

The Wear Resistance of Cr-C-Al₂O₃ Composite Deposits Prepared on a Cu Substrate using Cr³⁺-based Plating Baths

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Abstract. Cr-C-Al₂O₃ deposits with different Al₂O₃ concentrations were successfully prepared on a Cu substrate using Cr³⁺-based electroplating baths. The microstructures of the Cr-C-Al₂O₃ deposits were examined using optical, scanning and transmission electron microscopes. The hardness values, the corrosion and wear resistance of the Cr-C and Cr-C-Al₂O₃ deposited specimens were evaluated. Based on the experimental results, the hardness values of the Cr-C-Al₂O₃ deposits increased with increasing Al₂O₃ concentration in the electroplating bath. According to our microstructure study, Al₂O₃ nanoparticles are uniformly distributed within the Cr-C deposits after electroplating in a Cr³⁺-based plating bath. The wear resistance of the Cr-C-deposited specimens could be noticeably improved by adding Al₂O₃ nanoparticles to the deposit. The Cr-C-Al₂O₃ deposited specimens, which were prepared in a plating bath with an Al₂O₃ concentration of 50 gL⁻¹, had a relatively high wear resistance compared to the other specimens.

1. Introduction

Due to the material's lustre appearance, as well as superior corrosion and wear resistance, Cr electroplating has been widely used in industrial applications for almost a century. Conventional Cr electroplating is performed in an electroplating bath containing highly toxic Cr⁺⁶ ions [1]. In February of 2003, the Restriction of Hazardous Substances Directive (RoHS) was announced by the European Union. This directive restricts the use of six toxic substances, including Cr⁺⁶ ions, in the manufacturing process for electrical and electronic products. Therefore, the development of alternative coatings has become an important topic in recent years [2,3]. Trivalent Cr electroplating, among all of the alternative options, is considered to have a great potential in replacing conventional hexavalent Cr electroplating for its relatively low toxicity and high current efficiency [4-6].

In our previous works, we proposed that the hardness value of an as-plated Cr-C deposit increased from ca. 780 Hv to ca. 1600 Hv after annealing at 600 °C for 1 h [7] or to ca. 1600 Hv through reduction flame heating for 1 s [8]. However, the cracks in the Cr-C deposits severely widened after annealing, reducing the corrosion protection of the coating.

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Hence, increasing the mechanical properties of Cr-C deposits without weaken the corrosion resistance is important. Composite electroplating may be a useful method for strengthening as-plated Cr-C deposits [9,10]. In general, ceramic particles, such as SiC or Al₂O₃, are often used as hardening phases to form composite coatings via electroplating [11,12]. The aim of this study is to fabricate Cr-C-Al₂O₃ composite deposits using Cr³⁺-based plating baths with different Al₂O₃ concentrations. The microstructures, hardness values, and wear resistances of the resulting Cr-C-Al₂O₃ deposits will be investigated and discussed.

2. Experimental Procedure

A commercially pure Cu disc with a diameter of 20 mm and a thickness of 2 mm was used as the substrate for Cr-C-Al₂O₃ electroplating. Before electroplating, the Cu substrate was mechanically polished with 600-grid emery paper, ultrasonically cleaned in an alcohol bath, and dried with an air blaster. The trivalent Cr plating bath was composed of 0.8 M CrCl₃·6H₂O as the main metal salt, urea as a complex agent and a small amount of buffer salts to maintain a pH value of 1.1 [7]. Al₂O₃ particles with an average size of 100 nm were added to the plating bath at concentrations of 0, 50, 100 and 150 gL⁻¹ to produce the Cr-C and Cr-C-Al₂O₃ deposits on the Cu substrate. A deposit with a thickness of ca. 50 μm was prepared with an electroplating current density of 35 Adm⁻² for 1500 s. The bath temperature was kept at 30 ± 1 °C during electroplating. To increase its circulation, the plating bath was stirred with a magnetic stirrer during electroplating.

After electroplating, the surface and cross-sectional morphologies were studied with a scanning electron microscope (SEM; Hitachi S-3000N) and an optical microscope (OM; Olympus BH2-HLSH). The hardness values of the Cr-C and Cr-C-Al₂O₃ deposits were measured using a micro-hardness tester (Matsuzawa Digital, Model MXT-α7e) with a load of 25 g. The mean hardness and standard deviation of a Cr-C or Cr-C-Al₂O₃ deposit were evaluated by measuring at five arbitrary positions that were approximately in the centre of its cross section mounted in epoxy. The microstructures of the as-plated Cr-C and Cr-C-Al₂O₃ deposits were characterised using optical, scanning and transmission electron microscopes (TEM; Philips Tecnai F30).

The wear resistance of the Cr-C and Cr-C-Al₂O₃ deposited specimens was evaluated using a ball-on-plate wear tester, in which a 6 mm counterpart ball made of steel with a hardness value of ca. 450 Hv was used. During the wear-resistance test, a constant load of 10 N was applied normally to the Cr-C or Cr-C/Al₂O₃ deposited specimens under an unlubricated condition at 25 °C. The wear-resistance test was conducted with a circular track with a diameter of 3 mm, a frequency of 10 Hz, and a total ground distance of 50 m. The weight-difference value of the Cr-C or Cr-C-Al₂O₃ deposited specimens was measured before and after the wear-resistance test using a scale with a precision of 0.01 mg. Optical microscopes was used to examine the surface morphologies of the Cr-C and Cr-C-Al₂O₃ deposited specimen before and after the wear tests.

3. Results and Discussion

3.1 Microstructure Study

Figs. 1 (a, b) show the SEM micrographs of the Cr-C and Cr-C-Al₂O₃ deposit surfaces and their chemical composition analyses, which were performed using an energy-dispersive x-ray spectrometer (EDS). It can be observed that the Al₂O₃ nanoparticles, shown in a bright colour, were uniformly distributed on the deposit surface (see Fig. 1(b)). The results

of the EDS analysis, shown in Fig. 1 (b), show the co-deposition of Cr-C and Al_2O_3 nanoparticles. Typical nodular surfaces were observed in the Cr-C and Cr-C- Al_2O_3 deposits, but narrow cracks were also found in the Cr-C- Al_2O_3 deposits.

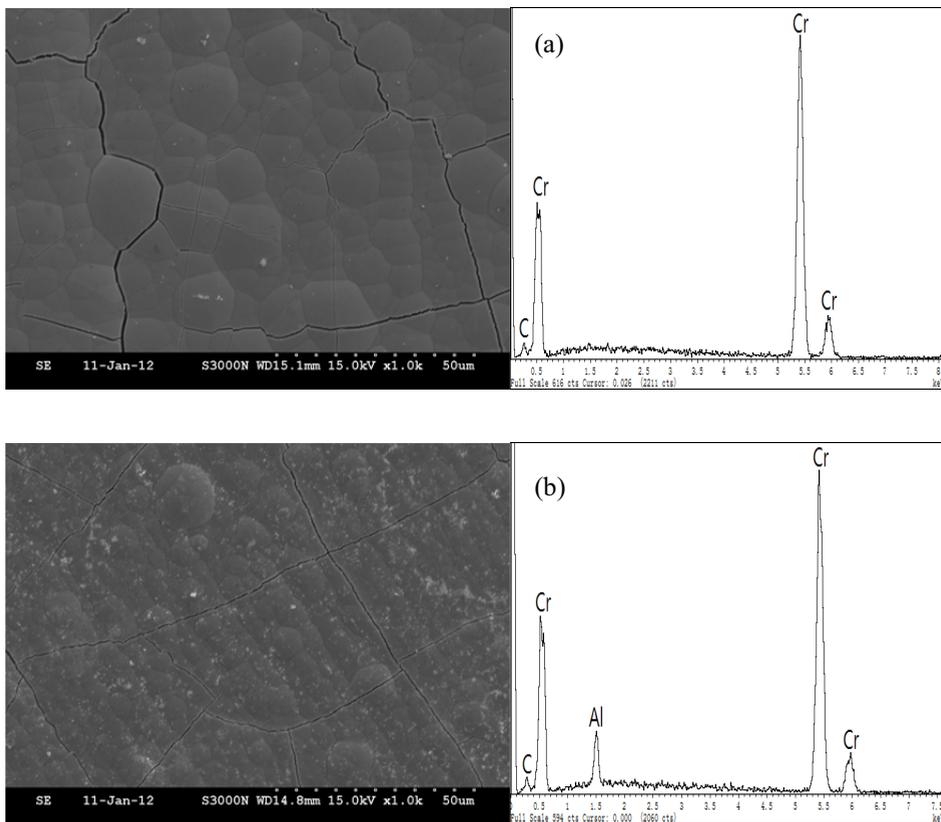


Fig. 1 Surface morphologies and EDS-analysis of (a) Cr-C deposits and (b) Cr-C- Al_2O_3 deposits prepared in an electroplating bath with $50 \text{ gL}^{-1} \text{ Al}_2\text{O}_3$.

A TEM micrograph of an as-plated Cr-C- Al_2O_3 deposit prepared in a plating bath with $50 \text{ gL}^{-1} \text{ Al}_2\text{O}_3$ is shown in Fig. 2. Al_2O_3 nanoparticles with an average size of 100 nm can be clearly seen in the deposit. The Al_2O_3 nanoparticles in the deposit were uniformly distributed, although a few aggregates of Al_2O_3 nanoparticles were found. It can be expected that the hardness of the Cr-C deposits could be reinforced via co-deposition of Al_2O_3 nanoparticles.

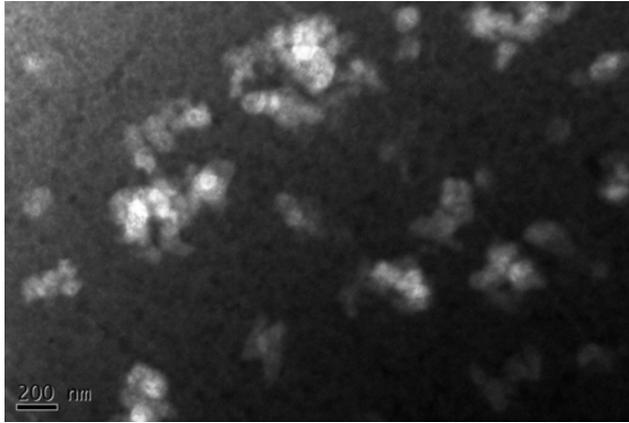


Fig. 2 TEM micrograph of an as-plated Cr-C-Al₂O₃ deposit prepared from an electroplating bath with 50 gL⁻¹ Al₂O₃.

3.2 Hardness Measurement

Fig. 3 shows the hardness and standard deviation values of the Cr-C-Al₂O₃ deposits with different Al₂O₃ concentrations. The hardness of the as-plated Cr-C deposits is 683 Hv, whereas the values of 791, 814 and 852 Hv were detected for the Cr-C-Al₂O₃ deposits prepared in the baths with 50, 100 and 150 gL⁻¹ of Al₂O₃, respectively. That is, the hardness values of Cr-C-Al₂O₃ deposits increased with an increasing Al₂O₃ concentration in the Cr³⁺-based plating bath.

According to our previous study [8], the hardness of the as-plated Cr-C deposits can be significantly increased to 1600 Hv after flame heating for 1 s. The wear resistance of the as-plated Cr-C deposited specimen could also be obviously improved through flame heating. However, the cracks in the flame-heated Cr-C deposits became wider and longer, leading to decrease in their corrosion resistance. In this study, we confirmed that the crack density could be significantly reduced and the crack width could be narrowed in the Cr-C deposits in the presence of Al₂O₃ nanoparticles. Moreover, the as-plated Cr-C-Al₂O₃ deposits have a relatively high hardness value, above 790 Hv, which is higher than that of fully quench-hardened steels that are used as tool and cutting materials.

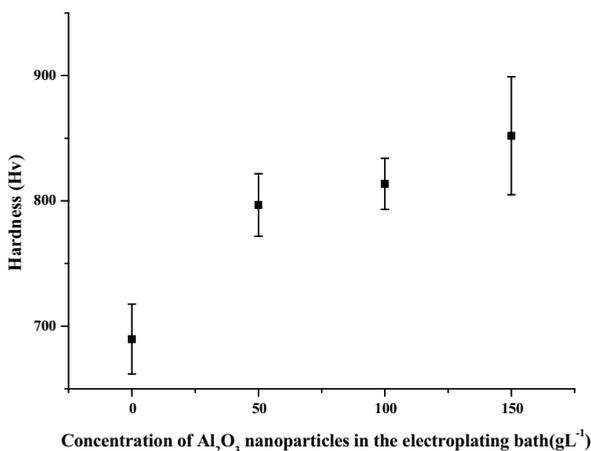


Fig. 3 Hardness values and standard deviations of as-plated Cr-C deposits and Cr-C- Al_2O_3 deposits prepared from electroplating baths with varying concentrations of Al_2O_3 .

3.3 Wear Resistance

The weight-difference values of the Cr-C and Cr-C- Al_2O_3 deposited specimens, before and after the wear-resistance test, are shown in Fig. 4. Clearly, a weight loss of 0.43 mg was detected from the Cr-C deposited specimen after the wear-resistance test. However, weight gains were found from the worn Cr-C- Al_2O_3 deposited specimens prepared from the plating baths with 50 and 100 gL^{-1} of Al_2O_3 . A slight weight loss of 0.02 mg was detected from the Cr-C- Al_2O_3 deposited specimens prepared in the electroplating bath with 150 gL^{-1} of Al_2O_3 . This indicates that the addition of Al_2O_3 nanoparticles to the Cr-C deposits noticeably increased their wear resistance.

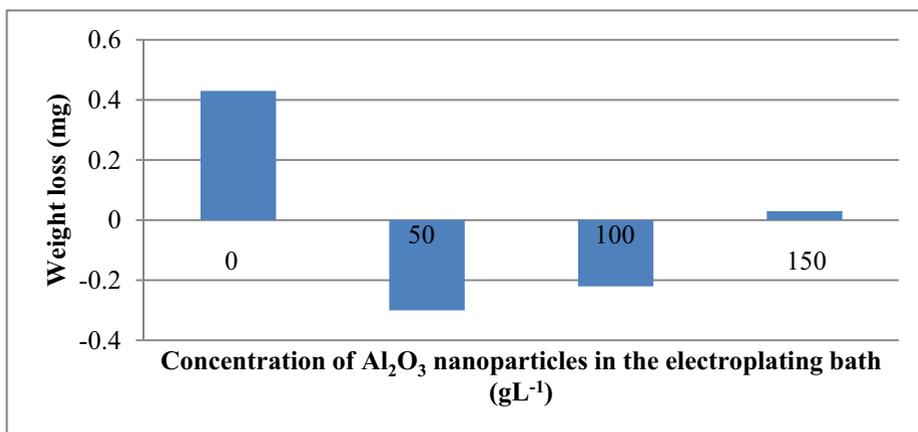


Fig. 4 Weight-difference values of as-plated Cr-C and Cr-C- Al_2O_3 deposited specimens after the wear-resistance test.

The surface morphologies of the Cr-C and Cr-C- Al_2O_3 deposited specimens after the wear-resistance test are shown in Figs. 5(a)-(d). As shown in Fig. 5(a), approximately half

of the surface of the as-plated Cr-C deposits was covered, whereas the other half did not markedly change, revealing a typical nodular surface. However, the nodular surface of the worn Cr-C-Al₂O₃ deposited specimens was no longer observed; the surface had a circular scratched appearance. Because weight gains could be detected from the Cr-C-Al₂O₃ deposited specimen prepared in the plating baths with 50 and 100 gL⁻¹ of Al₂O₃, it can be expected that the circular scratched marks were possibly ground and cold-welded by the steel counterpart.

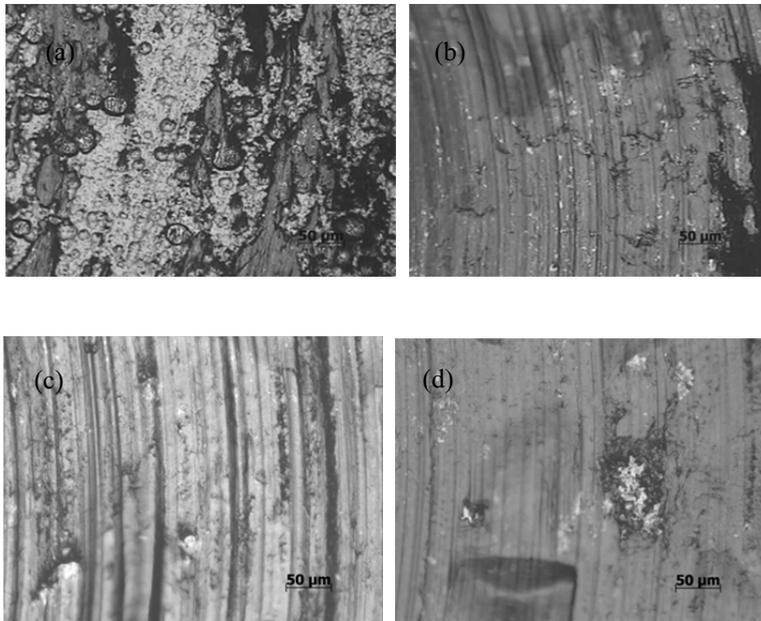


Fig. 5 Surface morphologies of (a) Cr-C deposited specimens and Cr-C-Al₂O₃ deposited specimens prepared in electroplating baths with (b) 50, (c) 100, and (d) 150 gL⁻¹ Al₂O₃, after the wear-resistance test.

The cross-sectional morphologies of the Cr-C and Cr-C-Al₂O₃ deposited specimens after the wear-resistance tests are shown in Figs. 6(a) and (b), in which the specified specimens have either an inferior or superior wear resistance, respectively. The surface profile of the Cr-C deposited specimens levelled off significantly after the wear resistance test; however, the worn Cr-C-Al₂O₃ deposited specimens did not significantly alter their surface profiles. These findings suggest that the addition of Al₂O₃ nanoparticles within the Cr-C deposits could increase their wear resistance. As shown in Fig. 6(b), a cold-welded layer smeared from the steel counterpart can be found on the surface of the Cr-C-Al₂O₃ deposits after the wear-resistance test. This result could explain the weight gain that was detected in the Cr-C-Al₂O₃ deposited specimens after the wear-resistance test. As shown in Fig. 5(d), some shallow holes were observed in the Cr-C-Al₂O₃ deposits that were prepared in the electroplating bath containing 150 gL⁻¹ Al₂O₃ after the wear resistance test. This result implies that some fragments of the Cr-C-Al₂O₃ deposits were peeled off during the wear-resistance test, resulting in a slight weight loss, though a smeared steel counterpart covered its surface after the wear-resistance test.

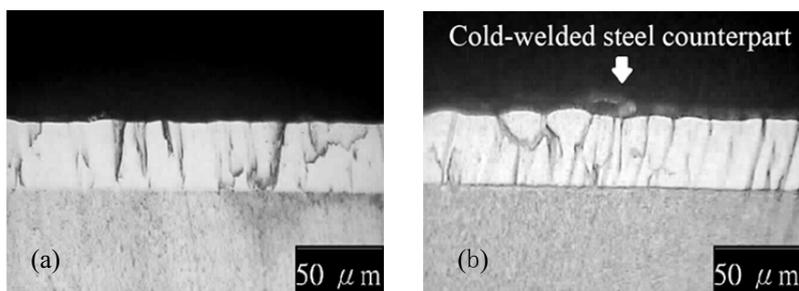


Fig. 6 Cross-sectional morphologies of (a) Cr-C deposited specimens and (b) Cr-C-Al₂O₃ deposited specimens prepared in an electroplating bath with 50 gL⁻¹ Al₂O₃ after the wear-resistance test.

The wear resistance of the as-plated and anneal-hardened Cr-C deposited specimens was evaluated in our previous study [13]. We found that the wear resistance of the as-plated Cr-C deposited specimens could be significantly improved after anneal-hardening. A slight weight loss was detected from the anneal-hardened Cr-C deposited specimens after the wear-resistance test. In this study, a cold-welded layer, smeared from the steel counterpart, was detected on the surface of the Cr-C-Al₂O₃ deposited specimens, leading to an increase in their weight. Although the hardness of the anneal-hardened Cr-C deposits is much higher than that of the Cr-C-Al₂O₃ deposits, a slight weight loss was detected from the anneal-hardened Cr-C deposited specimens. Because Al₂O₃ particles are widely used as an abrasive substance for grinding, the steel counterpart could be abraded by the Cr-C-Al₂O₃ deposits during the wear-resistance test and cold-welded on the deposited specimens.

4. Conclusion

In this study, Cr-C-Al₂O₃ deposits with different Al₂O₃ concentrations could be successfully prepared in Cr³⁺-based electroplating baths. After electroplating, the corrosion and wear resistance of the Cr-C and Cr-C-Al₂O₃ deposited specimens were investigated. The hardness values of the Cr-C-Al₂O₃ deposits increased with increasing concentrations of Al₂O₃ nanoparticles in the Cr³⁺-based electroplating baths. The wear resistance of the Cr-C deposited specimens can be markedly increased via co-deposition with Al₂O₃ nanoparticles. Through-deposit cracks in the Cr-C deposits were reduced by adding Al₂O₃ nanoparticles to the deposits. The Cr-C-Al₂O₃ deposited specimens prepared in the electroplating bath with 50 gL⁻¹ Al₂O₃ had relatively high wear resistances compared to the other specimens.

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