



Corrosion behavior of Cr electrodeposited from Cr(VI) and Cr(III)-baths using direct (DCD) and pulse electrodeposition (PED) techniques

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ABSTRACT

A comparison was made between the electrochemical corrosion behaviors of chromium deposited from hexavalent [Cr(VI)] and trivalent [Cr(III)] chromium baths using direct current (DCD) and pulse electrodeposition (PED) techniques. Chromium coatings were deposited on mild-steel (MS) substrate. The corrosion behavior of both DCD and PED chromium from Cr(VI) and Cr(III)-baths in 3.5%NaCl solution was studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results indicated that PED chromium from Cr(VI) and Cr(III)-baths have higher charge-transfer resistance R_{ct} and very low I_{corr} than that of DCD chromium on mild-steel substrate.

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1. Introduction

Hexavalent chromium [Cr(VI)] plating has been commercialized many years before. A Cr(VI) plating bath operates at an elevated temperature and produces a mist of chromic acid. Since Cr(VI) plating produces hazardous air emissions, all Cr(VI) electro depositors must control and monitor the bath surface tension periodically. Cr(VI) widely recognized as a human carcinogen was reported to cause increased incidences of lung cancer. A United States Environmental Protection Agency (EPA) report [1] implicates Cr(VI) as a Group A known human carcinogen. The EPA also found that Cr(III) is much less toxic, classifies as a Group D carcinogen not classifiable as to carcinogenicity in humans. Cr(III) is rather insoluble and does not oxidize organic materials, poorly absorbed from gastrointestinal tract and is not considered to be a carcinogen. Cr(VI) is very reactive and causes ulceration of nasal septum and other tissues upon exposure as well as reproductive and gastrointestinal effects. The use of Cr(III) in industrial and commercial processes is preferred over Cr(VI) on the basis of comparison of the toxicities. Chromium is used in industry because of its excellent wear, corrosion resistance and attractive appearance [2,3]. The main advantage of Cr(III) plating bath in comparison with a Cr(VI)-bath is that Cr^{3+} ions are nontoxic environmentally benign [4]. However, it is almost impossible to deposit the Cr coating from a simple aqueous Cr(III) solution due to a very stable $[Cr(H_2O)_6]^{3+}$ complex [5]. According to the published data [6] the slow deposition rate in Cr(III) chloride electrolyte is related to the appearance of very

stable μ -hydroxo-bridged oligomeric species of Cr(III). To destabilize the strong hexa-aqua chromium(III) complex, some of the complexing agents (glycine, urea, dimethyl formamide, formic acid, acetate, sodium citrate, DL-aspartic acid, etc) may be used [7–11]. Chromium plating from Cr(VI) solution is now under scrutiny due to its toxicity and carcinogenicity; therefore, significant efforts have been applied to the development of alternative process for chromium plating from Cr(VI) solution [12]. The present work was important in terms of a Cr(VI)-free process, using Cr(III)-glycine solution as an alternate bath. Therefore, in the present work the aim was to compare the DC and PE-deposited chromium using a Cr(III)-glycine bath with Cr(VI)-bath. The microstructure and corrosion behavior were analyzed in 3.5%NaCl solution using potentiodynamic polarization and EIS.

2. Experimental

2.1. Materials preparation

Chromium coatings were electrochemically deposited from Cr(VI)-bath consisting of 250 g/L CrO_3 , 2.5 g/L H_2SO_4 and Cr(III)-bath consisting of 212 g/L $CrCl_3 \cdot 6H_2O$, 26 g/L NH_4Cl , 36 g/L NaCl, 20 g/L $B(OH)_3$, 75 g/L glycine and 200 ml methanol. AR grade chemicals and double distilled water were used to prepare the solution. The coatings were deposited on polished and electro-cleaned substrate of mild steel. The pH value of 2 ± 0.2 was maintained for Cr(III)-bath and stirred by mechanical stirrer. Graphite and lead were used as the anode for Cr(III) and Cr(VI)-baths, mild-steel plates were used as the cathode. The samples obtained

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Table 1
Pulse parameter used for pulse plating of chromium.

Duty cycle (%)	Pulse frequency and pulse on-off times (ms)				Current density (A/dm ²)			
	10 Hz	25 Hz	50 Hz	100 Hz	Cr(III)-bath		Cr(VI)-bath	
					Peak	Average	Peak	Average
10	10–90	4–36	2–18	1–9	104	10.4	200	20
20	20–80	8–32	4–16	2–8	52	10.4	100	20
40	40–60	16–24	8–12	4–6	26	10.4	50	20
80	80–20	32–8	16–4	8–2	13	10.4	25	20

for mild steel, DC and PE-deposited chromium from Cr(VI) and Cr(III) were represented by (MS), Cr-(DCD)/MS from Cr(VI)-bath, Cr-(DCD)/MS from Cr(III)-bath, Cr-(PED)/MS from Cr(VI)-bath, and Cr-(PED)/MS from Cr(III)-bath, respectively. Pulse plating was done using Dynatronix (USA) DPR20-10-5 Model. The pulse parameters used are given in Table 1 [13]. The formula used in pulse plating is given below

$$\% \text{Duty cycle} = \frac{\text{ON time}}{\text{ON time} + \text{OFF time}} \times 100$$

$$\text{Average current} = \frac{\text{ON time}}{\text{Total time}} \times \text{peak pulse current}$$

$$\text{Peak current} = \frac{\text{Average current}}{\text{Duty cycle}} \times 100$$

The surface morphologies of the electrodeposits were characterized by SEM, and grain size and texture were assessed by X-ray diffraction (XRD) technique.

2.2. Corrosion measurements

2.2.1. Cell apparatus

Corrosion measurements were performed in a three-electrode cell with the volume of 150 mL. The samples (MS), Cr-(DCD)/MS from Cr(VI)-bath, Cr-(DCD)/MS from Cr(III)-bath, Cr-(PED)/MS from Cr(VI)-bath, and Cr-(PED)/MS from Cr(III)-bath were used as the working electrodes (WE). A platinum foil and a saturated calomel electrode (SCE) were used as the auxiliary electrode and reference electrode, respectively. The electrodes were connected to a potentiostat (PARSTAT 2273). The corrosion resistance parameters were obtained with inbuilt software package (powerCORR). All potentials in this work are referred to SCE.

2.2.2. Electrochemical procedures

Corrosion behavior was examined in neutral 3.5% NaCl solution at 30 ± 1 °C. Potentiodynamic polarization curves were measured for all the samples between -0.9 and -0.2 V at a scan rate of 5 mV/s. Impedance spectra were conducted at open circuit potential over a frequency range from 10^5 Hz to 10^{-2} Hz. The amplitude of potential modulation was 5 mV. All the recorded impedance spectra were shown as Bode and Nyquist diagrams.

3. Results and discussion

3.1. Microstructural characteristics

The morphology of chromium deposits on mild-steel substrate was examined under a scanning electron microscopy (SEM). In Figs. 1A and B and 2A and B, the surface structure of pure chromium from Cr(III) and Cr(VI)-baths under scanning microscope is compared. Fig 1A and B are the SEM photomicrographs of DC electrodeposited chromium at 35 A/dm^{-2} for 30 min from Cr(III) and Cr(VI)-baths, respectively. Both deposits have a small nodular deposit with the particle size of about 2–2.5 μm with micro cracks.

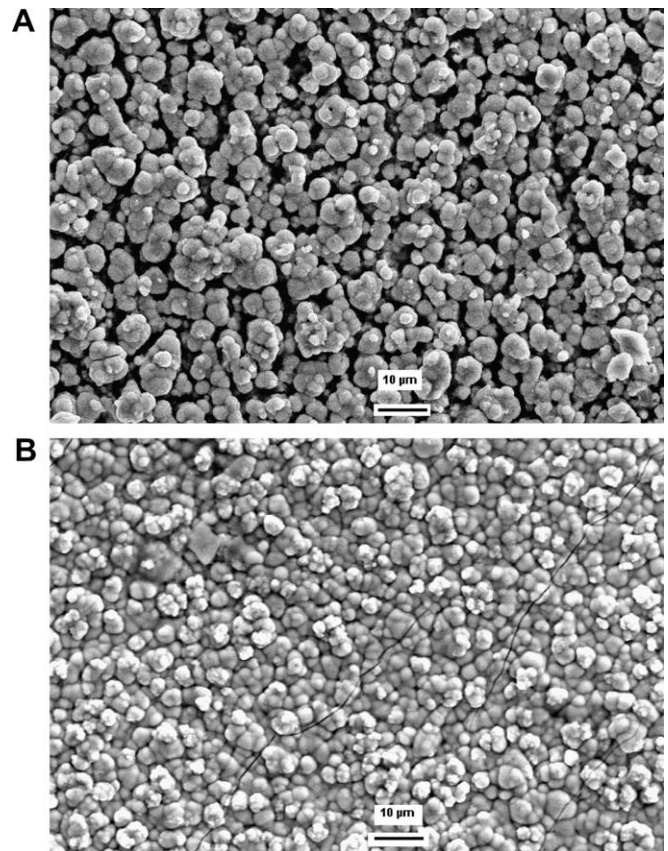


Fig. 1. (A and B) SEM surface morphology of DC-deposited chromium at 35 A/dm^{-2} in 30 min from Cr(III) and Cr(VI)-baths.

The micro cracks formed during electrodeposition is due to the adsorbed hydrogen gas. Similarly, Fig. 2A and B is the SEM photomicrographs of PE-deposited chromium at an average current density of 10.4 A/dm^{-2} for Cr(III) both and 20 A/dm^{-2} for Cr(VI)-bath in 30 min. Both the deposits have a very small nodular size with the particle size of about 1–1.4 μm . In the PE deposition, the peak current density is higher than average current density, this leads to a decreased grain size. The decreased porosity and denser packed surface are due to the desorption of hydrogen during the off time of pulse cycle [14].

3.2. X-ray diffraction analysis

Chromium may be electrodeposited in various phases (α -, β - and γ -phase) [15]. The phases obtained are dependent on plating conditions. α -Chromium [16,17] is the most predominant and stable phases; however, β -chromium only deposits under certain conditions and converts eventually to α -chromium over time or with annealing. Fig. 3 shows the X-ray diffraction pattern of the chromium deposited from hexavalent and trivalent chromium baths. The α -Cr(110) was peak obtained at $2\theta = 44.6992$ and $2\theta = 44.2276$ from trivalent and hexavalent chromium baths respectively. Similarly, α -Cr(200) peaks were obtained at $2\theta = 65.0869$ and $2\theta = 64.7460$ from trivalent and hexavalent chromium baths, respectively. Intensity of α -Cr(110) peak is higher in trivalent, whereas α -Cr(200) peak is higher in hexavalent chromium. The α -Cr(110) plane is having higher intensity in BCC structure from trivalent bath. Therefore, the α -Cr deposits tend to grow with the plane of highest intensity. In contrast to α -Cr(110), the preferred orientation in hexavalent chromium bath is α -Cr(200). The crystallite sizes of Cr coatings were calculated from Scherer's equation.

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