

# *High-rate plating of aluminium from the bath containing aluminium chloride and lithium aluminium hydride in tetrahydrofuran*

MASAKI YOSHIO\* AND NOBUHIKO ISHIBASHI†

\* *Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan*

† *Department of Applied Analytical Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan*

Received 13 December 1972

---

An electrolyte for the high-rate plating of aluminium from the tetrahydrofuran solutions of aluminium chloride and lithium aluminium hydride has been developed. A smooth and coherent deposit of aluminium has been obtained at the current density of  $18 \text{ A dm}^{-2}$  without stirring, whereas the conventional diethyl ether solvent bath allows good plating up to  $5 \text{ A dm}^{-2}$  under the same condition. The current densities applicable are increased with an increase in the molar fraction of aluminium chloride in tetrahydrofuran. The conductivity of the plating solution was measured at various molar ratios of aluminium chloride to lithium aluminium hydride. A plateau region of the conductivity curve plotted against the molar ratio is consistent with the composition of the plating bath giving a good plating. The plateau region is enlarged with an increase in total aluminium concentration.

---

## **1. Introduction**

The electrodeposition of aluminium from organic electrolyte systems has received considerable attention. Commercial applications of aluminium electrodeposition have been tried by using the NBS bath [1]. Diethyl ether, anhydrous aluminium chloride and lithium aluminium hydride are the components in the NBS bath. Schmidt and his co-workers [2] at General Electric electroformed 76 cm diameter parabolic mirrors. The NBS bath was used to electroform solar mirrors by the workers [3] at Electro-Optical Systems, and also used to clad uranium fuel elements by Battelle Memorial Institute [4]. High surface area electrodeposited aluminium for electrolytic capacitors was obtained by

Sprague Electric [5]. Volatility of ethyl ether and limited life were among the disadvantages of the NBS bath [6]. In order to eliminate the above disadvantages, a method was described for electrodepositing aluminium from tetrahydrofuran [7] or tetrahydrofuran-benzene mixed solution [8] of aluminium chloride and lithium aluminium hydride. The workers [9] at Nisshin Steel Co. scaled up the tetrahydrofuran-benzene process to a pilot plant in which they electrodeposited aluminium on alloy steel for integrated circuits. In a working plant, deposition of aluminium is carried out continuously by using a flow system.

High-rate plating is desirable from an industrial viewpoint. Holland [10] developed the bath containing formamide-nitrobenzene-benzoyl chloride solutions of aluminium chloride

and operated at 300–325 A ft<sup>-2</sup>, although it was reported that the bath is extremely difficult to operate [1]. Murphy and Dumas [12] claimed the deposition of bright, adherent aluminium from solutions of aluminium chloride and an amine dissolved in ether, and operated at 20–120 A ft<sup>-2</sup>. Generally, an electrolysis under high current densities is possible from the solutions of a low melting point eutectic. Beach and his co-workers [6] developed the Etmac bath composed of aluminium chloride-aluminium dichlorohydride-2-ethoxyethyl trimethylammonium chloride-diethyl ether complex, and Hisano and his co-workers [13] aluminium bromide-N.N dimethyl aniline complex. These baths operated at 15.6 and greater than 30 A dm<sup>-2</sup>, respectively.

The present paper describes a hydride type tetrahydrofuran solvent bath in view of high current densities available. Since aluminium chloride is one of the constituents of the bath, it was thought advisable to investigate the behaviour of baths containing higher concentrations of aluminium. Increasing the aluminium chloride content in the bath allowed a satisfactory deposit up to a current density of 18 A dm<sup>-2</sup>.

## 2. Experimental

### 2.1. Preparation of the bath

The plating solution was prepared by adding a tetrahydrofuran solution of lithium aluminium hydride to a saturated solution of aluminium chloride in the presence of excess undissolved aluminium chloride powder. Undissolved aluminium chloride is smoothly dissolved by the addition of lithium aluminium hydride solution. A tetrahydrofuran solution of lithium aluminium hydride was obtained by refluxing for 5–8 h. A considerable amount of undissolved residue was removed by filtration. The addition of aluminium chloride to tetrahydrofuran must be made carefully, otherwise foaming and decomposition of the solvent occurs which affect the conductivity of the plating solution. Cooling by dry ice-acetone is necessary. The freshly prepared solution of aluminium chloride is colourless, and then turns to light yellow with increasing temperature. Addition of hydride solution to the

aluminium chloride solution was made at 0 to –20°C.

### 2.2. Solubility measurements

The solubility of aluminium chloride is increased, when the solution is coloured by the violent reaction between aluminium chloride and tetrahydrofuran. Therefore, benzene (20 vol %)-tetrahydrofuran mixed solvent was used as a solvent. A slight excess of aluminium chloride was put in a benzene solution, and then tetrahydrofuran was added slowly with cooling. The solubility of aluminium compounds at the various concentrations of lithium aluminium hydride was determined by the analysis of aluminium in a supernatant portion of the solution after the separation of undissolved aluminium chloride.

### 2.3. Conductivity measurements

The conductivity of the plating solution containing a high concentration of aluminium gives various values whether the aluminium chloride solution used is colourless or not, in addition to its time dependency. Accordingly, the conductivity measurements were carried out on freshly prepared solutions each time the molar ratio of the solutes was varied, and the measurements were made just after preparation.

## 3. Results and discussion

### 3.1. Increase in the solubility of aluminium chloride by addition of lithium aluminium hydride

Aluminium chloride dissolves in pure tetrahydrofuran up to the concentration of 0.8 mol l<sup>-1</sup> at 20.0°C. The solubility is higher than 0.8 mol l<sup>-1</sup> when the solution is coloured by the violent dissolution reaction. It has been said that the plating solution is best prepared by making separate, ethereal solutions of aluminium chloride and of lithium aluminium hydride, and mixing them [14]. The aluminium content of the plating solution prepared by the mixing method is, however, lower than that of the NBS bath using diethyl ether as solvent.

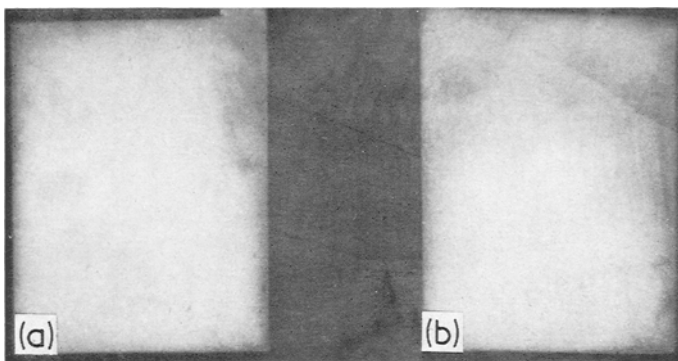


Fig. 2. Appearance of aluminium deposits ( $1.5 \times 2.0$ )  $\text{cm}^2$  from tetrahydrofuran solution of  $1.17 \text{ mol l}^{-1} \text{ AlCl}_3$ - $0.23 \text{ mol l}^{-1} \text{ LiAlH}_4$   
(a) c.d. =  $10 \text{ A dm}^{-2}$  (b) c.d. =  $15 \text{ A dm}^{-2}$

As shown in Fig. 1, the solubility of aluminium chloride is increased by the small addition of lithium aluminium hydride. The curve shows that two or three moles of aluminium chloride, supposedly, react with one mole of lithium aluminium hydride to form soluble mixed hydrides. But at concentrations of lithium aluminium hydride greater than  $0.3 \text{ mol l}^{-1}$ , the measurements cannot be made because of the presence of a viscous layer.

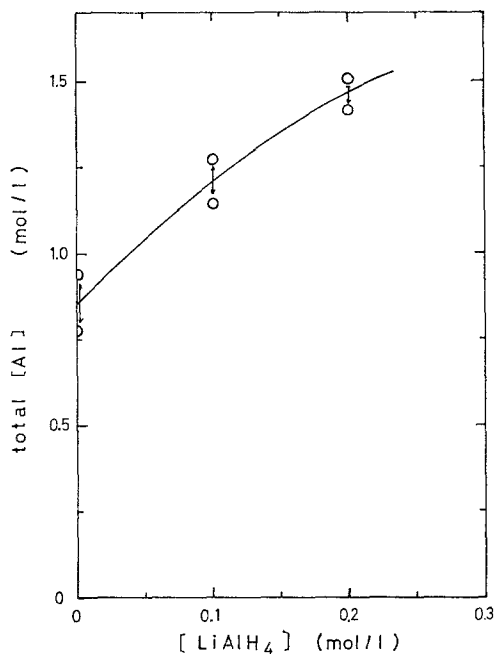


Fig. 1. Effect of addition of lithium aluminium hydride on the solubility of aluminium chloride in tetrahydrofuran (80 vol %)-benzene (20 vol %) mixed solution at  $20^\circ\text{C}$ .

### 3.2. Electrodeposition of aluminium at high current densities

A current density less than  $5 \text{ A dm}^{-2}$  tends to give a smooth aluminium deposit from the conventional tetrahydrofuran bath [7, 8], as well as from the NBS bath. As the current density is increased, the deposits tend to become nodular, and at current densities greater than  $10 \text{ A dm}^{-2}$  dendritic growth becomes rapid. Table 1 shows the current density ranges applicable. At a molar ratio of  $\text{AlCl}_3/\text{LiAlH}_4$  equal to 2, current densities less than  $5 \text{ A dm}^{-2}$  may be used. By further

Table 1. Effect of the bath composition and current density on electroplating

Molar ratio [AlCl <sub>3</sub> ]/[LiAlH <sub>4</sub> ]	Current density, A dm <sup>-2</sup>						
	1	3	5	8	10	13	15 18
1	○	○	⊗	⊗			
2	○	○	○	△	⊗	⊗	
3	○	○	○	○	○	○	⊗ ⊗
5	○	○	○	○	○	○	○ ○

[AlCl<sub>3</sub>] + [LiAlH<sub>4</sub>] =  $1.50 \text{ mol l}^{-1}$ , tetrahydrofuran  
 ○ silver-white coherent deposit; △ silver-white deposit with dendrites at edges; ⊗ black deposit.

increasing the aluminium chloride concentration in the bath under the condition of constant total aluminium content, the applicable current density range is greatly enlarged. Smooth metallic deposits were obtained at  $18 \text{ A dm}^{-2}$  from the high molar ratio ( $>5$ ) bath. Use of stirring made an electrolysis using more than  $30 \text{ A dm}^{-2}$ , possible. Most electrolyses were carried out at  $40\text{--}50^\circ\text{C}$  because of the ohmic heating of the baths. The appearance of the deposited aluminium obtained after 10 min of electrolysis is seen in Fig. 2. The deposits shown in Fig. 2 were obtained from a solution containing the minimum amount of aluminium chloride for a high current density operation. The use of a higher aluminium chloride concentration, for example  $1.50 \text{ mol l}^{-1} \text{ AlCl}_3$  and  $0.23 \text{ mol l}^{-1} \text{ LiAlH}_4$ , made the deposit glossy.

The composition of the high-rate plating bath is as follows:

LiAlH <sub>4</sub>	at least $0.2 \text{ mol l}^{-1}$
AlCl <sub>3</sub> /LiAlH <sub>4</sub>	over 5
solvent	tetrahydrofuran

Higher current density electrolyses are possible, the higher the concentration of the total aluminium and the higher the molar ratio of aluminium chloride to lithium aluminium hydride. However, it is difficult to prepare a bath solution containing more aluminium chloride than  $2.5 \text{ mol l}^{-1}$ .

According to Brenner [15], many addition agents have been added to the bath in an attempt to obtain thick deposits. From a tetrahydrofuran solvent bath, thick deposits were easily obtained without addition agents by controlling the bath

composition. For example, deposited aluminium of 2–3 mm thickness on average and about 5 mm at edges, was obtained from the bath of molar ratio 3, whereas it was difficult to deposit aluminium of 1 mm thickness from molar ratio 1 baths under a constant concentration of aluminium of  $1.30 \text{ mol l}^{-1}$ . The bath containing the higher concentration of aluminium chloride is desirable to obtain a good deposit of aluminium on substrates with complicated shapes.

### 3.3. Specific conductivity of the bath

Fig. 3 shows the conductivity of the bath at various molar ratios of aluminium chloride to lithium aluminium hydride. The conductivity curves exhibit a plateau, in which range good deposits are obtained. The plateau is enlarged by increasing the total aluminium concentration.

Since the conductivity varies with time, the

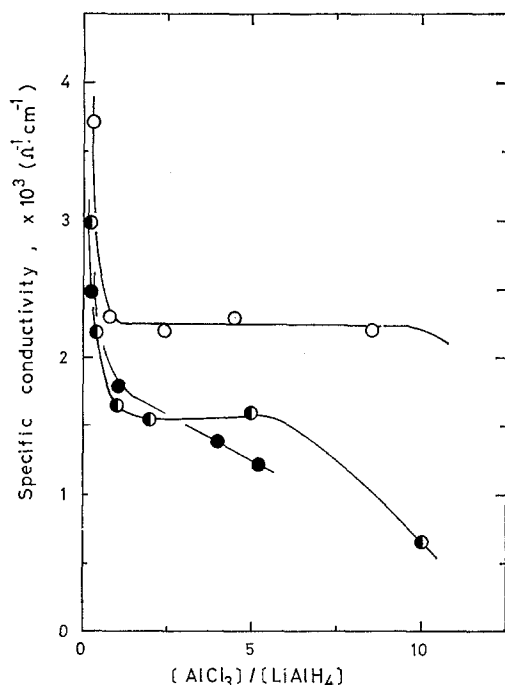


Fig. 3. Specific conductivity of a tetrahydrofuran (tetrahydrofuran-benzene mixed) solution of aluminium chloride and lithium aluminium hydride as a function of the molar ratio of aluminium chloride to lithium aluminium hydride at 20°C.

(○)  $[\text{AlCl}_3] + [\text{LiAlH}_4] = 1.25 \text{ mol l}^{-1}$ , tetrahydrofuran.

(○)  $1.00 \text{ mol l}^{-1}$ , tetrahydrofuran (55 vol %)–benzene.

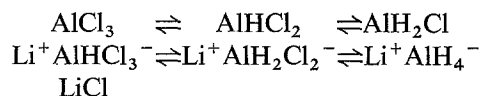
(●)  $0.80 \text{ mol l}^{-1}$ , tetrahydrofuran.

conductivity is measured just after the preparation, and the coloured aluminium chloride solution is not used for the conductivity measurements. However, the electroplating bath prepared from coloured aluminium chloride solution and lithium aluminium hydride solution has a larger conductivity, about 1.5 times, than that of the bath made from colourless aluminium chloride solution, and has no plateau range in the conductivity curve. Use of slightly coloured solution may be profitable because of its high conductivity.

### 3.4. Complex species in the bath

The aluminium dissolved from the anode does not deposit at the cathode from the NBS bath [15]. Life tests of the tetrahydrofuran solvent bath showed, however, that operations were not limited to consuming only the initial aluminium content. For example, 10.8 g of deposited aluminium were obtained from 170 ml of the bath consisting of tetrahydrofuran solutions of  $0.95 \text{ mol l}^{-1} \text{ AlCl}_3$  and  $0.30 \text{ mol l}^{-1} \text{ LiAlH}_4$ , and further electrolysis was possible. The amount of aluminium deposited was about 2.5 times that of the aluminium chloride used in the preparation of the bath.

The solution prepared from various molar ratios of aluminium chloride to lithium aluminium hydride contain the following chemical species [16]:



and the principal current-carrying ions are  $\text{Li}^+\text{AlHCl}_3^-$  and  $\text{Li}^+\text{AlH}_2\text{Cl}_2^-$  in tetrahydrofuran. Lithium chloride is insoluble in diethyl ether which is the solvent of the NBS bath, although it is dissolved in tetrahydrofuran up to  $1.5 \text{ mol l}^{-1}$  at 25°C. Accordingly, the main species at the higher molar ratio than 3 are  $\text{AlCl}_3$ ,  $\text{AlHCl}_2$  and  $\text{Li}^+\text{AlHCl}_3^-$  in diethyl ether, and  $\text{AlCl}_3$ ,  $\text{AlHCl}_2$ ,  $\text{LiCl}$  and  $\text{Li}^+\text{AlHCl}_3^-$  in tetrahydrofuran, respectively. Furthermore, in diethyl ether solution the species  $\text{Li}^+\text{AlH}_2\text{Cl}_2^-$  cannot exist at the lower molar ratio than 3 because of the formation of lithium chloride precipitate. The absence of  $\text{Li}^+\text{AlH}_2\text{Cl}_2^-$  and

LiCl species seems to explain the different anodic dissolution behaviour of Al in the tetrahydrofuran and NBS baths. The exact nature of the species present in the plating solution is complex. Aggregates such as triplet could be formed in the solutions containing large concentrations of aluminium,  $\text{Li}_2\text{AlHCl}_3^+$ ,  $\text{Li}(\text{AlHCl}_3)_2^-$ ,  $\text{Li}_2\text{AlH}_2\text{Cl}_2^+$ ,  $\text{Li}(\text{AlH}_2\text{Cl}_2)_2^-$ .

#### Acknowledgements

The authors wish to express their thanks to the Nisshin Steel Co. Ltd. for financial support of this work, and to Mr T. Sonoda for his assistance in the experiments.

#### References

- [1] J. J. Utz and S. Kritzer, *Materials in Design Engineering*, **49** (1959) 88.
- [2] F. J. Schmidt and I. J. Hess, *Plating*, **53** (1966) 229
- [3] R. N. Hanson, D. G. DuPree and K. Lui, *Plating*, **55** (1968) 347.
- [4] J. G. Beach and C. L. Faust, *J. Electrochem. Soc.*, **106** (1959) 654.
- [5] R. J. Roethlein, *J. Electrochem. Soc.*, **117** (1970) 931.
- [6] J. G. Beach, L. D. McGraw and C. L. Faust, *Plating*, **55** (1968) 936.
- [7] N. Ishibashi, Y. Hanamura, M. Yoshio and T. Seiyama, *Denki Kagaku*, **37** (1969) 73.
- [8] N. Ishibashi and M. Yoshio, *Electrochim. Acta*, **14** (1972) 1343.
- [9] M. Koike and K. Sekimoto, *Kinzoku*, No. 4 (1972) 77.
- [10] B. O. Holland, *J. Australian Inst. Metals*, **6** (1961) 212.
- [11] I. A. Menzies and D. B. Salt, *Trans. Inst. Metal Finishing*, **43** (1965) 186.
- [12] N. F. Murphy and A. C. Dumas, *Proc. Amer. Electroplater's Soc.*, **43** (1956) 162.
- [13] T. Hisano, T. Terazawa, I. Takeuchi, S. Inohara and H. Ikeda, *Bull. Chem. Soc. Japan*, **44** (1971) 599.
- [14] F. A. Clay, W. B. Harding and C. J. Stimetz, *Plating*, **56** (1969) 1027.
- [15] A. Brenner, *Adv. Electrochem. and Electrochem. Eng.* **5** (1967) 205.
- [16] M. Yoshio, N. Ishibashi, H. Waki and T. Seiyama, *J. Inorg. Nucl. Chem.*, **34** (1972) 2439.