Int. J. Electrochem. Sci., 14 **(2019)** 3281 – 3290, doi: 10.20964/2019.04.52

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Effect of Pretreatment Process on the Adhesion and Corrosion Resistance of Chromium-Carbon Coatings Deposited on Copper Substrates

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Received: 11 December 2018 / *Accepted:* 20 February 2019 / *Published:* 10 March 2019

In this work, the copper substrates are pretreated by chemical polishing and mechanical polishing to change their surface roughness. Then, the effects of the substrate surface roughness on adhesion and corrosion resistance of chromium-carbon coatings electrodeposited onto copper substrates are investigated. The surface roughness of chromium-carbon coatings are analyzed by a surface roughness measuring system. An ELCOMETER-106 adhesion tester is utilized to measure the adhesion strength of chromium-carbon thin films electrodeposited on copper substrates. The highest adhesion strength of 8.1 MPa is obtained for chromium-carbon thin film electrodeposited on mechanically polished copper substrate. The electrochemical behavior tested by potentiodynamic for two scans in 3.5 wt.% NaCl solution shows that the chromium-carbon thin film electrodeposited on mechanically polished copper substrate exhibits better corrosion resistance than that of chromium-carbon coating electrodeposited on unpolished and chemically polished substrates. The chromium-carbon thin film electrodeposited on mechanically polished copper substrate with the least roughness has the relatively highest corrosion resistance and adhesion force and this can be attributed to the chromium-carbon thin film has a crack-free structure when the copper substrate is polished mechanically.

Keywords: chromium-carbon thin films, adhesion strength, mechanical polishing, chemical polishing

1. INTRODUCTION

Recently, trivalent chromium-carbon coatings have been developed and applied as the anti-corrosion and anti-wear materials due to its excellent corrosion resistance, high hardness, good hydrophobicity and lower toxicity than hexavalent chromium [1-10]. Trivalent chromium-carbon coating shows its high potentiality to substitute the conventional coatings, such as the hexavalent hard chrome coatings. Chromium-carbon coatings can be prepared by different methods including chemical vapor deposition (CVD) techniques [11], arc evaporation [12], physical vapor deposition (PVD) methods [13] and pulsed laser deposition [14], all of the above-mentioned methods have similar drawbacks such as unable to deposit the thin films on the complex surfaces, surface treatment for large size workpiece and high cost. The electrodeposition technique is a quite suitable way to solve the above problems.

Generally, the trivalent chromium-carbon coatings were electrodeposited from an electrolyte based on trivalent chromium such as chromium sulfate and chromium chloride [15-20]. Our previous study had indicated that the trivalent chromium-carbon coatings electrodeposited from a chromium sulfate bath can obtain a thicker coatings (approximately at 20 μm) with a loosen microstructure. In addition, the coatings were peeled off easily from metal substrates. On the contrary, a thinner (only approximately at 5 μm) and denser microstructure was observed for chromium-carbon coatings which were electrodeposited from a chromium chloride bath. The good adhesion between chromium-carbon coating and substrate results in the corrosion resistance of coatings electrodeposited from chromium chloride bath is better than that of electrodeposited from chromium sulfate bath [21]. In order to promote the reduction reaction of Cr ions, a complex agent such as formic acid must be added into the bath. The carbon existing in the complex agent in the bath will get incorporated in the coating accompanying the reduced chromium metal. Our previous study [22] showed that the content of carbon in the coating affected the hardness of chromium-carbon coatings.

Although the anti-corrosion and anti-wear behaviors of trivalent chromium-carbon coatings are mainly governed by their mechanical properties, the adhesion between the trivalent chromium-carbon coating and substrate is also a very important factor on the anti-corrosion and anti-wear behavior of coatings. It is known that proper treatment of the substrate surface before plating is important for good adhesion [23-24]. The effect of substrate surface roughness on the adhesion between electroplated coating and substrate was investigated [25-26]. However, their results are controversial. Hayakawa et al. [25] deposited hydroxyapatite (HA) onto un-etched and etched Ti substrates by electrodeposition and reported that the Ti metal etched by sulfuric acid before plating can improve adhesive force, which can be attributed to the enhancement of anchoring effect due to the surface roughness. On the other hand, Zhao et al. [26] studied the effects of the surface roughness on properties of the electroplated nickel coating on the 45# steel and found that the sample with moderate surface roughness ($Ra \approx 0.1 um$) had the relatively higher adhesion force than the samples with higher and lower surface roughness. Prior to the electroplating of chromium-carbon coatings, the substrates were only simply treated by an ultrasonic cleaning process, activation by NaOH solution and soaking into a hydrochloric acid solution [16, 27-30]. Therefore, in this study the surface roughness of copper substrates was modified by chemical and mechanical polishing treatments and the effect of substrate surface roughness on the adhesion and corrosion behaviors of trivalent chromium-carbon coatings was investigated.

2. EXPERIMENTAL

The chromium-carbon thin films were electroplated on copper substrates with a dimension of 50 × 50 × 2 mm. The copper substrates were cleaned by ultrasonic in ethanol for 10 minutes, rinsed with distilled water, activated in 3 wt.% NaOH solution for 1 min and soaked into a 15 wt.% hydrochloric acid solution for 0.5 min before electroplating process. The chemical polishing and mechanical polishing were utilized to pretreat the surface of copper substrates. The chemical polishing process of copper substrates were carried out in a chemical polishing solution containing H_2O_2 (450 ml/L), H_2SO_4 (110 ml/L), the additive (1.5 ml/L), and remainder DI water. The copper substrates were immersed into chemical polishing solution for 5 mins. For mechanical polishing, the copper substrates were grinded with #1000 silicon sandpaper and polished with a cloth buffing wheel for 3 mins.

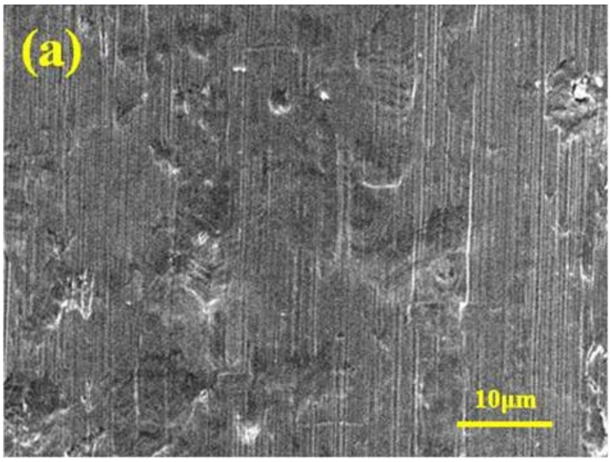
The chromium-carbon deposits were electroplated in a bath containing 0.3 M $CrCl_3 \cdot 6H_2O$ as the main metal salt, 1 M ammonium formate as complexing agent, 0.03 M KBr, 0.5 M KCl and 0.5 M $B(OH)_3$. The optimal condition for preparing chromium-carbon deposit was electroplated at 10 ASD for 15 mins [22,31].

The measurement of potentiodynamic polarization were analyzed from a standard three-electrode cell system using an Autolab-PGSTAT30 potentiostat/galvanostat controlled by a GPES (General Purpose Electrochemical system) software and stabilized at open circuit potential (OCP) before electrochemical test. The potentiodynamic polarization curves of chromium-carbon coatings were measured after 20 min immersion of specimens in a 3.5 wt.% NaCl aqueous solution at room temperature in the potential range between −0.4 V and 0.6 V with a scanning rate of 0.45 mV s^{-1}. Before the measurement, the samples were degreased and rinsed with DI water.

The surface morphologies and cross-sectional images were measured with a scanning electron microscopy (SEM, HITACHI S-3000 N, operating at 15 kV). The surface roughness of chromium-carbon coatings were analyzed by a surface roughness measuring system (Mitutoyo, SV-3200, Japan). The adhesion strength of chromium-carbon thin films electrodeposited on copper substrates was measured by using an ELCOMETER-106 adhesion tester [31].

Apply evenly a small amount of metal glue between the sample and the terminal of adhesion tester, dried at 110 ° C for 30 mins, then carried out an adhesion test process and the ELCOMETER-106 adhesion tester will show the adhesion strength value of thin films [31].

3. RESULTS AND DISCUSSION



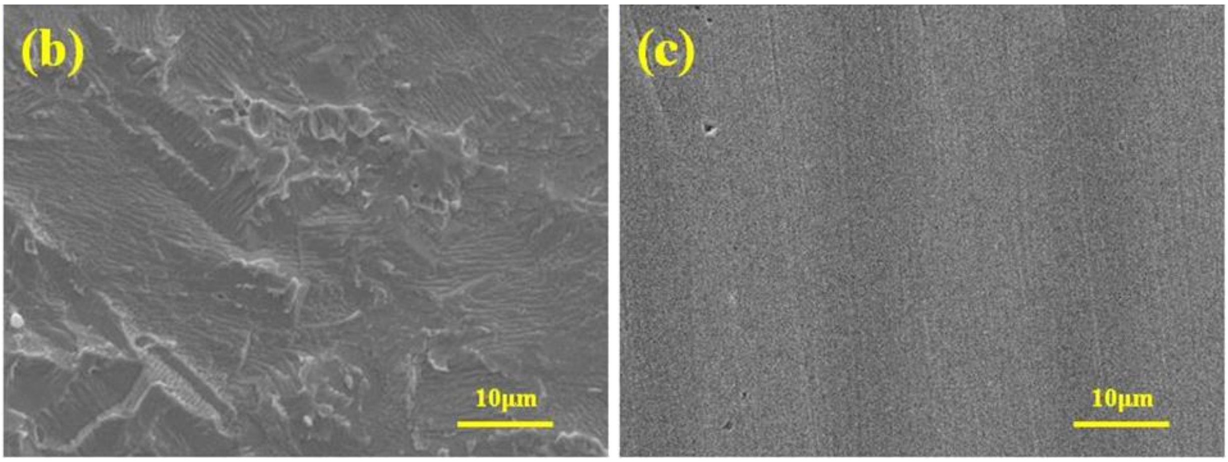


Figure 1. The SEM morphologies of copper substrates treated with different methods: (a) unpolished, (b) after chemical polishing and (c) after mechanical polishing.

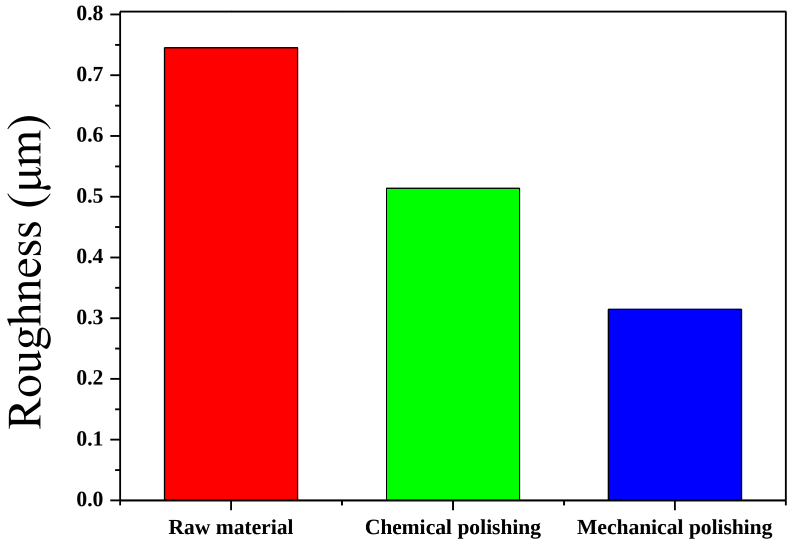


Figure 2. The surface roughness of unpolished, chemically polished and mechanically polished copper substrates.

Fig. 1 shows the surface morphology of unpolished, chemically polished and mechanically polished copper substrates, respectively. The unpolished substrate still retains its cutting trace on the surface (Fig. 1a). After chemical polishing, a rough surface can be clearly seen in Fig. 1b despite of the cutting trace on the copper surface disappears. In contrast, the substrate becomes smooth after mechanical polishing (Fig. 1c). The average roughness of the unpolished and polished substrates is shown in Fig. 2. The roughness of pristine, chemically polished and mechanically polished copper substrates is 0.75 µm, 0.52 µm, and 0.32 µm, respectively. The result indicates that the smallest average roughness value was observed for mechanically polished copper substrate, which is consistent with the SEM finding as shown in Fig. 1.

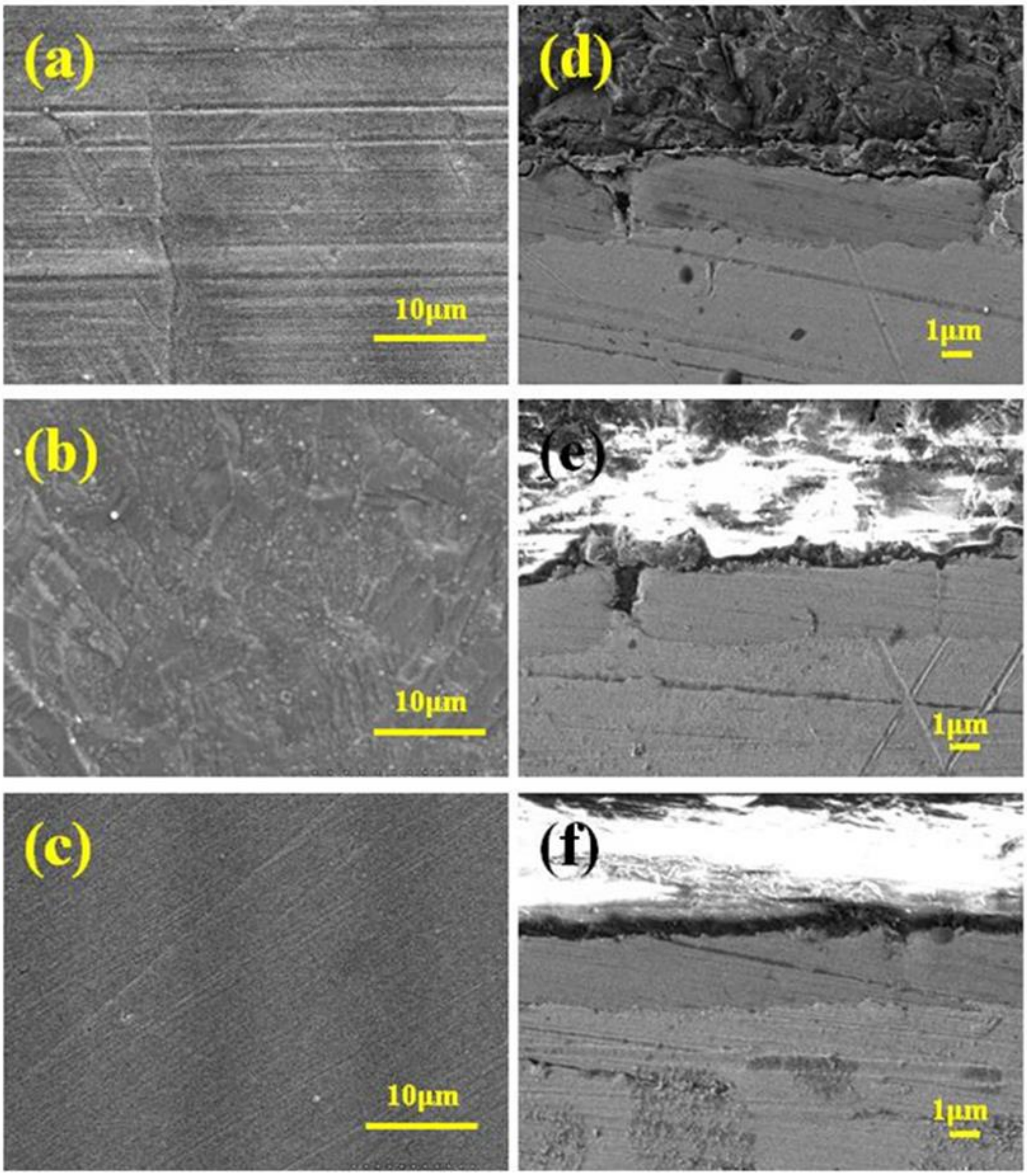


Figure 3. SEM morphologies and cross-sectional images of chromium-carbon coatings electrodeposited on copper substrates treated with different methods: (a)(d) unpolished, (b)(e) after chemical polishing, (c)(f) after mechanical polishing.

Fig. 3 presents the surface morphology and cross-sectional images of chromium-carbon thin films electrodeposited on the copper substrates treated with different processes. The thicknesses of the three chromium-carbon coatings are all about 3 µm. Fig. 3(a) shows the surface morphology of chromium-carbon thin films deposited on unpolished substrate, cutting marks still can be clearly observed on the deposited thin films. The cross-sectional SEM image (Fig. 3(d)) shows the severe cracks penetrate through chromium-carbon thin films to the copper substrate. Fig. 3(b) shows the surface morphology of chromium-carbon films deposited on the chemically polished substrate. It shows from Fig. 3(b) that many uneven regions caused by chemically corroded appear on the sample surface. This uneven structure distributed throughout the substrate likes a sharp mountain peak. This sharp mountain peak structure will induce the formation of cracks (or a discontinuous structure) during electroplating process (see Fig. 3(e)). Fig. 3(c) shows the chromium-carbon film deposited on the mechanically polished copper substrate. By comparing Fig. 3(a), Fig. 3(b) and Fig. 3(c), the result suggests that a relative smoother coating was achieved when the electrodeposition is carried out on the Cu substrate with least surface roughness than the substrates with more roughness. The SEM cross-sectional image presents that a crack-free chromium-carbon thin film is uniformly deposited on the mechanically polished copper substrate (see Fig. 3(f)).

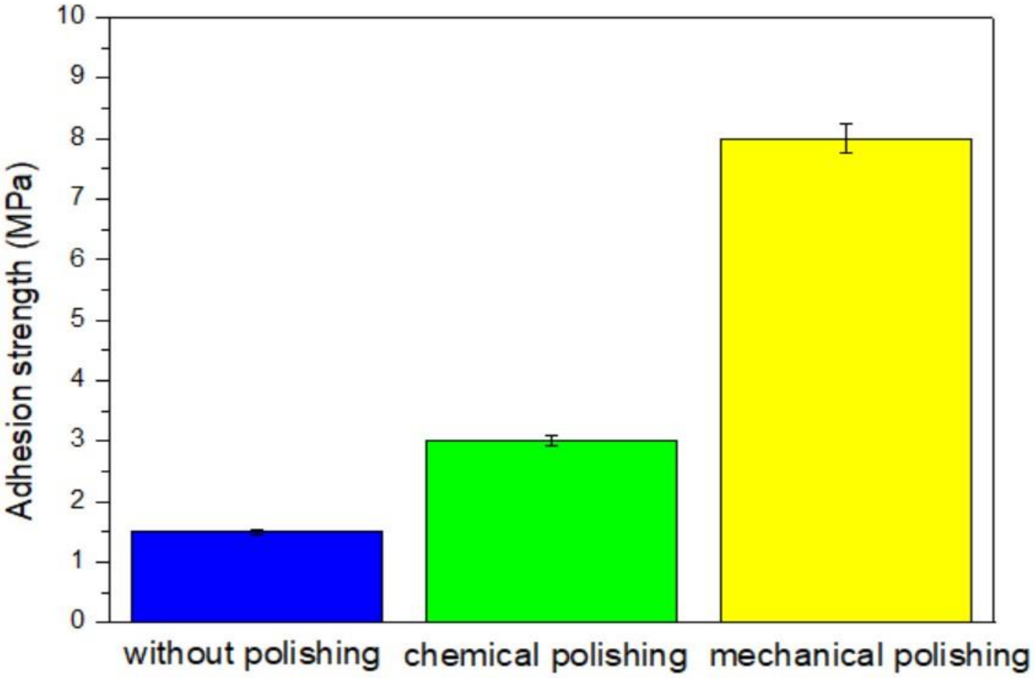


Figure 4. The adhesion strength of chromium-carbon thin films electrodeposited on unpolished, chemically polished and mechanically polished copper substrates.

Fig. 4 shows the adhesion strength of chromium-carbon thin films electrodeposited on unpolished, chemically polished and mechanically polished copper substrates. The adhesion strength of chromium-carbon thin film deposited on the unpolished substrate is about 1.5 MPa. The adhesion strength of chromium-carbon thin films deposited on the chemically polished and mechanically polished substrates is about 3.2 and 8.1 MPa, respectively. Significant influence of surface roughness was observed on the adhesion strength. Our results suggest that the film prepared on the rougher surface exhibits poorer adhesion, which may be attributed to the formation of many cracks within the chromium-carbon thin films due to the higher surface roughness of copper substrates (see the SEM cross-sectional images at Fig. 3(d) and Fig. 3(e)). On the contrary, a smooth substrate surface leads to a crack-free structure within the chromium-carbon thin films. The interface between chromium-carbon thin film and copper substrates has a close contact without any cracks (Fig. 3(f)). Huang et al. [27] indicated that the Cr-C coatings deposited on steel substrates will formed many cracks in the Cr-C coatings and has bed adhesion on steel substrate, they used a "Ni undercoat" method to improve the adhesion and the corrosion resistance of samples, but did not get good results. How to improve the adhesion between Cr-C coatings and substrates become an important topic. In previous studies [32-34], the surface treatment of substrates only used a conventional grinding by fine-grite size SiC sandpaper, the effect of different pretreatment process on the adhesion between Cr-C coatings and substrates are seldom studied. In this study, the experimental results show that the mechanically polished substrate with the least roughness exhibits the maximum substrate/coating bonding force.

The potentiodynamic polarization curves of chromium-carbon coatings electrodeposited on unpolished, chemically polished and mechanically polished copper substrates for the first scan in 3.5 wt.% NaCl aqueous solution at room temperature are shown in Fig. 5. Corrosion current densities (i_{corr}) and corrosion potentials (E_{corr}) were evaluated from the intersection of the linear anodic and cathodic branches of the polarization curves, and are listed in Table 1. The corrosion currents (i_{corr}) for the chromium-carbon coatings electrodeposited on unpolished, chemically polished and mechanically polished copper substrates were 1.25×10^{-6}, 1.85×10^{-6} and 1.62×10^{-6} A/dm^2, respectively, whereas the corrosion potentials (E_{corr}) for these three tested specimens were -0.12 V, -0.12 V and -0.1 V, respectively. As seen, the values of i_{corr} and E_{corr} for these three specimens are similar to each other, indicating the corrosion behavior for chromium-carbon coating electrodeposited on mechanically polished copper substrate was similar to that of coating electrodeposited on unpolished and chemically polished substrates on the first scan. The corrosion resistance of Cr-C coatings deposited on steel substrates (only carried out a conventional grinding) which i_{corr} is only approximately at 2.5×10^{-4} A/dm^2 due to a bad adhesion between Cr-C coatings and substrates and serious cracks within Cr-C coatings [35]. In this work, the experimental prove the mechanically polished process will significantly improve the corrosion resistance of samples due to a good adhesion between Cr-C coatings and substrates and a crack-free structure in the Cr-C coatings.

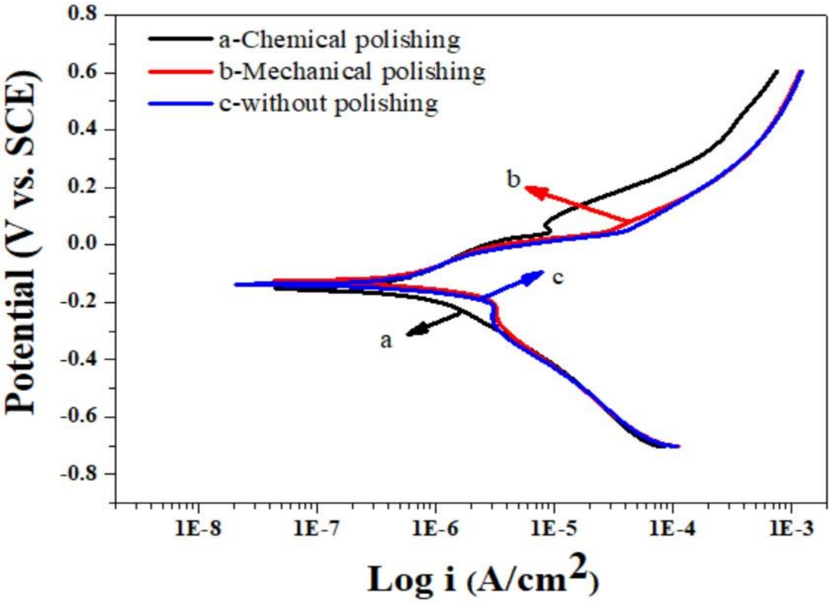


Figure 5. Polarization curves of chromium-carbon coatings electrodeposited on unpolished, chemically polished and mechanically polished copper substrates measured in 3.5 wt.% NaCl aqueous solution at room temperature for the first scan.

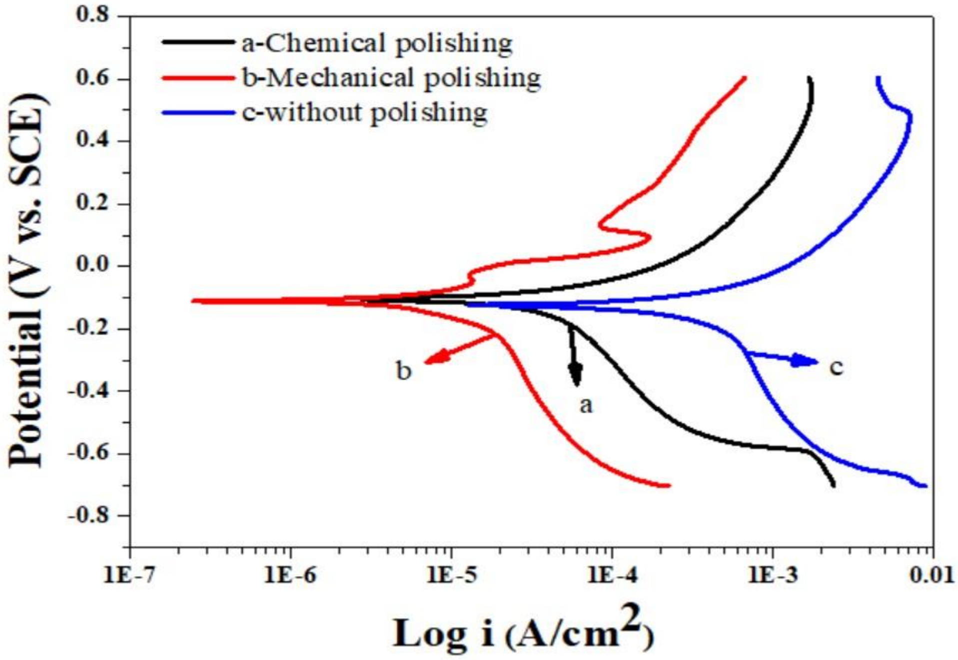


Figure 6. Polarization curves of chromium-carbon coatings electrodeposited on unpolished, chemically polished and mechanically polished copper substrates measured in 3.5 wt.% NaCl aqueous solution at room temperature for the second scan.

Table 1. The electrochemical parameters (E_{corr} and i_{corr}) of potentiodynamic polarization curves the chromium-carbon coatings recorded in 3.5 wt.% NaCl aqueous solution at room temperature for the first scan and second scan.

Sample code	i_{corr} (A/dm^2)	E_{corr} (V vs. SEC)
without polishing	1.25×10^{-6}	-0.12
chemical polishing	1.85×10^{-6}	-0.12
mechanical polishing	1.62×10^{-6}	-0.1
After second scan		
without polishing	9.65×10^{-4}	-0.12
chemical polishing	1.35×10^{-4}	-0.1
mechanical polishing	2.25×10^{-5}	-0.1

To assure the corrosion behavior, each sample was then successively scanned two times and the polarization curves are shown in Fig. 6. The corrosion potentials (E_{corr}) and corrosion current densities (i_{corr}) of the chromium-carbon thin films after two polarization scans are also listed in Table 1. As Table 1 indicated, the corrosion current density for the chromium-carbon thin film deposited on the unpolished copper substrate increases from 1.25×10^{-6} to 9.65×10^{-4} A/dm^2 after two polarization scans. Similarly, the corrosion current density for the chromium-carbon thin film deposited on the chemically polished copper substrate increases from 1.85×10^{-6} to 1.35×10^{-4} A/dm^2 after two polarization scans. Among these three specimens, the chromium-carbon thin film deposited on the chemically polished copper substrate shows it has the lowest corrosion current density of 2.25×10^{-5} A/dm^2 after two polarization scans. This result indicates that the best corrosion resistance was achieved for chromium-carbon thin film deposited on the mechanically polished substrate. The best corrosion resistance behavior of chromium-carbon thin film deposited on the mechanically polished substrate can be attributed to the crack-free structure within the thin film and its good adhesion on copper substrates (see Fig. 3(d),(e),(f)).

4. CONCLUSIONS

The effects of pretreatment process such as chemical polishing and mechanical polishing on the adhesion strength and corrosion resistance of chromium-carbon coatings electrodeposited on copper substrates were investigated. Both polishing process can effectively reduce the roughness of the copper substrate. The best adhesion strength of about 8.1 MPa was achieved for chromium-carbon coating deposited on a mechanically polished copper substrate. When substrate was polished by mechanical procedure, the coating exhibited the best corrosion resistance. The best adhesion strength and corrosion resistance of the chromium-carbon coating deposited on mechanically polished copper substrate can be attributed to the mechanical polishing provides a very smooth surface of copper substrate and favors forming a crack-free chromium-carbon coating on copper substrate.

ACKNOWLEDGEMENTS
The authors would like to thank the Ministry of Science and Technology of the Republic of China, Taiwan, for financially supporting this research under Contract No. MOST 104-2622-E-606-002-CC2.

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