Studies on Immersion Deposition of Copper on Aluminium

K. KARUNAKARAN AND B. NAYAK

Depart of Chemistry, Indian Institute of Technology, Kharagpur-721 302

THE effect of chloride and copper (II) concentrations on the amonunt of copper deposited by displacement mechanism on commercial aluminium from a copper oxalato complex bath was studied. The amount of copper deposited was found to increase with the increase of chloride and copper (II) concentrations in the bath. At constant copper (II) concentration, the amount of copper deposited increased upto certain value of chloride ion concentration beyond which there was slight decrease. For a given chloride ion concentration the amouut deposited increased with increase on eopper (II) concentration. Using a higher but optimum chloride ion concentration and a higher copper (II) concentration, it was possible to deposit copper at a much faster rate. The deposits were smooth and fairly adherent but as expected somewhat porous.

INTRODUCTION

Imemrsion plating differs from electroplating and electroless plating in the sense that it does not require an external source of current or chemical reducing agents in the bath. Although such deposits are porous, the advantages of immersion coatings are their simplicity and minor capital expense for equipments. Immersion plating on aluminium has attracted the attention of many research workers since it is very much useful in providing an undercoat over which adherent electroplates may be built up subsequently (1,2).

It is well known that any metal having more negative standard reduction potential (E° value) will displace another metal which has less negative E° value from the aqueous solutions of its salts. Although the standard reduction potential aluminium ($E^\circ_{25^\circ} = -1.66$) is more negative than that of copper ($E^\circ_{25^\circ} = 0.337$) yet aluminium does not displace copper from the aqueous solutions of many of its simple and complex salts. But we have found that on the introduction of Cl^- ion (as KCl or in any other form) or Br^- ions into such solutions enable aluminium to displace copper from the solution which then forms a coating on aluminium itself. Thus immersion coating of copper on aluminium can be obtained in the presence of chlorides and bromides from the solutions containing copper (II) either in hydrated or in complexed form. In the present communication we report the results of our studies on the effect of $[Cl^-]$ on the immersion deposition of copper on aluminium from a copper oxalato complex bath.

EXPERIMENTAL

The compositions of the bath used are given below :

Bath I	Copper sulphate ($CuSO_4.5H_2O$)	....	3.0202 g/l
	Sodium oxalate ($Na_2C_2O_4$)	...	15.0354 g/l
	Potassium chloride	....	0.3339 — 1.3356 g/l
Bath II	Copper sulphate ($CuSO_4.5H_2O$)	....	6.0404 g/l
	Sodium oxalate ($Na_2C_2O_4$)	....	15.0354 g/l
	Potassium chloride	....	0.3339 — 1.6695 g/l
Bath III	Copper sulphate ($CuSO_4.5H_2O$)	....	9.0606 g/l
	Sodium oxalate ($Na_2C_2O_4$)	...	15.0354 g/l
	Potassium chloride	....	0.3339 — 1.6695 g/l

All the chemicals used in the bath were of BDH 'AnalaR' grade. The bath solution for immersion plating was prepared by adding concentrated solution of cupric sulphate to a hot solution of sodium oxalate and the deep blue coloured solution was made upto 1 litre in a volumetric flask after cooling it to room temperature and adding the necessary amount of potassium chloride.

Commercial aluminium wire of diameter 3 mm was used as the substrate. It was polished by 180, 1/0, 2/0, 3/0, 4/0 emery polishing paper successively, degreased with toluene, cleaned with

5% sodium hydroxide at 60°C, dipped in 50% nitric acid, cleaned with tap water, distilled water and then immediately dipped into the bath. The immersion plating was carried out at 30°C.

The amount of copper deposited was determined by the following method. The deposit was stripped wrth a little amount of concentrated nitric acid, diluted and dilute ammonium hydroxide solution was added so that the solution is slightly acidic. The solution was made upto 50 ml in a volumetric flask and 20 ml of this solution was pipetted out into a conical flask and titrated against 0.01 M ETDA solution using pyridine as buffer and pyrocatechol violet as the indicator as mentioned by A.I. Vogel (3).

RESULTS AND DISCUSSION

The immersion coating of copper on aluminium from the copper oxlaato complex dath was quite facile and took place readily at the room temperature (30°C). The experimental data relating to the amount of copper deposited produced a certain degree of scatter due to some inexplicable reason, but the general trend was not difficult to establish. The amount of copper deposited was found to increase not only with time of immersion but also with concentrations of Cl^- and Cu (II) present in the solution. For a given concentration of Cu (II) present in various forms, the amount of copper deposited increased with the concentration of Cl^- upto certain value of concentration beyond which there was a slight decrease (Fig. 1). At low Cl^- concentrations, such ions present in the bath

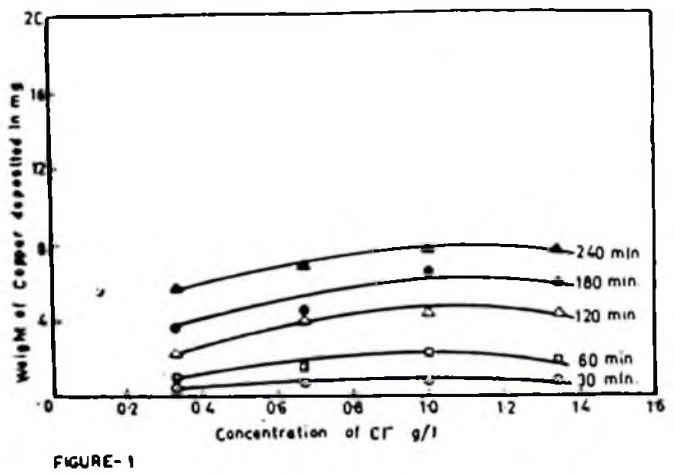


FIG. 1 Effect of $[Cl^-]$ amount of copper deposited for various periods of immersion : $[Cu(II)] = 3.0205$ g/l. Temperature : 30°C

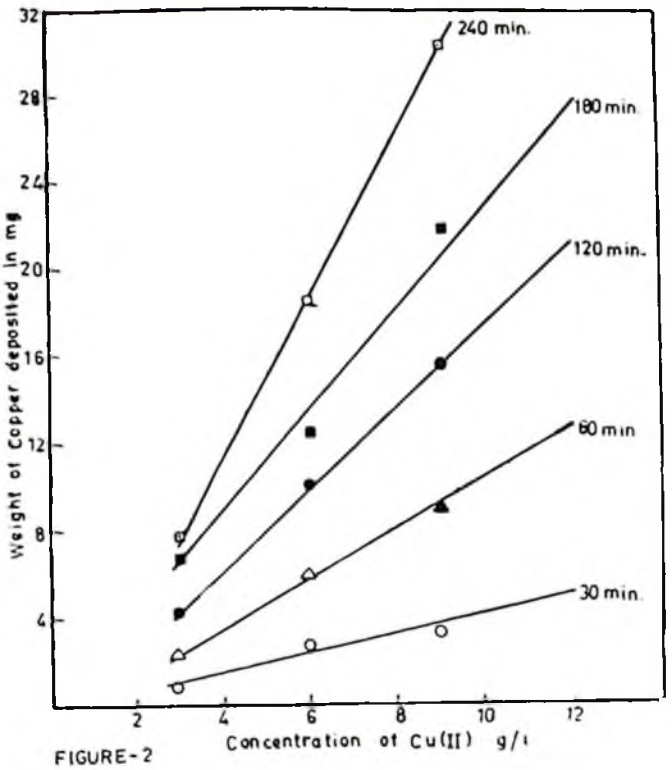


FIG. 2 Effect of Cu(II) concentration on the amount of copper deposited for various periods of immersion : $[Cl^-] = 1.0067$ g/l Temperature : 30°C

possibly promote the dissolution of aluminium into the solution through the overall process,

$$Al + 4\,Cl^- \longrightarrow AlCl_4^- + 3e^-$$

which may occur in one are several steps.

The electrons thus released reduce the Cu (II) present in the vicinity of the substrate surface to give the immersion coating of copper on aluminium It is not easy to state precisely the actual form of Cu (II) that receives the electrons released by process (I), but the most likely form appears to be Cu^{2+} (aq) which is formed by the dissociation of the oxalato complex

$$[Cu(C_2O_4)_2(H_2O)_2]^{2-} \rightarrow Cu^{2+}(aq) + 2H_2O + 2C_2O_4^{2-} \quad (II)$$

The lower rate of deposition at $[Cl^-]$ may be due to the fact that some of the Cu^{2+}(aq) ions may get converted into $CuCl^+$ or higher chloro complexes to which electron transfer is somewhat hindered.

A mentioned earlier the amount of copper deposited at a given $[Cl^-]$ increased with the concentration of Cu (II). Fig. 3 is the typical graph which shows the effect of Cu (II) concentration at fixed $[Cl^-]$. At higher concentration of

Cu (II) the rate of deposition was much faster but the quality of the deposit was somewhat inferior as more number of pits started to appear. In all the cases the amount of copper deposited ihcreased linearly with time (Fig. 3) which means that the

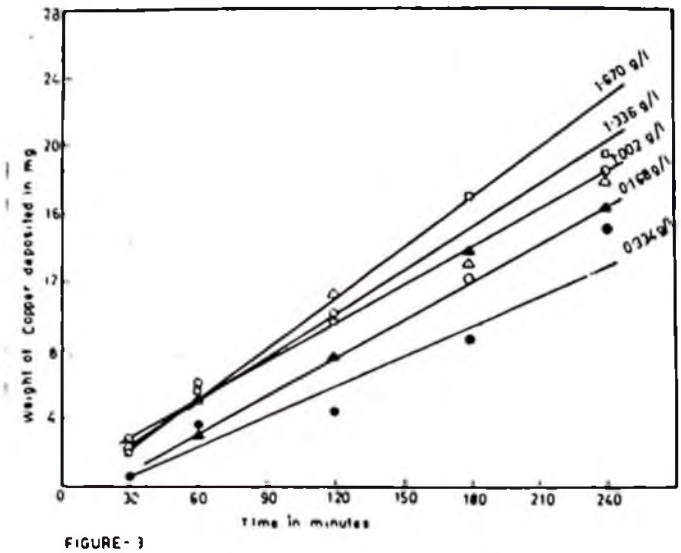


FIGURE- 3

FIG. 3 Effect of time period of immersion on the amount of copper deposited at various chloride ion concentration : *[*Cu(II)*]* = 6.0404 g/l Temperature : 30°C

coating continued to remain porous even after attaining highar thickness of the order of 12μ. The coating thickness achieved over a period of 4 hours for various runs are shown in Table 1.

The coatings in most cases except those obtained at higher Cu(II) and *[*Cl^-*]* and those above 5μ thick were smooth, fairly adherent but

TABLE 1

Bath composition		Thickness in μ (micron)
Concentration of Cu (II) g/l	Concentration of Cl^- g/l	
3.0202	0.3339	2.164
3.0202	0.6678	2.660
3.0202	1.0017	2.989
3.0202	1.3356	2.934
6.0404	0.3339	5.851
6.0404	0.6678	6.237
6.0404	1.0017	7.099
6.0404	1.3356	6.823
6:0404	1.6695	7.504
9.0606	0.3339	6.695
9.0606	0.6678	8.295
9.0606	1.0017	11.660
9.0606	1.3356	8.551
9.0606	1.6695	10.360

porous. Above 5μ thickness the coatings started to peel off on bending through an angle of 180°,

REFERENCES

1. J. Fischer, *U.S. Patent*, 2, 036, 962 (1936).
2. M. F. McFadden, *'Aluminium finishing seminar'*, Paper AP—14 (1968).
3. A. I. Vogel, *'Quantitative Inorganic Analysis'*, The English Language Book Society and Longman, London, 3rd edition, 1961, page 445.