Study on the Electrodeposition of Chromium from Cr(III) Solution in the Presence of Oxalate and Acetate Anions

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A Hull cell was used to evaluate a chromium(III) plating bath based on the combination of oxalate and acetate anions. The bath contains chromium(III) sulfate, ammonium oxalate, sodium acetate, boric acid, potassium sulfate, sodium sulfate and sodium dodecyl sulfate (SDS). The working pH was 3.5, and all species were protonated. The chromium(III) plating bath had a faradaic efficiency of 37%, high covering power at 8.2 cm, low deposition potential of 7.3 V, and a deposition rate of 0.4 $\mu\text{m}/\text{min}$. Chromium coatings were obtained at a current density ($30\text{A}/\text{dm}^2$). This chromium(III) plating bath is competitive considering the state of the art of the electrodeposition of Cr(III). SDS was used as a surfactant to prevent the formation of polymeric oxides (olation reactions) by decreasing the number of nearby ions of Cr(III). Boric acid successfully maintained the pH as a buffer because after 2 h of the electrodeposition process, the pH values change only 0.2 units. The bath was analyzed after electrolysis to check the formation of Cr(VI) ions, and after 2 h of electrodeposition, this cation was not detected. The voltammetry results showed a very high noise with a potential of -0.8 V due to the abundant bubbles that formed and suggest a reduction in a step from Cr(III) to Cr(0). In the literature, the use of oxalate anions is explained by the reaction of exchange of ligands between these anions and the water of the first solvation sphere of Cr(III). In our study, it is postulated that electrostatic interactions of ion-ions and ion-solvents should be very present, and that oxalate and acetate anions are very likely to be in the second sphere of solvation and not in the first as other authors propose. The water molecules in the first solvation sphere are very stable and difficult to replace because they are exposed to two opposite electrostatic forces at their ends.

Keywords: chromium(III) plating bath, solvation sphere, ligands, chromium electrodeposits, hull cell.

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