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# A STUDY ON COPPER DEPOSITION PROCESS DURING ANODIC OXIDATION OF ALUMINIUM ALLOY

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#### Abstract

The structure and composition of anodic films, formed on 6063 commercial aluminium alloy at constant current density of  $1.5 \text{A/dm}^2$  with various superimposed cathodic current ratio, in the range  $0 \sim 33\%$ , in the  $11\% \text{ H}_2\text{SO}_4$  with various concentration of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , in the range  $0 \sim 75 \text{ g/l}$ , without cathodic current are generally porous-type and no sign of Cu co-deposition appearance, suggesting that cathodic current is an important factor in the Cu co-deposition. Comparison with the anodic film thickness measurement results obtained from anodic film formed by direct anodic current and anodic film formed by superimposed various portion of cathodic current, the portion of cathodic current of input current increases with decrease of anodic film thickness and increases with increase of concentration of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$  in the anodic film.

Keywords: Anodic oxidation, Copper deposition, Aluminum alloy, Cathodic current, Anodic current,

### 1. INTRODUCTION

Most of electrolytic colouring processes are used to produce range of bronze or black finishes using electrolytes based on copper, nickel, cobalt or tin electrolytes. Various types of anodizing electrolytes can be used for producing the initial anodic coating<sup>1)-3)</sup> but, in practice, sulfuric acid coatings are almost always used <sup>4)</sup>. The work is anodized under conventional conditions

to anodic film thicknesses appropriate to the application, and it is then immersed in the metal salt solution and coloured, usually under A. C. condition<sup>4)–6)</sup>. In order to provide further understanding of electrolytic colouring process in this research, anodizing was performed 1 step colouring process i. e. anodic oxidation in situ metal codeposition process in metal salt electrolytes with various ratios of cathodic current.

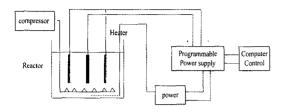


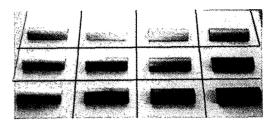
Fig. 1 Schematic diagram of experimental apparature setup

## 2. EXPERIMENTAL RESULTS

The structure and composition of anodic films, formed on 6063 commercial aluminium alloy at constant current density of  $1.5 \,\mathrm{A/dm^2}$  with various superimposed cathodic current ratio, in the range  $0 \sim 33\%$ , in the  $11\% \,\mathrm{H_2O_4}$  with various concentration of  $\mathrm{CuSO_4 \cdot 5H_2O}$ , in the range  $0 \sim 75 \,\mathrm{g/l}$ , without cathodic current are generally porous-type and no sign of  $\mathrm{Cu}$  co-deposition appearance, suggesting that cathodic current is an important factor in the  $\mathrm{Cu}$  co-deposition.

Increase Cu colour appearance of specimen surface with increase of cathodic current portion in input current is related to Cu deposition reaction by cathodic current. Furthermore, increase Cu colour intensity of specimen surface with increase of CuSO<sub>4</sub> concentration in 11% H<sub>2</sub>SO<sub>4</sub> electrolyte is also related to Cu concentration on specimen surface.

Elemental composition profiles, from X-ray photoelectron spectrometry, through the Cu coloured porous films, formed in 11% H<sub>2</sub>SO<sub>4</sub> +75g/ l CuSO<sub>4</sub>·5H<sub>2</sub>O aqueous electrolyte, show that Cu<sub>2</sub> S and Cu<sub>2</sub>O is formed in the inner anodic film region. Thus, it appears that development of Cu<sub>2</sub>O within the surrounding amorphous alumina is related to cathodic reaction effects, associated



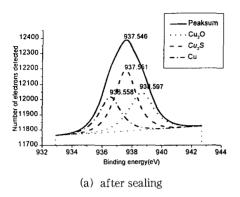
Wav Time	e DC	DC:AC:10:1	DC:AC:3:1	DC:AC:2:1
10min	Silver	Silver	Silver	Silver
20min	Silver	Light Brown	Light Brown	Brown
30min	Silver	Brown	Brown	Dark Brown

Fig. 2 Change of colour of anodic film(Current Density: 1.5Adm<sup>-2</sup>, Electrolyte Temp: 22±2℃ Current frequency: 27Hz, under Air agitation Constant current density mode, Counterelectrode: Pb

with the chemical oxidation process through the strong acidity in the pore of the anodic film. Furthermore, development of Cu<sub>2</sub>S in the anodic film is supposed to the co-deposition reaction process within the film by cathodic current.

Direct interpretation of the results of the formation of Cu<sub>2</sub>S and Cu<sub>2</sub>O in the film suggests that the film formed in 11% H<sub>2</sub>SO<sub>4</sub>+ CuSO<sub>4</sub> electrolytes by cathodic current portion of input current during anodizing, developed both formation of Cu and S by electrolytic reduction reaction process and formation of Cu<sub>2</sub>S and Cu<sub>2</sub>O by chemical reaction process under high acidity within the pore of anodic film.

This trend is also revealed in X-ray diffractometer analysis. From the results of the Cu concentration measurement by scanning electron microscopy with energy dispersive X-ray analysis, it is apparent that the concentration of Cu in the film formed in the electrolytes increases with increase of concentration of CuSO<sub>4</sub> amount in the electrolyte and decreases with decrease of ca-



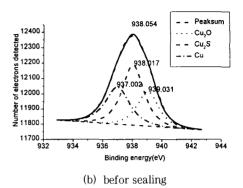


Fig. 3 XPS profile of anodic film formed in 10w/o H₂SO₄+75g/l CuSO₄ at constant density of 1.5A/dm² during 30 min at 22±2℃

thodic current portion of input current ratio to total input current.

Comparison with the anodic film thickness measurement results obtained from anodic film formed by direct anodic current and anodic film formed by superimposed various portion of c athodic current, the portion of cathodic current of input current increases with decrease of anodic film thickness and increases with increase of concentration of Cu<sub>2</sub>S and Cu<sub>2</sub>O in the anodic film.

## REFERENCES

- J. P. O'Sullivan, Ph. D. Thesis, University of Manchester (1978)
- G. E. Thompson, R. C. Furneaux, J. S. Goode and G. C. Wood, Trans. Inst. Metal Finish., 56, p159-179 (1978)
- 3. J. P. O'Sullivan and G. C. Wood, Proc. Royal Soc. London, A317, p511-535 (1970)
- 4. S. H. Tan, Ph. D. Thesis, University of Manchester (1982)
- G. E. Thompson and G. C. Wood, Nature, London, 290, p230–265 (1981)
- 6. G. A. Dorsey, Plating, 57, p1117-1135 (1970)