JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 235–239

A xylene electrolyte modified by trimethylchlorosilane for electrodeposition of aluminium

A. LISOWSKA-OLEKSIAK, S. BIAŁŁOZÓR, M. LIEDER

Technical University of Gdańsk, Faculty of Chemistry, Majakowskiego 11/12, 80-952 Gdańsk, Poland

Received 17 January 1991; revised 23 June 1991

The addition of 2–5 vol % of trimethylchlorosilane to a 2 M solution of $AlBr_3$ in xylene gives a very convenient aluminium electroplating bath. Tendency to dendritic growth ceases and the quality of aluminium improves. Electrodeposition proceeds with high cathodic efficiency. The additive has extended the use of the electrolyte up to 1 year.

1. Introduction

Among electrochemical methods proposed for obtaining aluminium coatings electrolysis of aromatic electrolytes composed of alkylbenzene solutions is the simplest and cheapest [1–3]. Unfortunately, in spite of great interest in aromatic electrolytes, they have not been used in practice up to the present due to their low conductivity which causes bad current distribution and dendritic metal growth. As a consequence the aluminium coatings are loose and highly porous. Recently, methods have been proposed for obtaining compact and thick aluminium coatings from 2 M $AlBr_3$-xylene electrolytes [4]. Pulse electrolysis suppresses dendritic growth. Also the application of additives such as $SnBr_2$ or 2,2′-dipirydyl gives good, adherent and compact deposits. Unfortunately, the proposed method based on the addition of a small quantity of $SnBr_2$ has a general drawback. It is difficult to maintain the concentration of the additive at the same level throughout the bath working period. In this paper a very convenient method of modification of Al_2Br_6-xylene electrolytes by addition of trimethylchlorosilane $(CH_3)_3SiCl$ (TMCS) has been proposed.

2. Experimental details

The electrolytes were prepared by dissolution of $AlBr_3$ in xylene and addition of TMCS. Pure anhydrous $AlBr_3$ (p.a.) and TMCS (p.a.) were used without further purification. The solvent was dried on 0.4 nm sieves and then distilled over sodium. All operations with the solution were carried out in a dry glove box under an argon atmosphere.

An undivided electrolysis cell was used in all experiments. An aluminium rod (99.9% purity) was used as anode and also as reference electrode. Electrodeposition was carried out on a polycrystalline disc platinum electrode (geometrical area of $0.2\,mm^2$) and a copper sheet (99.99% purity) with geometrical surface of $1\,cm^2$. Linear scan voltammetry (LSV) chronoamperometry (CA) and constant current electrolysis were applied. LSV, CA and electrolysis measurements were carried out at 303 K. Scanning electron microscopy was employed to indicate the morphology of deposited layers. A more detailed description of the experimental techniques was given in earlier publications [5, 6].

3. Results and discussion

It is well known that aluminium can be deposited from aromatic solutions provided that the electrolyte is aged for at least 3 days [1, 4]. In the fresher electrolytes no electrodic process takes place. However, after introducing 2 vol % of $(CH_3)_3SiCl$ to a 2 M solution of $AlBr_3$ in xylene a brown layer containing mainly silicon can be deposited. Figure 1 shows the morphology of such a deposit obtained in the first day. Figure 2 shows the LSV curve recorded in the same solution 2 days after preparation. The cathodic process proceeds with a significantly higher overpotential and, moreover, oscillations can be seen in the anodic branch of the curve. Characteristic data for the LSV curves are shown in Table 1. The shape of the cathodic branch of the curve indicates that the electroreduction process is accompanied by an increase in the surface

Table 1. Some characteristic data for aluminium electrodeposition by voltammetry in 2 M $AlBr_3$ solution in xylene with TMCS, on the Pt electrode. Scan rate: $0.01\,V\,s^{-1}$*

[*TMCS*] (*vol %*)	E_λ (V_{Al})	E_{nuc} (V_{Al})	E_{pa} (V_{Al})	j_c ($-0.1\,V\rightarrow$) (*mA cm*$^{-2}$)	j_c ($-0.05\,V\leftarrow$) (*mA cm*$^{-2}$)
–	−0.12	−0.07	0.12	2.8	1.75
2	−0.12	−0.05	0.10	5.0	3.30
5	−0.12	−0.05	0.09	6.0	4.8
6†	−0.20	−0.18	0.13	–	–
6	−0.12	−0.05	0.10	8.0	5.0
8	−0.12	−0.05	0.06	8.0	4.2

* *Nomenclature*:

E_λ	switching potential
E_{nuc}	nucleation potential
j_c ($-0.1\,V\rightarrow$)	cathodic current density measured at an overpotential of −0.1 V in the forward branch
j_c ($-0.05\,V\leftarrow$)	cathodic current density measured at an overpotential of −0.05 V in the backward branch

† Voltammogram recorded during the first day of electrolyte use.

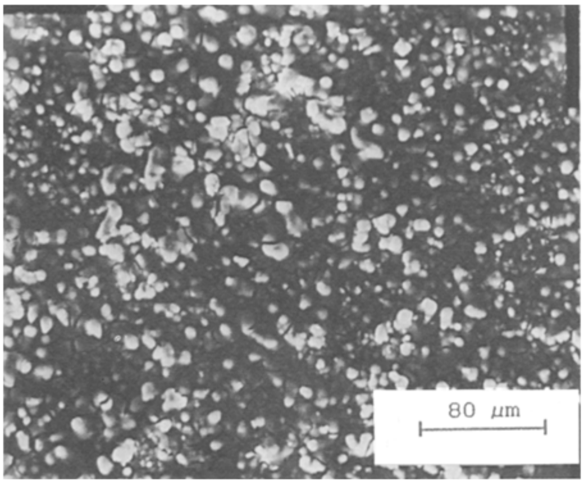

Fig. 1. SEM of a coating on the copper electrode on the first day of using the electrolyte composed of 2 M $AlBr_3$ and 6 vol % of TMCS in xylene, j_c = 12 mA cm^{-2}, t_c = 1 h.

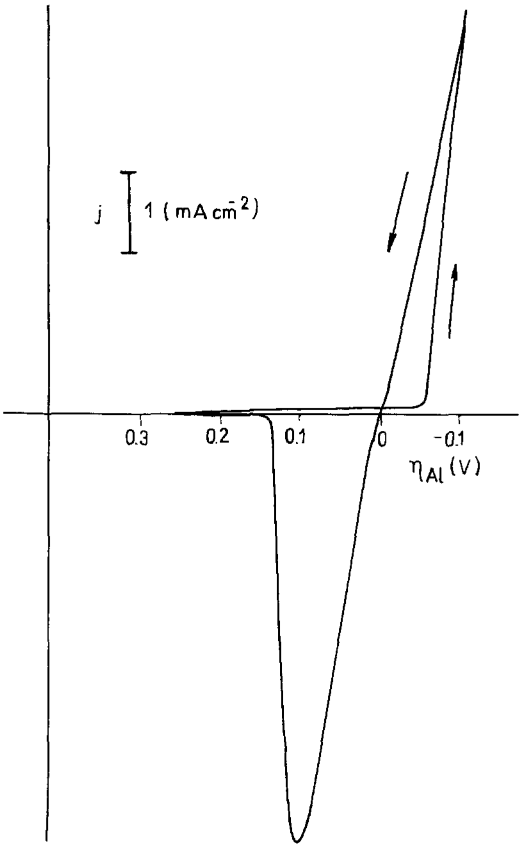

Fig. 3. Voltammogram recorded in the aged electrolyte composed of 2 M $AlBr_3$ and 2 vol % of TMCS in xylene on the Pt electrode. Scan rate 0.01 V s^{-1}.

area. However, the observed oscillations of the anodic current may be brought about by a passive layer being formed. It may be assumed that the oscillations in the anodic branch of the LSV curve are caused by the semiconductor silicon dissolution process. The oscillations ceased in the solution aged for at least 3 days. Similar oscillations were also observed in the reduction–oxidation process of SiF_6^- in molten fluoride media [7].

Figure 3 shows the LSV curve obtained on the Pt electrode in the aged solution containing 2 vol % of $(CH_3)_3SiCl$. The shape of the curve is typical for the electrodeposition of the metal in a reversible process with interfacial control [8]. Figure 4 shows the voltammogram in the same solution at a high scan rate of 0.3 V s^{-1}. In the anodic branch an extra hump can be seen, which does not show up at the low scan rate. The hump may indicate the presence of two chemical species in the surface layer. The cathodic current efficiencies calculated from the voltammograms obtained at a low scan rate are higher than 90% (Table 2). The cathodic deposits obtained from the aged solutions contain only aluminium. Silicon was detected only at a contamination level (below 1%). The corrosion potentials (E_{corr}/SCE) of the aluminium coatings on copper, measured in 0.1 M $(Na_2SO_4)_{aq}$ are shown in Table 3. The values of E_{corr} are similar to the potentials of the passive aluminium electrodes.

The addition of 2–5 vol % of silane to the electrolyte resulted in an increase in the cathodic current and a decrease in the overpotential of nucleation (E_{nuc}). A further increase in the TMCS concentration up to 8 vol % did not influence the values of the cathodic

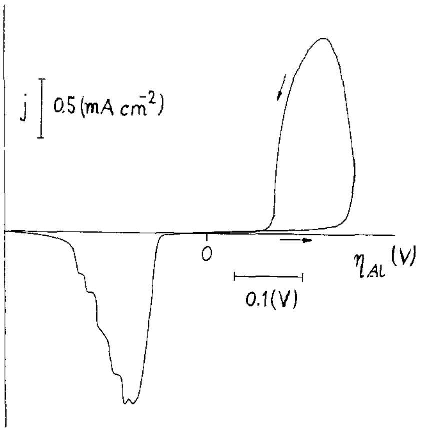

Fig. 2. Voltammogram after 2 days of the use of the electrolyte composed of 2 M $AlBr_3$ and 6 vol % of TMCS in xylene on the platinum electrode. Scan rate: 0.01 V s^{-1}.

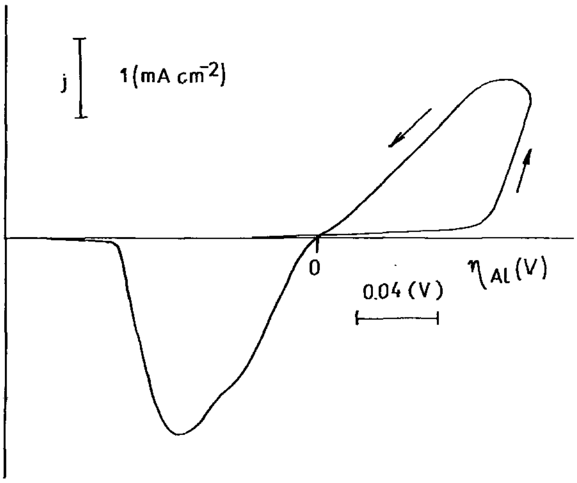

Fig. 4. Voltammogram recorded in the aged electrolyte composed of 2 M $AlBr_3$ and 2 vol % of TMCS in xylene on the platinum electrode. Scan rate: 0.30 V s^{-1}.

Table 2. The cathodic current efficiency (W_{Al}) of aluminium electrodeposition from 2 M $AlBr_3$ solution in xylene

Electrode	*[TMCS] (vol%)*	*Storage time (days)*	j_c *(mA cm^{-2})*	t_c *(min)*	E_c *(V)*	*Method*	W_{Al} *(%)*
Cu	2	4	12	60	–	gravim	70
		30	12	60	–		70
		365	12	60	–		70
Pt	2	3	–	–	–	LSV	98
		30	–	–	–	LSV	98
		4	–	0.5	−0.1	CA	99
		4	–	1	−0.1	CA	99
		4	–	2	−0.1	CA	98
Cu	6	1	12	60	–	gravim	40
Pt		1	–	–	–	LSV	68
Cu		4	12	60	–	gravim	70
Pt		4	–	–	–	LSV	98

current densities, j_c (see Table 1). It may be assumed that TMCS affects the reaciton kinetics due to its surface activity.

The addition of TMCS also brought about radical changes in the structure of the deposited layer. In our previous papers [4, 6] it was shown by CA and SEM that nucleation and growth of aluminium from 2 M $AlBr_3$-xylene electrolytes proceeds as an instantaneous process with three dimensional (3-D) crystal growth. With few centres of crystallization the growth results in porous coatings. The CA results indicate that the addition of TMCS to the electrolyte changes the type of crystallization from 3-D to two dimensional (2-D). The slope of the log (j_c) against log (t_c) plots for a typical CA curve (Fig. 5) is close to 1, which is characteristic for 2-D instantaneous crystallization. A typical electron micrograph of the aluminium coatings is shown in Fig. 6. It is well known that silanes are often used as a means of modifying the electrode surface [9, 10]. The electrode is modified by binding silanes to the surface through oxide bridges between silicon and the metal atoms. In our studies of the crystallization of aluminium the electrode surfaces were cleaned in such a way that they were free from oxides. Nevertheless in order to show that silane is bound to the electrode surface through the oxide bridges, further experiments, also on the electrochemically oxidized platinum electrode, were carried out in the solution without TMCS. The electrodes were exposed to silane separately.

The platinum electrodes were prepared for the experiments by several methods:

(i) A standard procedure based on cleaning with diamond paste, activation in 30% H_2SO_4, rinsing and drying was used. Next the electrode was transferred to a dry box where, under nitrogen, a final polishing on filter papers was performed (denoted as Pt–X).

(ii) The clean and polished electrode was exposed to $(CH_3)_3SiCl$ for 0.5 min (denoted as Pt–Si–X).

(iii) The clean and polished electrode was exposed to a 2 M $AlBr_3$ solution followed by immersion in TMCS for 0.5 min (denoted as Pt–X–Si).

(iv) The electrode was electrochemically oxidized in a 1 M H_2SO_4 solution [10], then rinsed and dried (denoted as Pt–O–X).

(v) The dry, clean and oxidized platinum electrode was exposed to TMCS (denoted as Pt–O–Si).

All these electrodes were used in CA studies of the crystallization of aluminium in 2 M $AlBr_3$ solution without TMCS. The (log j_c against log t_c) plots yielded straight lines, the slopes of which, shown below, allow identification of the crystallization type [11].

Table 3. The corrosion potentials (E_{corr}) of aluminium coatings on copper substrate, measured at 1 h exposure in 0.1 M Na_2SO_4 aqueous solution

[TMCS] (vol%)	*Storage time (days)*	*Deposition duration (h)*	j_c *(mA cm^{-2})*	E_{corr} *(V/SCE)*	*Deposit*
none	4	2	15	−0.34†	light, 3-D, W_c = 70%
2	3	1	12	−0.43	light, 2-D, W_c = 70%
6	1	1	15	−0.1	brown, porous, W_c = 45%
6	4	1	12	−0.46	light, 2-D, W_c = 70%

* 2 M $AlBr_3$ solution in xylene with TMCS
† E_{corr} of the Al rod is −0.47 V
E_{corr} of the Cu substrate is −0.06 V.

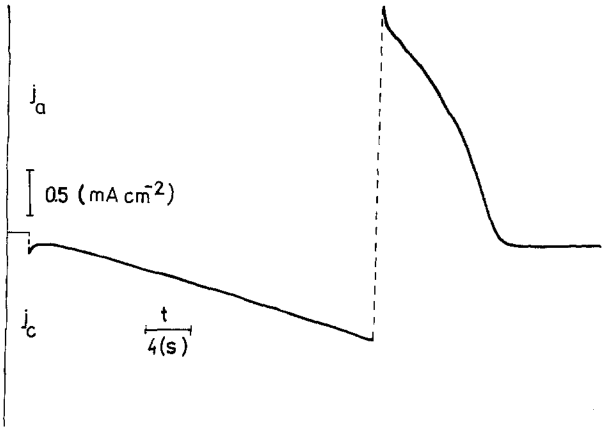

Fig. 5. Chronoamperometric curve recorded in the aged electrolyte composed of 2 M $AlBr_3$ and 2 vol % of TMCS in xylene on the platinum electrode, $E_c = -0.1$ V.

Electrode	*d log j_c/d log t_c*	*Crystallization type*
Pt-X	0.6	3-D, instantaneous
Pt-Si-X	–	electrode completely passive
Pt-X-Si	1	2-D, instantaneous
Pt-O-X	1.2	~ 1-D, instantaneous
Pt-O-Si	0.6	3-D, instantaneous

These values suggest that a change of the crystallization type takes place only if the electrode was previously wetted with the electrolyte. Otherwise, the silane renders the platinum surface completely passive. The presence of the Pt–O bonds is not essential for change in the type of crystallization. The voltammetric data show that the acceleration of the electrode processes takes place only in the case of the Pt–X–Si electrode. The results are presented in Table 4.

Figure 7 shows a plot of electrolyte conductivities of various composition which were stored for different durations as a function of temperature. It can be seen that the temperature dependence of charge carriers is virtually constant for the fresh solution but increases steadily as the storage time increases.

Traces of water are consumed by TMCS in the reaction [12].

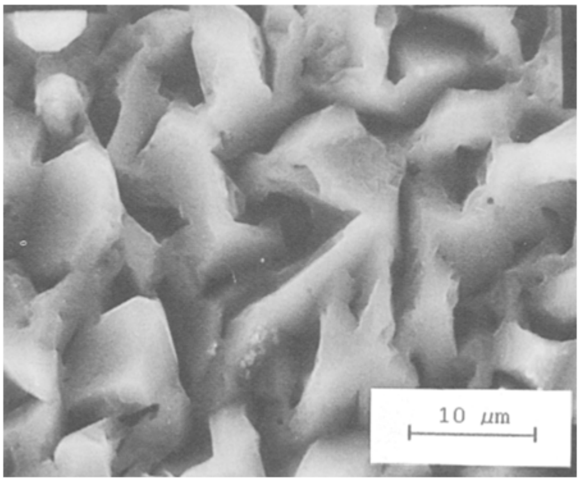

Fig. 6. SEM of a coating obtained from the aged electrolyte composed of 2 M $AlBr_3$ and 6 vol % of TMCS in xylene on the copper electrode, $j_c = 12\,mA\,cm^{-2}$, $t_c = 1$ h.

Table 4. Some characteristic data for electrodeposition of aluminium by voltammetry in 2 M $AlBr_3$ solution in xylene without TMCS on the platinum electrode, previously contacted with silane outside the solution. Scan rate: 0.01 $V s^{-1}$

Electrode	*E_{nuc} (V against Al)*	*j_c (η − 100→) (mA cm^{-2})*	*j_c (η − 50←) (mA cm^{-2})*
Pt-X	0.7	2.6	2.3
Pt-X-Si	0.6	5.2	4.8
Pt-O-Si	0.8	2.2	2.3
Pt-O-X	0.8	1.2	2.5

$$(CH_3)_3SiCl + H_2O \rightleftharpoons (CH_3)_3SiOH + HCl \quad (1)$$

Thus the hydrolysis of $AlBr_3$ is suppressed and the quality of the deposit does not deteriorate. Although traces of water are partly renewed according to the reaction

$$2(CH_3)_3SiOH \rightleftharpoons (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3 + H_2O \quad (2)$$

nevertheless Reaction 1 extends the period of use of the bath. In the presence of $AlBr_3$ siloxane molecules give silanes [13]:

$$(R_3Si)_2O + AlBr_3 \rightleftharpoons 2R_3SiBr + AlOBr \quad (3)$$

Reactions 2 and 3 show why no siloxanes or silanoles were detected by chromatography in a 3-month old solution of 2 M $AlBr_3$ in xylene with 5 vol % of TMCS.

4. Conclusion

The addition of 2–5 vol % of trimethylchlorosilane to Al_2Br_6-xylene electrolytes influences the stability of the plating bath by bonding traces of water. The electrocrystallization proceeds by a 2-D type of crystal growth due to the surface activity of the TMCS mol-

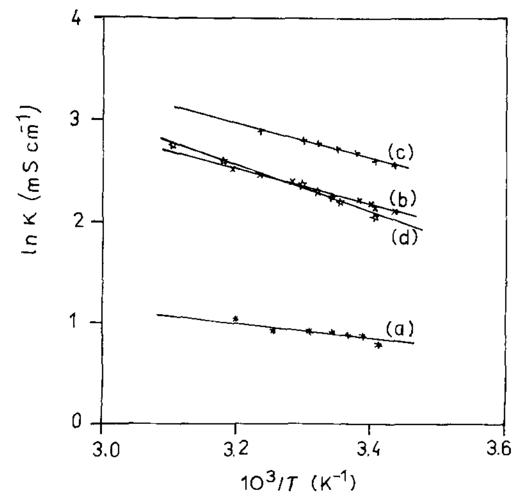

Fig. 7. Arrhenius plots for electrolytes containing TMCS stored for: (a) 1 day, electrolyte composition: 2 M $AlBr_3$ and 2 vol % of TMCS; (b) 6 days, 2.5 M $AlBr_3$ and 6 vol % of TMCS; (c) 27 days, 2.5 M $AlBr_3$ and 6 vol % of TMCS; and (d) 1 year, 2 M $AlBr_3$ and 2 vol % of TMCS.

ecules, which makes the deposit more coherent and compact. A very useful property of the proposed modification is that the concentration of added TMCS need not be corrected during use.

Acknowledgements

The authors wish to thank the Coordination Committee of Problem 01.15 for their financial support for this work.

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