

Electrodeposition of Chromium from Chromium(III) Sulphate Solutions

Mika EGUCHI, Yuji KOMAGINE and Yoshihiro MOMOSE

Department of Materials Science, Faculty of Engineering, Ibaraki University.

Nakanarusawa 4-12-1, Hitachi, Ibaraki, 316-8511, Japan

INTRODUCTION

Chromium platings bring on material surfaces mirror-brightness, high corrosion resistance and also high wear resistance. These properties provide many application fields of this platings, such as decoration, electronic machines and parts of motor vehicles, etc. As most chromium plating baths contain toxic chromium(VI) ions as a source of chromium, it is desirable to replace chromium(VI) to less-toxic chromium(III). In this study, chromium(III) sulphate ($\text{Cr}_2(\text{SO}_4)_3$) baths were used and effects of bath composition, especially of additives, and plating conditions on properties of deposited films were investigated.

EXPERIMENTAL

Basic composition of the plating bath were composed of $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$, H_3BO_4 (as pH buffering agent), NH_4Br (as inhibitor for oxidation of Cr(III) to Cr(VI) at a counter electrode) and KCl (for high electrolytic conductivity). Ammonium formate (HCOONH_4) was used as a complexing agent and glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) as a brightening agent. Four baths with different compositions were prepared as shown in Table 1, and pH values were adjusted to 2.7 using H_2SO_4 or NH_4OH solutions.

The cathode chamber of a square-shaped electrolytic cell was separated from anode chamber by a filter paper diaphragm, and the catholyte was under a stirred condition. Bright nickel-plated copper plates ($2 \times 3 \text{ cm}^2$) and an iridium oxide coated titanium plate were used as cathodes (working electrodes) and anode, respectively. Plating procedures were carried out at 30°C with current densities of $1 \sim 30 \text{ A dm}^{-2}$ under coulombstatic conditions.

Prepared electrodeposits were analysed using X-ray diffraction (XRD) and EDAX, as well as using an optical and scanning electron microscopes (SEM).

RESULTS AND DISCUSSION

In bath A only green powdery precipitates were found on the cathode. The precipitates were presumably Cr_2O_3 , as oxygen and chromium were found by EDAX analysis. No metallic deposits were found in the bath A and almost same situation was found in the bath B. In baths C and D, both of which contained glycine, metallic deposits were obtained, and better appearance of the deposits was observed in the bath D. These observations suggested that existence of glycine seemed to be necessary for obtaining metallic electrodeposits and further addition of ammonium formate caused smoothness of deposits.

Current efficiency of the deposition using the

bath D was calculated from weight changes before and after the deposition process and amount of electricity passed through the cell. The current efficiency depended on the current density, as shown in Fig. 1, and a maximum of the efficiency was obtained at the current density of about $7\text{--}9 \text{ A dm}^{-2}$. Under 4 A dm^{-2} almost no deposition occurred, and best appearance of the deposits was observed at about $5\text{--}6 \text{ A dm}^{-2}$.

Deposited film had a broad diffraction line at about 74° in XRD patterns, as other possible diffraction lines were covered by those of nickel substrate. The diffraction line was ascribed to (200) of metallic chromium and possibly to (081) of chromium carbide Cr_7C_3 . Possibility of deposition of carbide was not rejected, as much larger amount of carbon than that of ordinary contamination was observed by EDAX measurement and carbon source was exist as glycine.

Table 1 Composition and a kind of bath.

Basic bath	$\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	110 g/L
	H_3BO_3	30 g/L
	NH_4Br	130 g/L
	KCl	210 g/L
Addition agent	HCOONH_4	30 g/L
	$\text{H}_2\text{NCH}_2\text{COOH}$	75 g/L
A bath	Basic bath	
B bath	Basic bath + HCOONH_4	
C bath	Basic bath + $\text{H}_2\text{NCH}_2\text{COOH}$	
D bath	Basic bath + HCOONH_4 + $\text{H}_2\text{NCH}_2\text{COOH}$	

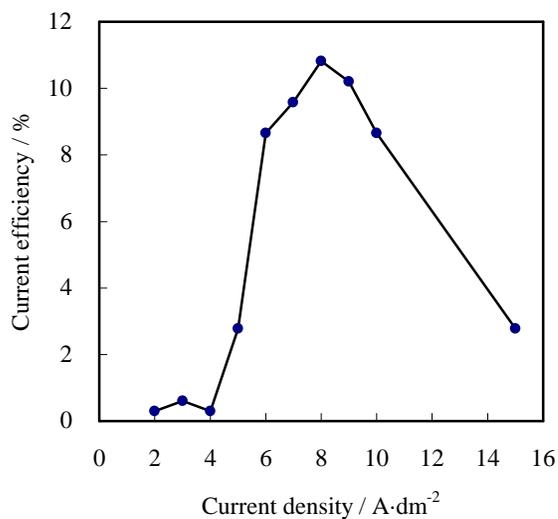


Fig. 1 Dependence of current efficiency on current density. (Bath D)