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Preparation of Crystalline Chromium Coating on Cu Substrate Directly by DC Electrodeposition from Wholly Environmentally Acceptable Cr(III) Electrolyte



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ABSTRACT

Almost all of the currently achievable chromium coatings using Cr(III) electrolytes are amorphous. In this work, a crystalline chromium coating with an attractive appearance was produced on Cu substrates. This was achieved using direct current (DC) electrodeposition of a wholly environmentally acceptable sulfate Cr(III) electrolyte without a subsequent heat treatment. Structural characterization revealed that the crystalline chromium coating deposited at 5 A/dm² from the electrolyte solution is composed of body-centered cubic (bcc) Cr crystals, which demonstrated significant preferred orientation and a size range of 50–60 nm. The results also show that, in general, the color and luster of the chromium coating are greatly affected by the current density employed, and the larger the current density is, the dimmer the coating.

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1. Introduction

Presently, almost all of the chromium coatings that are electrodeposited using Cr(III) electrolytes are amorphous [1–5], with their X-ray diffraction (XRD) patterns showing a characteristic broad bread-like peak. G. Saravanan et al. prepared a nanocrystalline chromium coating using a pulsed electrodeposition method of Cr(III) electrolytes containing a large amount of dimethylformamide (DMF) [6]. This process for the production of a chromium coating is destined to be rejected by industries because DMF has been introduced as a new source of toxic pollution, although the harm of Cr(VI) was avoided. In addition, F. I. Danilov et al. also claim to have prepared a nanocrystalline, hard chromium coating from Cr(III) electrolytes containing urea and formic acid, but the XRD pattern they provided revealed that the coating possessed a main phase that was amorphous, which is not distinctly different from the phase structures of previously reported chromium coatings [7].

As is well known, the chromium coating produced by a traditional Cr(VI) electrodeposition process is nanocrystalline, which has been widely used in industry due to its excellent toughness, hardness, and comprehensive performance. The properties of the coatings are dependent on their microstructures, and compared with the conventional chromium coatings obtained from Cr(III) electrolytes,

the amorphous chromium coatings using Cr(III) electrolytes show obvious flaws, such as insufficient toughness, high brittleness and internal stress, and a poor binding force between the coating and the substrate [8,9].

The goal of this study was to prepare crystalline chromium coatings by the direct current electrodeposition of Cr(III) electrolytes without the use of a subsequent heat treatment. At the same time, we aimed to avoid the introduction of other harmful substances, which is the most significant contribution of trivalent chromium electrodeposition. For this aim, we attempted to use direct current (DC) in the present research.

2. Experimental section

Two types of Cr(III) electrolytes were employed in this research. One is a chloride system electrolyte, and the other is a sulfate system electrolyte. The chloride electrolyte has the following main components: 0.4 mol/L CrCl₃·6H₂O, 0.6 mol/L HCOOH, 2.6 mol/L NH₄Cl, 0.6 mol/L H₃BO₃, 1.0 mol/L KCl, and 0.2 mol/L CH₃COOH. In this system, the current densities used for electrodeposition were between 5 A/dm² and 30 A/dm². The electrolyte temperature was controlled in the range of 15–55 °C, and the pH was maintained at 2.1. Highly pure graphite was used as the anode. The main components of the sulfate electrolyte used in this work are as follows: Cr₂(SO₄)₃·6H₂O 0.06 mol/L, K₂SO₄+Na₂SO₄ 1.5 mol/L, H₃BO₃ 1.0 mol/L, hydroxyl succinic acid 0.07 mol/L, and sulfur-containing

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additive (SA, whose main composition is $\text{CH}_4\text{N}_2\text{S}$) 1.2 mmol/L. The current densities used in the system were in the range of 5–15 A/dm^2 , and the temperature and pH of the electrolyte solution were adjusted to 50 °C and pH 3.4, respectively. An iridium/tantalum oxide-coated electrode was used as the anode. For both of the two electrolytes, a high purity copper sheet was employed as the cathode.

The structures of the chromium coatings obtained were analyzed using an X-ray diffractometer (XRD, Panalytical X'Pert PRO, PHILIPS, Netherlands) with a small incidence angle ($\sim 1^\circ$) and a high-resolution transmission electron microscope (HRTEM, JEM-3010, JEOL, Japan).

3. Results and discussion

There are many electrolyte systems used for Cr(III) electrodeposition [7,10–13], but for those systems based solely on chromium salts, Cr(III) electrolytes can be simply classified into two groups: chloride electrolytes and sulfate electrolytes. A large number of studies are focused on the electrodeposition of a chromium coating using chloride Cr(III) electrolytes. To produce a crystalline chromium coating by the direct electrodeposition of Cr(III) electrolytes, we first chose chloride as the electrolyte for our experiment.

The temperature of the electrolyte solution has an important influence on the microstructure and properties of the electrodeposited coating [14]. Generally, raising the electrolyte temperature can promote the diffusion and transference of metal atoms deposited at the cathode surface, consequently inducing the formation of metallic crystals.

For a chloride Cr(III) electrolyte solution, electrodeposition is usually performed at room temperature [15–18]. Because some volatile organics are contained in the chloride electrolyte solution in this research, raising the electrolyte temperature will intensify the volatilization of these constituents. The conventional electrodeposition temperature is below 60 °C. Therefore, in this work, we selected a temperature range of 15–55 °C to study the effect of electrolyte solution temperature on the coating microstructure.

In this temperature range, a uniform and flat chromium coating can be produced using the chloride electrolyte solution. XRD analysis was performed on two coatings electrodeposited at either 15 °C or 55 °C. The phase structure of the chromium coatings did not change by increasing the electrodeposition temperature (Fig. 1). The XRD patterns clearly reveal the feature of a bread-like wide peak, which is typical of an amorphous substance. From these data, it was determined that it was impossible to electrodeposit a crystalline chromium coating by varying the deposition

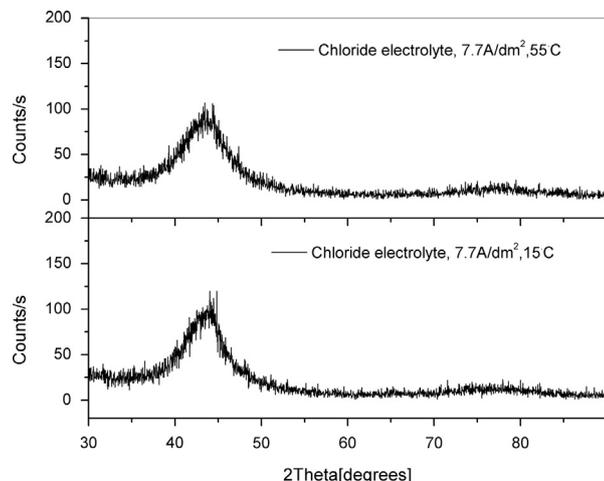


Fig. 1. XRD patterns of the chromium coatings prepared from the chloride electrolyte at 15 °C and 55 °C separately.

temperature within this range while employing the chloride electrolyte solution. Apparently, raising the electrolyte temperature in this range (15–55 °C) is not enough to accelerate the diffusion and migration of the electrodeposited atoms to form a crystalline chromium coating.

For certain electrolyte systems, among the process parameters for electrodeposition, besides the electrolyte temperature, the current density also has a significant effect on the electrodeposition behavior and coating structure [14]. To prepare a crystalline chromium coating from the chloride electrolyte solution, we tried varying the current density. It was observed that chromium coatings with a uniform and flat appearance can be deposited using the chloride electrolyte solution at a current density within the range of 5–30 A/dm^2 . No diffraction peak arising from the Cr crystals was observed in the XRD pattern of the chromium coating produced at 5 A/dm^2 (Fig. 2a). All of the peaks in this pattern belonged to the Cu substrate, although the characteristic bread-like peak associated with amorphous matter could be seen in its amplified pattern (Fig. 2b). However, in the XRD pattern for the coating deposited at 30 A/dm^2 , the diffraction peaks originating from the crystal faces (1 1 0), (2 0 0), (2 1 1) and (2 2 0) of body-centered cubic (bcc) Cr also appear in addition to the diffraction peaks of Cu. Therefore, it was determined that a crystalline chromium coating is able to be prepared directly by the electrodeposition of the chloride electrolyte when the current density is increased to 30 A/dm^2 .

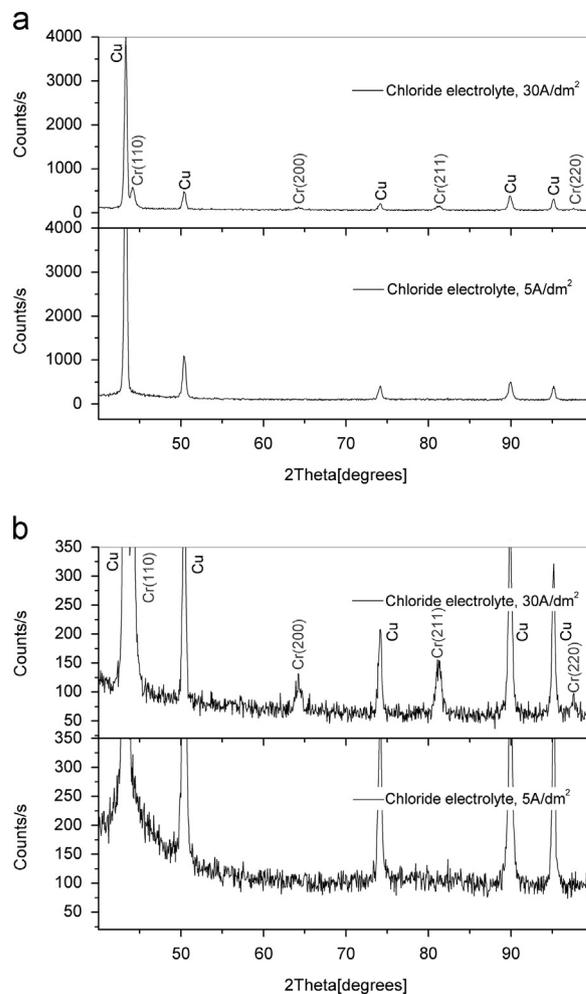


Fig. 2. (a) XRD patterns and (b) the amplified XRD patterns of the chromium coatings prepared from the chloride electrolyte at 5 A/dm^2 and 30 A/dm^2 separately.

Unfortunately, the crystalline chromium coating produced from the chloride electrolyte could not be used as a decorative coating due to its dim appearance. In addition, the chloride electrolyte solution has severe disadvantages, as follows.

- 1) The electrolyte solution contains relatively volatile carboxylic acids (e.g., HCOOH), resulting in the instability of the electrolyte solution.
- 2) Formic acid is toxic and causes irritation, which can harm factory workers and the environment.
- 3) A large amount of Cl^- ions exists in the electrolyte solution. The evolution of chlorine gas at the anode surface also introduces a toxic substance as well as pollution.

To prepare a crystalline chromium coating with an attractive appearance using Cr(III) electrolytes that do not produce pollution, we aimed to find another way. The current density seems to have a more significant influence on the structure of the deposited chromium coating than the electrolyte temperature, so more attention should be paid to this parameter.

As the chloride electrolyte solution has some notable disadvantages, we then carried out experiments employing a sulfate system Cr(III) electrolyte, which does not use volatile formic acid. After the optimization of the electrolyte solution composition and repeated tests, a crystalline chromium coating was directly electrodeposited from a sulfate Cr(III) electrolyte solution, whose composition was shown in the experimental section.

Uniform and smooth chromium coatings can be produced using this sulfate electrolyte solution at current densities between 5 A/dm^2 and 15 A/dm^2 . Fig. 3a gives the XRD patterns of the two coatings deposited at 5 A/dm^2 and 15 A/dm^2 separately. In addition to the diffraction peaks that correspond to the Cu substrate, the peaks corresponding to the crystal faces (1 1 0), (2 0 0) and (2 1 1) of bcc Cr appear in both XRD patterns of the two coatings. By carefully comparing the XRD data of the coating deposited at 5 A/dm^2 with those of the coating deposited at 15 A/dm^2 , we found that the diffraction peaks of the latter had noticeable broadening, which indicates that either crystal grain refining or microscopic stress must exist in the bcc Cr crystals of the coating because both of these two factors can result in diffraction peak broadening.

Thus, crystalline chromium coatings can be produced successfully by the direct electrodeposition of a sulfate-system Cr(III) electrolyte solution in the current density range of $5\text{--}15 \text{ A/dm}^2$. The smaller the current density employed, the better the crystallinity of the bcc Cr phase in the obtained coating.

Furthermore, the diffraction peak of crystal face (1 1 0) of bcc Cr found in the crystalline chromium coatings, deposited from either the chloride electrolyte solution or the sulfate electrolyte solution, is much stronger than those of the (2 0 0) and (2 1 1) crystal faces. In this research, a small angle incident mode was adopted for the XRD analysis, and the intersection angle between the incident X-ray and the coating sample surface was approximately 1° . According to the principles of XRD and the 2θ angle ($\sim 44.37\text{--}44.38^\circ$) corresponding to the crystal face (1 1 0), it can be calculated that the majority of the crystalline grains of bcc Cr in the coatings arrange in such a way that their crystal face (1 1 0) has an intersection angle of approximately 21° with the coating surface.

Whether a chromium coating electrodeposited from a Cr(III) electrolyte solution is bright and white is not relevant to its main phase, but it is undoubtedly related to its fine microstructure and composition distribution. Furthermore, the color and luster of the electrodeposited chromium coating is significantly affected by the current density employed (Table 1). It was observed that the larger the current density is, the dimmer the color of the coating.

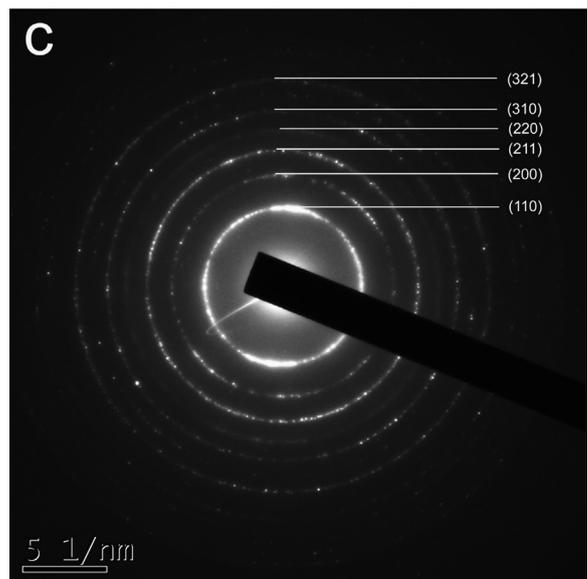
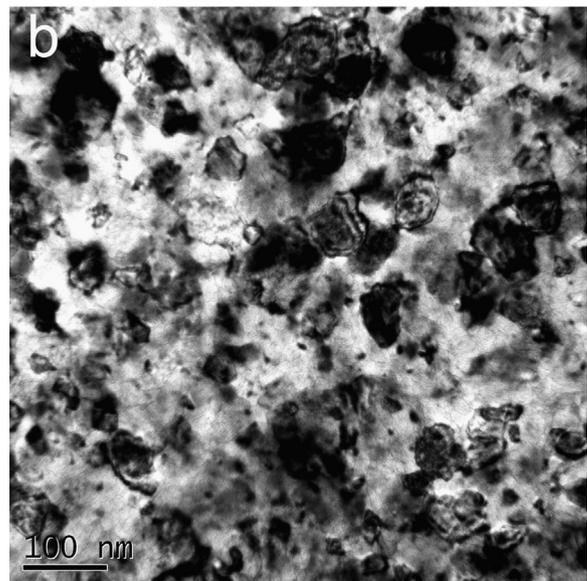
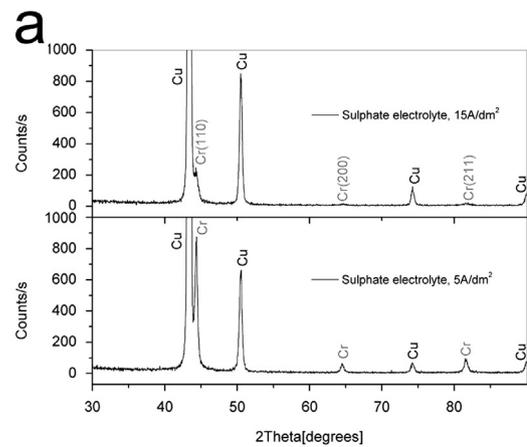


Fig. 3. (a) XRD patterns of the chromium coatings prepared from the sulfate electrolyte at 5 A/dm^2 and 15 A/dm^2 separately, and (b) TEM photo and (c) SAED pattern of the chromium coating prepared from the sulfate electrolyte at 5 A/dm^2 .

The microstructure of the attractive crystalline chromium coating, which was produced using the sulfate electrolyte solution at a current density of 5 A/dm^2 , was further investigated using selected area electron diffraction (SAED) and transmission electron

Table 1
Phase structure and color characteristics of chromium coatings prepared under different process conditions.

Process	Phase	Color & luster
Chloride electrolyte 5 A/dm ²	Amorphous	Uniform, white, bright
Chloride electrolyte 30 A/dm ²	Crystalline	Uniform, dim
Sulfate electrolyte 5 A/dm ²	Crystalline	Uniform, white, bright
Sulfate electrolyte 15 A/dm ²	Crystalline	Uniform, dim

microscopy (TEM). The main phase in the coating is bcc Cr crystal, identified by its SAED pattern and TEM photos (Fig. 3), which conforms with the above results from XRD. The chromium coating's diffraction rings are composed of a series of dots attributed to the diffraction of slightly large crystals (~50–60 nm) with distinct edges and angles (Fig. 3b).

For the first time, this research reveals that a crystalline chromium coating can be directly electrodeposited using a Cr(III) electrolyte solution that does not contain constituents that may cause pollution (e.g., Cl⁻, HCOOH, DMF). Without SA in the sulfate electrolyte solution, no chromium coating could be obtained at any current density, but when a very small amount of SA (~1.2 mmol/L) was added, a crystalline chromium coating was able to be electrodeposited immediately. Obviously, the sulfur-containing additive plays a special role in the catalysis of the electrochemical reduction of the active Cr³⁺ complex, the relevant detailed mechanism of which will be the subject of our future research.

4. Conclusions

A crystalline chromium coating with a good appearance can be electrodeposited using a wholly environmentally acceptable sulfate Cr(III) electrolyte. A significant preferred orientation of bcc Cr crystals occurs in the crystalline chromium coatings using the Cr(III) electrolytes. The color and luster of the electrodeposited chromium coating do not appear to be relevant to its main phase but are significantly influenced by the current density used. Generally, the larger the current density is, the dimmer the color of the coating.

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