Effect of Cr(III) solution chemistry on electrodeposition of chromium

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Abstract

This work provides a new insight into the interaction of urea with formate during the chromium electrodeposition from a sulphate-based Cr(III) solution. The influence of solution chemistry on chromium electrodeposition in a Cr(III) bath containing sodium formate and urea as complexing agents was studied by FT-IR, XPS and AFM. The results show that good quality Cr coatings may be obtained only in those cases when the secondary ligand with the carbamidic group predominates over urea in the electrolyte. This suggests that electrodeposition of good quality chromium deposit is possible due to the formation of active chromium–carbamid complexes \([\text{Cr(carbamid)}_n(\text{H}_2\text{O})_{6-n}]^{3+}\). These complexes delay the formation of the stable oligomeric species, and thus provide a prolonged working lifetime in the Cr(III) formate-urea electrolyte.

1. Introduction

The main advantage of a Cr(III) plating bath in comparison with a Cr(VI) bath is that Cr\(^{3+}\) ions are non-toxic. However, it is almost impossible to deposit the Cr coating from a simple aqueous Cr(III) solution due to a very stable \([\text{Cr(H}_2\text{O})_{6}]^{3+}\) complex. According to the published data [1] the slow deposition rate in Cr(III) sulphate electrolyte is related to the appearance of very stable \(\mu\)-sulphato-bridged oligomeric species of Cr(III). To destabilize the strong hexa-aqua chromium(III) complex some of the complexing agents (formic acid, urea, acetate, glycine, etc.) may be used [1–7]. The most important fact is that Cr(III) does not oxidize organic compounds. Although the pH in the bulk of the electrolyte may be about 1–2, the diffusion layer pH can reach 4. At this pH co-coordinated water molecules may be converted to OH\(^-\) groups, which leads to the formation of \(\mu\)-hydroxo bridged species. This reaction may continue with the formation of larger and larger molecules where the chromium atoms are linked with OH\(^-\) groups (olated compounds). This is the cause of losses in both the deposition rate and the quality of Cr deposit [2, 8]. The coordinated water molecules, OH\(^-\) groups, or other ligands may be replaced by anions in the solution. Anions that easily enter into the co-coordinated sphere and displace OH\(^-\) groups can effectively prevent olation [8]. Some of organic ligands influence the plating rate and the quality of the coatings due to the formation of Cr(III) active complexes [1–5]. However, the reasons why thick chromium coatings are difficult to obtain in Cr(III) baths have not been fully clarified.

The purpose of this work was to examine the effect of solution chemistry on the quality of Cr deposit and to find optimum plating conditions for chromium electrodeposition from Cr(III) bath containing both sodium formate and urea as complexing agents.

2. Experimental details

Chromium coatings were plated on steel containing 99.4% iron (Steel-3) in solution containing 0.3 m of \(\text{Cr}_2(\text{SO}_4)_3\), 6H\(_2\text{O}\), 0.6 m of \(\text{Na}_2\text{SO}_4\), 0.5 m of \(\text{H}_3\text{BO}_3\), 0.2 m of \(\text{Al}_2(\text{SO}_4)_3\), 18H\(_2\text{O}\), 0.5 m of \(\text{NaF}\) and additionally 0.4 m of \(\text{HCOONa}\) and 0.75 m of \((\text{NH}_2)_2\text{CO}\) as complexing agents. To study the effect of complexing agents on chromium electrodeposition the solutions without and with complexing agents were used. The pH of these solutions was adjusted to 2.0 ± 0.1 by addition of \(\text{H}_3\text{SO}_4\) or KOH. The polarization measurements were conducted in a three-electrode electrochemical cell using a PI-50-1 potentiostat under potentiodynamic conditions with a potential scan rate of 10 mV s\(^{-1}\) at a temperature of 20 °C. A saturated Ag/AgCl electrode was used as reference and Pt plate served as a counter electrode. The steel (99.4% purity) cathode was mechanically polished, degreased with a mixture of calcium and magnesium oxides, rinsed thoroughly, activated in a diluted (1:1) hydrochloric acid and then rinsed with deionised water. To study the properties of the Cr
coatings the steel samples were plated at a current density \( (i_c) \) of 20 and 30 A dm\(^{-2} \) and a temperature of 50 °C. The quality of Cr deposits was assessed visually and by using an optical microscope. A light metallic deposit of good appearance and good adhesion was defined as a high quality deposit. The electrodeposition rate of Cr was determined gravimetrically.

Elemental analysis of coatings was carried out using X-ray photoelectron spectroscopy (XPS). Spectra were recorded by an ESCALAB MK-II spectrometer (VG Scientific, UK) using MgK\( \alpha \) anode radiation. The spectrometer had a base pressure of 1.33×10\(^{-7} \) Pa in the analyser chamber. For sputter etching the argon gas pressure was maintained at 5×10\(^{-3} \) Pa in the preparation chamber. Under these conditions the chromium phase can be etched at a rate of \( \approx 0.2 \) nm min\(^{-1} \). The quantity of each element in at % was calculated from the area of the single peak. Empirical sensitivity factors of the elements were taken from [9] and the spectra recorded were compared with the standard ones. No less than five spectra were recorded for every element. The maximum accuracy of the method was 0.1 at %. A standard program was used for data processing. Bands were determined according to their energy, intensity, width, and shape.

The surface of Cr plated sample was examined by means of contact mode atomic force microscopy (AFM) on a scanning probe microscope Explorer (ThermoMicroscopes, USA). 50, 10 and 2\( \mu \)m scans in distinct areas of surface near the center of the specimen were performed collecting topography and internal sensor data. The most common statistical parameters \( R_a \) and \( R_{\text{rms}} \) (the average roughness deviation and the root-mean-square roughness deviation, respectively) were calculated from the topography data using SPMLab 5.01 software. The calculation of these parameters is shown in (1) and (2):

\[
R_a = \frac{1}{N} \sum_{j=1}^{N} |Z_j - \bar{Z}|
\]

(1)

\[
R_{\text{rms}} = \sqrt{\frac{1}{N} \sum_{j=1}^{N} (Z_j - \bar{Z})^2}
\]

(2)

Areas with erroneous data, noise spikes and noise lines were excluded before the calculations.

The infrared spectra were recorded as KBr discs using a Fourier transformation infrared spectrometer (Hartman & Braun, Canada) with 2 cm\(^{-1} \) scale resolutions in the region of wave numbers between 3600 and 400 cm\(^{-1} \).

3. Results and discussion

The voltammograms recorded on steel and Cu in both Cr(III) baths without and with complexing agents (Figure 1) show no current until the electrode potential reaches \(-0.64 \) V, then the current increases with the potential sweep. This value agrees with the potential for the onset of reduction of Cr(III) to Cr(II) [6]. The current increases more dramatically in bath containing complexing agents for both Fe and Cu cathodes. In the absence of complexing agents the current increases slowly until the electrode potential reaches about \(-1.3 \) V and then increases dramatically. The curves show the erratic current response when the potential is more negative than \(-1.65 \) V, which may be due to hydrogen evolution. Inhibition of the cathodic process observed in the absence of complexing agents (curves 1, 3) suggests the formation of some inactive species in diffusion layer. Adsorption of these species into the crystal growth site of the metal is believed to cause the loss of metallic quality. For example, electrode surfaces corresponding to curves 1 and 3 in Figure 1 were covered with a thin layer of dark substance, whereas the electrode surfaces corresponding to curves 2 and 4 were covered with a thin layer of light chromium.

The effect of complexing agents on Cr electrodeposition was studied in Cr(III) bath containing sodium formate alone and in bath containing both sodium formate and urea. It was found that the current efficiency (CE) of Cr in Cr(III) bath containing both HCOONa and (NH\(_2\))\(_2\)CO was twofold higher than that in bath containing HCOONa alone. The optimum concentrations of complexing agents in the electrolyte are 0.4 m HCOONa and 0.75 m (NH\(_2\))\(_2\)CO. The working lifetime of the electrolyte containing HCOONa alone is very short and the maximum thickness of Cr