ composite plating with different MoS₂ concentrations.

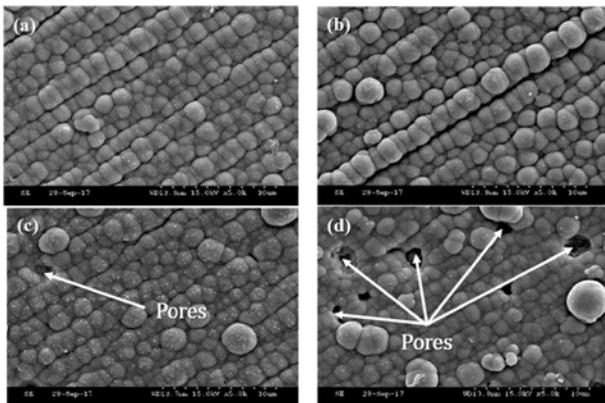


Fig. 2. Surface morphology images of Cr-P-C/MoS₂ composite plating with different MoS₂ concentrations; (a) 0.5 g/l, (b) 1.0 g/l, (c) 1.5 g/l, and (d) 2.0 g/l.

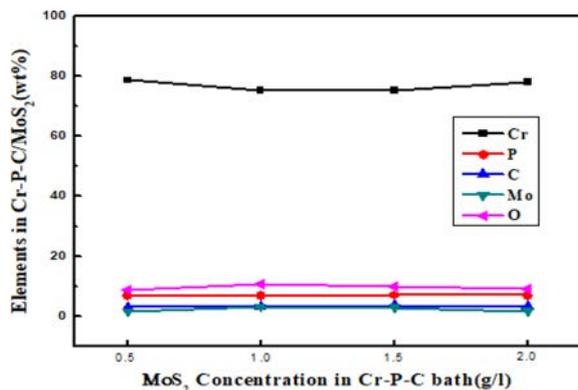


Fig. 3. EDS analysis of Cr-P-C/MoS₂ composite plating with different MoS₂ concentrations.

plating was finely dispersed with MoS₂ particles. Also, there was a difference in surface uniformity in the content of MoS₂. In the case of 0.5 and 1.0 g / l, the size of the nodular structure was constant and uniformly formed. On the other hand, the nodular structure was irregular and pore formed in the MoS₂ of 1.5, 2.0 g/l and showed a large nodular structure was irregular and pore formed.

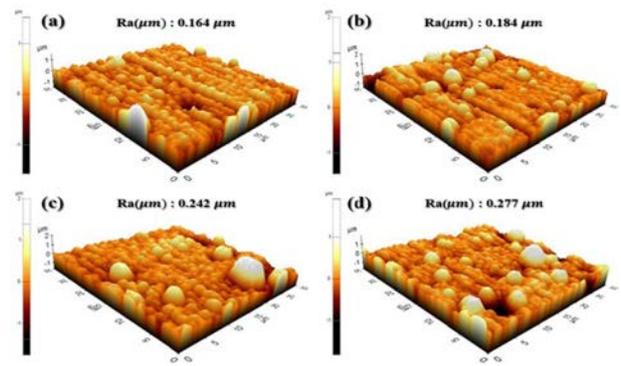


Fig. 4. Typical three-dimensional AFM image of Cr-P-C/MoS₂ composite plating layers with different MoS₂ concentrations; (a) 0.5 g/l, (b) 1.0 g/l, (c) 1.5 g/l, and (d) 2.0 g/l.

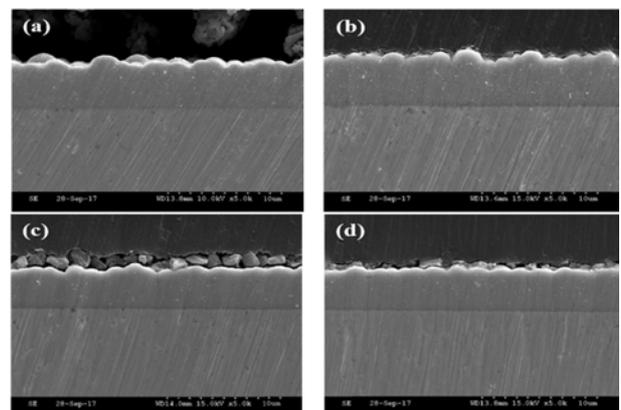


Fig. 5. Cross-section morphology images of Cr-P-C/MoS₂ composite plating layers with different MoS₂ concentrations; (a) 0.5 g/l, (b) 1.0 g/l, (c) 1.5 g/l, and (d) 2.0 g/l.

Based on the above results, it is suggest that MoS₂ particles adsorbed around the surface cathode and increasing according to amount of MoS₂ particles which are separated and formed into pores by increasing the collision between the particles. Fig. 3 presents the EDS analyses of the electrodeposited Cr-P-C/MoS₂ composite plating. Chromium, phosphorus, oxygen, carbon, and molybdenum elements are detected on the surface composite plating. It is indicate that these changes in the amount of incorporation can be explained by Guglielmi's three-step absorption model an increase in the electric field strength and coulomb force to an increase in the incorporation rate of the MoS₂ particles [7, 11].

Fig. 4 shows that the surface roughness of Cr-P-C/MoS₂ composite plating with different MoS₂ concentrations. It was found that the Ra values were 0.164, 0.184 0.242 and 0.277 μm, respectively. The lowest Ra values were obtained when 0.5 and 1.0 g/l. This result may be ascribed to incorporated MoS₂ particles. The nodular size decreases and the surface roughness decreases. It is also believed that the surface roughness is increased due to the generation of pores due to particle separation and the uniformity due to cohesion on the surface of

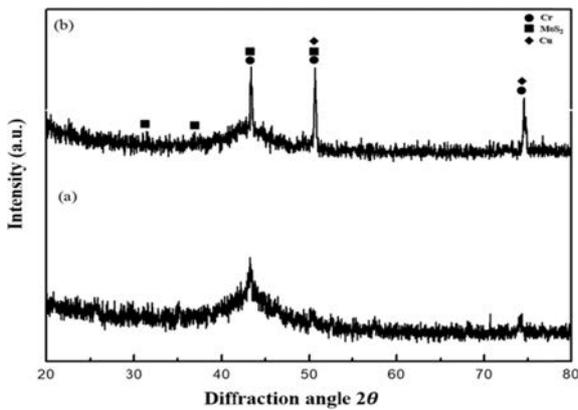


Fig. 6. XRD analysis of Cr-P-C alloy plating and Cr-P-C/MoS₂ composite plating.

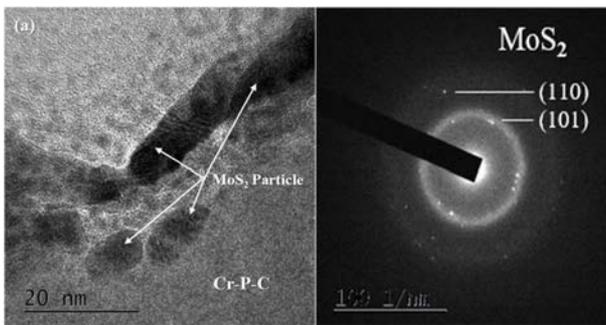


Fig. 7. HR-TEM images and selected area diffraction pattern for the Cr-P-C/MoS₂ composite plating layer; (a) HR-TEM image, and (b) SADP pattern.

the cathode [12].

Fig. 5 shows that the cross-section of Cr-P-C/MoS₂ composite plating layers according to the content of MoS₂ particles. When the content of MoS₂ was 0.5, 1.0, 1.5 and 2.0 g/l electrodeposited thickness of 4.60, 4.90, 4.02, and 4.04 μm, respectively. It was confirmed that the highest electrodeposited thickness was formed at 1.0 g/l. In the EDS analysis, the molybdenum content was the highest at 1.0 g/l of MoS₂.

Fig. 6 shows the XRD analysis of Cr-P-C/MoS₂

composite plating analyzed with a specimen of 1 g/l of MoS₂ and compared with the Cr-P-C alloy plating. It can be observed that The Cr-P-C alloy plating has an amorphous structure with broadened Cr peaks at 43.5°. In case of Cr-P-C/MoS₂ composite plating, MoS₂ peaks observed at 32.9° and 52.1°, confirming that MoS₂ was dispersed in the electrodeposited layer.

The TEM analysis of Cr-P-C/MoS₂ composite plating are shown in Fig. 7. It can be observed that the chromium carbide was composed of an amorphous structure, which has plate type MoS₂ incorporated and a typical amorphous halo pattern and dot pattern. The results indicated that Cr-P-C/MoS₂ composite plating mixed in the amorphous chromium carbide and incorporated in (101) and (110) diffraction patterns in the form of MoS₂ particles

The scratch test of Cr³⁺, Cr-P-C alloy and Cr-P-C/MoS₂ composite plating are shown in Fig. 8. For each specimen, the critical load at which the composite coating layer was peeled was measured by applying a vertical load of 10 mN. LC1, LC2, and LC3 represent the points at which the composite plating layer begins to be deformed. LC1 is the buckling crack begins to be deformed by pressure, LC2 is the delamination of the plating layer, and LC3 is the delamination of the plating layer

The lubrication characteristics were confirmed to be excellent in lubrication characteristics of Cr-P-C/MoS₂ composite metal > trivalent chromium > Cr-P-C alloy casting. The Cr-P-C/MoS₂ composite plating were found to crack from 1.1 mm completely peeled off at 2.4 mm, which confirmed the best lubricity, adhesion, and abrasion resistance.

Based on the above results, it is suggested that the MoS₂ effect in the Cr-P-C/MoS₂ composite plating improves the lubricity, adhesion and abrasion resistance. [13, 14]. Therefore, scratch test showed that the mechanical properties of Cr-P-C/MoS₂ composite coating were improved by MoS₂ addition.

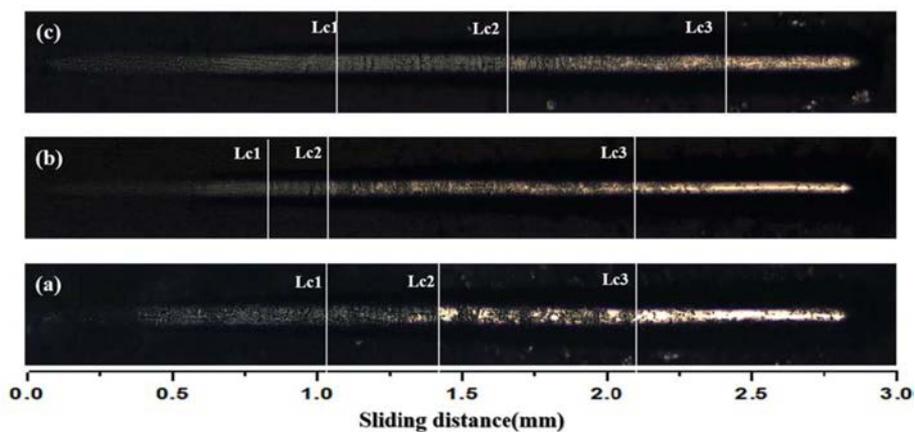


Fig. 8. Optical micrographs of the scratch track showing the failure characteristics; (a) Cr³⁺, (b) Cr-P-C alloy and (c) Cr-P-C/MoS₂ composite plating layer.

Conclusions

In this study, we aimed to improve the lubricity and abrasion resistance of Cr-P-C alloy plating by adding MoS₂ particles, since molybdenum disulfide (MoS₂) has low reactivity with chromium plating solution. The physical properties were investigated and the following characteristics were confirmed:

1. Cr-P-C/MoS₂ composite plating: electrodeposition of MoS₂ increases the current efficiency. However, when the current density exceeds a certain level, collision as the particles content increases, the particle incorporation decreases during plating time

2. The crystal structure of Cr-P-C/MoS₂ composite is a mixed diffraction pattern of the amorphous and crystalline phases MoS₂; it appears as a halo pattern of amorphous chromium carbide and a dot pattern of MoS₂. The diffraction pattern of the MoS₂ particles were confirmed

3. Scratch test showed that the mechanical properties of Cr-P-C / MoS₂ composite coating were improved by MoS₂ addition.

Acknowledgments

This work was supported by the Inha University Research Grant.

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