A New Cathode Film Mechanism for Hexavalent Chromium (Cr) Electrodeposition Using Hybrid Additives

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The requirement of increasing cathode current efficiency, thus, to save labor and decrease the environment pollution, has motivated research topics on finding new additives for hexavalent chromium electrodeposition and studying their mechanisms as well. We have successfully developed a hybrid additive solution consisting of $KBrO_3$, Sulfonic acid (CH_3SO_3H), H_2SO_4 and DI water, which can increase the cathode current efficiency of hexavalent Cr electrodeposition from 17% to more than 28% at a current density of 60A/dm^2. [1]

The mechanism of the above hybrid additives for chromium electrodeposition was studied by electrochemical testing techniques including cathodic polarization curves, electrochemical impedance spectroscopy (EIS), and differential capacitance curves. The cathodic polarization curves showed that the additives increase the chromium deposition potential (Fig.1). The results of EIS and differential capacitance curves suggested that CH_3SO_3H could adsorb on the cathode and increase the reaction resistance (R_r). The effect of additives on cathodic process kinetics was investigated by measuring the volume of hydrogen (H_2) evolves in Cr electrodeposition. It was found, the additives greatly inhibited the hydrogen evolution reaction while had slight effect on Cr^{3+} oxidation reaction ($Cr^{3+} \rightarrow 3e^- + Cr^{6+}$). Inspired by these facts and the tradiontial cathode film mechanism, the authors proposed that a new cathode film, $CH_3SO_3(OH)_nCrOHCrO4+Cr(OH)_3CrOHCrO_4$, formed when hybrid additives were used. This new cathode film is referred to as hybrid cathode film because a part of traditional cathode film still existed. BrO_3^- did not take part in forming the hybrid cathode film but could dissolve it; thus, CrO_4^- could be reduced to Cr.

The proposed cathode film mechanism successfully explains some phenomena in Cr electrodeposition with hybrid additive, such as the depolarization effect of additives, the increase of reaction resistance and the decrease of differential capacitance. XPS (X-ray Photoelectron Spectroscopy) analysis of chromium deposits showed that the valence of Cr at the surface was different from that inside the films. Br, C and O elements can be co-deposited with Cr. Their mass fractions in the Cr deposits were measured by XPS with Ar^+ sputtering (Fig 2). The valence of Br at the surface was also different from that inside the film, which may be contributed to the dissolution of the hybrid cathode film. These results support the proposed hybrid cathode film mechanism.

REFERENCES

1. S. Guan, Q, Zhang and R.N Hu, "chromium electroplating technique with high current efficiency", Corrosion Science and Protection technique, 2001, (5), (Written in Chinese)

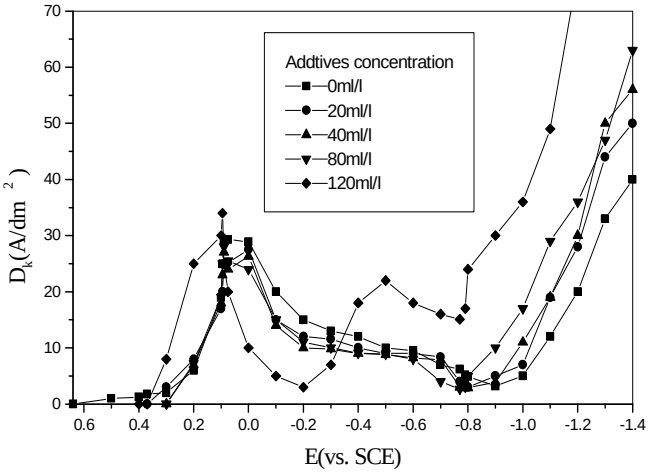

Figure 1. The effect of additives on cathode polarization curves

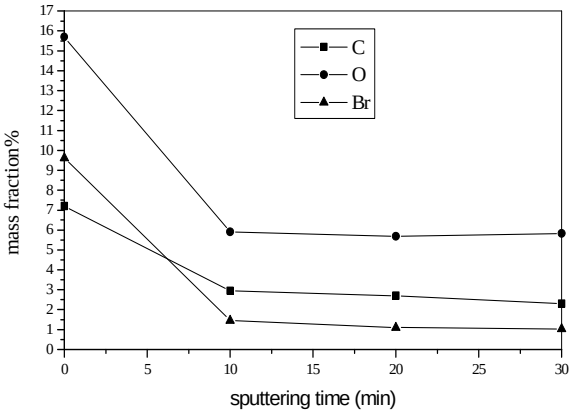

Figure 2. Mass fraction analysis of C, O, Br vs. sputtering time(~200Å/min) in Cr deposits by XPS