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Electrodeposition of aluminium-copper alloys from alkyl benzene electrolytes

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An experimental programme in which aluminium–copper alloys were electroplated from alkyl benzene/$AlBr_3$ electrolytes is described. The investigation showed that Al–Cu alloys (0–3.5 wt% Cu) can be plated onto steel and that the resulting coatings are bright, adherent and less porous than equivalent coatings of pure aluminium. The composition of the cathode deposits can be readily controlled by using Al–Cu anodes of specified copper content. About half the copper dissolved from the anodes is transferred to the cathode, the remainder being precipitated from the electrolyte as CuBr. Coating composition varies with current density and this parameter can also be used to control the process. In a parallel investigation, potential differences between aluminium and a number of other metals (Zn, Pb, Cd, Sn, Cu, Ag) were measured. Potential differences in the alkyl benzene electrolytes were found to be 10–30 times less than in aqueous electrolytes which indicates that the alkyl benzenes should be useful for plating other alloys in addition to those of aluminium and copper.

1. Introduction

Aluminium–copper alloys are used extensively as a replacement for pure aluminium in certain applications, principally because of their superior physical strength. Likewise, electrodeposited aluminium–copper alloys are likely to be superior, for certain applications, than the pure metal. Aluminium–copper alloy coatings appear, for example, to best meet the requirements for metallized silicon circuits [1]. These coatings are currently prepared by vapour deposition but electrodeposition might be more satisfactory, particularly to avoid Al–Si alloy formation and to control deposit thickness.

Electrodeposition of aluminium and its alloys from aqueous solutions is impossible because the water component of the electrolyte decomposes and hydrogen evolves at a lower voltage than is required to plate the metal. However, organic electrolytes are suitable for this purpose as was first shown by Blue and Mathers [2] who deposited several aluminium alloys from electrolytes containing aluminium bromide, aluminium chloride, ethyl bromide, benzene and xylene. These authors reported that in most cases the deposits were dark and granular.

Successful aluminium plating by the present authors [3–5] from ethylbenzene–toluene/aluminium bromide electrolytes (whose specific conductances are adjusted with HBr to between $2–4 \times 10^{-3} \Omega^{-1} cm^{-1}$) suggested that these electrolytes might also produce alloy coatings of good quality. An investigation was carried out, therefore, to ascertain the feasibility of producing aluminium–copper alloys (up to 5 wt% Cu) using much the same electrolyte but with aluminium–copper anodes.

2. Experimental

The experimental part of the work was divided into two sections:

(a) Determination of potential differences between aluminium and a number of other metals, specifically Zn, Pb, Cd, Sn, Cu and Ag (all 99.9+ wt% pure);

(b) Deposition of aluminium–copper alloys, 0·025 mm thick or greater, and an examination of the experimental factors affecting the plating process and coating quality.

2.1. *Apparatus and materials*

Most of the auxiliary apparatus, materials, electrolyte preparation techniques and plating procedures used in this work have been described in previous publications [3–5]. One new feature was the analysis for copper in the electrodes and electrolyte, which was performed colorimetrically [6] using neocuproin to form a colour complex followed by extraction of the complex into chloroform. In the case of electrolyte samples, the organic material was oxidized by exposure to sulphuric/nitric acid solutions prior to the analysis. This procedure also ensured that the copper in the electrolyte was in its cupric state.

The cell used for the experiments (both plating and potential measurements) is described in Fig. 1. For the plating experiments, the cell was arranged with four flat aluminium–copper anodes around a central cylindrical steel cathode. For the potential difference measurements a flat metal electrode (e.g. silver) was placed in one of the anode positions with a flat aluminium electrode placed in the central position.

Each flat electrode (1 mm thick, 1·8 cm wide) was suspended from the lid of the cell by means of a screw-tightened Teflon support (B in Fig. 1), inserted into a 24/40 ground glass joint. The central cylindrical electrode (1 cm diameter) was held similarly. Non-aqueous grease ensured tightness of the stoppers in their 24/40 joints.

In addition to receptacles for the electrodes, the lid had inlet and outlet tubes (L and M in Fig. 1) for the passage of inert gas through the cell, with the outgoing gas being bubbled through an ethylbenzene/toluene solvent in order to avoid any back diffusion of air into the cell. Lastly,

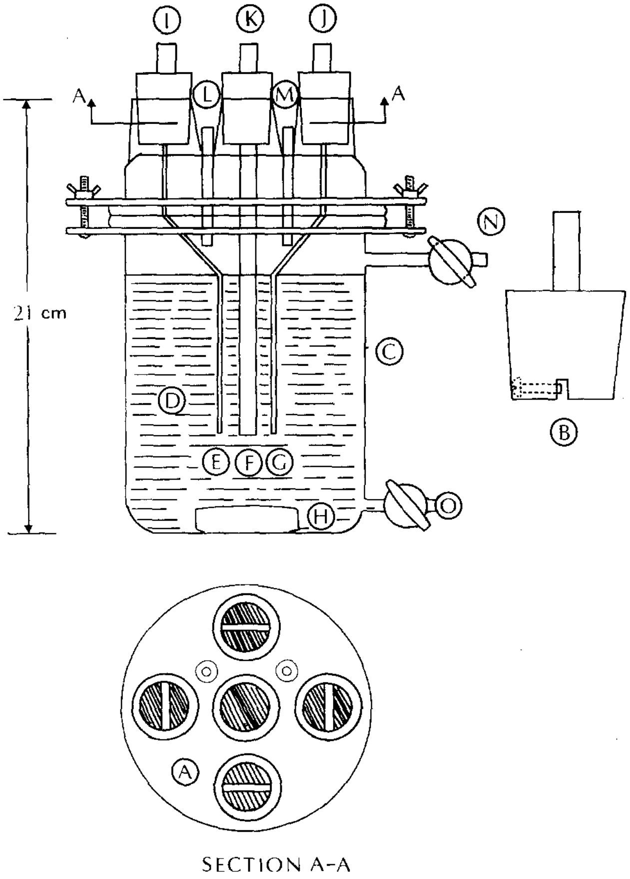

Fig. 1. Electrolytic cell: A, reaction kettle cover; B, electrode support (Teflon); C, reaction kettle; D, electrolyte; E and G, aluminium alloy anodes; F, steel cathode; H, magnetic stirring rod (Teflon covered); I, J and K, electrical contacts; L and M dry nitrogen inlet and outlet; N and O, filtration pump inlet and outlet.

the main body of the cell contained an inlet and outlet which permitted continuous filtration of the electrolyte.

3. Potentials of selected metals with respect to aluminium

All potentials were measured between a flat metal electrode and a central flat aluminium electrode, using a high impedance 'Tacussel' (TechnEurop Montreal) electronic millivoltmeter (type Aries-1000). The electrolyte was in all cases an ethylbenzene/toluene solution (1 :1 by volume) containing 50 wt% anhydrous aluminium bromide from which trace impurities had been removed by electrolysis with pure aluminium anodes for 24 hours. The specific conductance of the electrolyte was also adjusted (with HBr additions) to the normal operating level of $3–4 \times 10^{-3} \Omega^{-1} cm^{-1}$ during this preliminary electrolysis.

Prior to the potential measurements, each electrode was;

(a) degreased with trichloroethylene,

(b) immersed in a 30 wt% sodium hydroxide solution,

(c) rinsed in tap water then immersed in a 10 vol % HNO_3 solution (except for Sn which was immersed in 10 vol% HCl),

(d) rinsed in distilled water, immersed in methanol and dried in air.

Each electrode was then in turn suspended in the cell as described in the experimental section (Section 2). Contamination of the system by moisture-laden air was minimized by blowing argon through the cell during all electrode positioning manoeuvres.

The potential measurements were begun as soon as a particular pair of electrodes (Al plus one of the other metals) was in place, and they were continued until a constant potential was obtained (1–4 h). The temperature of the electrolyte was thermostatically controlled throughout the experiments at 18 ± 0·1° C. The results are tabulated in Table 1.

3.1. *Discussion: potentials of Zn, Pb, Cd, Sn, Cu and Ag with respect to Al*

Table 1 gives the standard potentials of the above metals with respect to hydrogen in aqueous solutions and their potentials with respect to aluminium in aqueous and non-aqueous media. The results show that:

(a) All of the tested metals are more noble than aluminium in both aqueous and organic media.

(b) The potential differences between the metals and aluminium are much smaller in the organic electrolytes than in aqueous solutions.

This latter result is important because it indicates that it should be possible in principle

Table 1. Potentials (in V) of selected metals with respect to aluminium in comparison with potentials in aqueous electrolytes

	Metal/ion system						
Conditions	*Al/Al^{3+}*	*Zn/Zn^{2+}*	*Pb/Pb^{2+}*	*Cd/Cd^{2+}*	*Sn/Sn^{2+}*	*Cu/Cu^{+}*	*Ag/Ag^{+}*
A. Organic solutions, potential relative to aluminium							
present work (ethyl benzene–toluene 1 : 1/50 wt% $AlBr_3$, 18° C)	0·00	0·03	0·054	0·059	0·159	0·210	0·230
Blue and Mathers [2] (benzene, toluene, xylene: $AlCl_3$, 25° C)	0·00	0·02	0·072	0·059	0·164	0·226	0·56
B. Aqueous solutions							
standard potential [6] versus hydrogen (20° C)	−1·66	−0·763	−0·126	−0·403	−0·136	0·136	0·799
potential relative to aluminium (20° C)	0·00	0·90	1·53	1·26	1·52	2·18	2·46

to plate aluminium/metal alloys with all of these metals.

4. Electrodeposition of aluminium–copper alloys

The electrodeposition study consisted of plating 0·025 mm Al–Cu coatings (0–3·5% Cu) onto cylindrical steel cathodes from flat aluminium–copper anodes.

The principal parameters investigated were:

(a) Cu content of cathode deposit as a function of anode Cu content (constant current density);

(b) Cu content of cathode deposit as a function of current density (constant anode composition); and

(c) cathode current efficiency.

The results of these three studies are described in Figs. 2–4 and the next three sections.

4.1. *Cu content of cathode deposits versus Cu content of anodes*

The anode composition tests were performed with six sets of anodes containing respectively 0·13, 0·38, 0·95, 1·25, 2·41, 5·04 wt% Cu. Each individual test consisted of plating for 100 min at a controlled current density of 11 ± 1 mA cm^{-2}, conditions which produced coatings of approximately 0·025 mm thickness. Twenty to forty tests were carried out with each set of anodes.

As the results (Fig. 2) show, there is an almost straight line relationship between the copper content of the cathode deposit and the copper content of the anode. This feature and the observation that only about half the copper in the anode is transferred to the cathode is discussed in detail below.

4.2. *Cu content of cathode deposit versus cathode current density*

The results of experiments performed with a single set of anodes (5·04 wt% Cu) but at various cathode current densities are shown in Fig. 3. As can be seen the copper carry-over from anode to cathode decreases with increasing current density. Approximately 70% of the copper is carried over at the lowest current density (5 mA cm^{-2}) while only 20% is carried over at 44 mA cm^{-2}.

4.3. *Cathodic current efficiency*

The results of cathode current efficiency tests with 5·04 wt% Cu anodes are presented in Fig. 4, where the cathode current efficiency takes into account the plating of both Al and Cu (from Al^{3+} and Cu^{+}). As was anticipated from previous pure aluminium studies [4], cathode efficiency tends to drop with

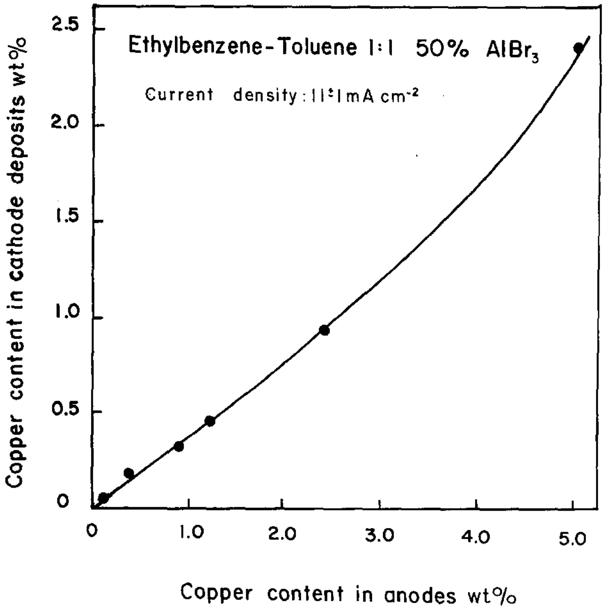

Fig. 2. Copper content of cathode deposits in relation to copper content of anodes, constant current density (11 ± 1 mA cm^{-2}). Each experimental point represents the average of twenty to forty experiments in which 0·025 mm deposits were plated on freshly prepared cathodes.

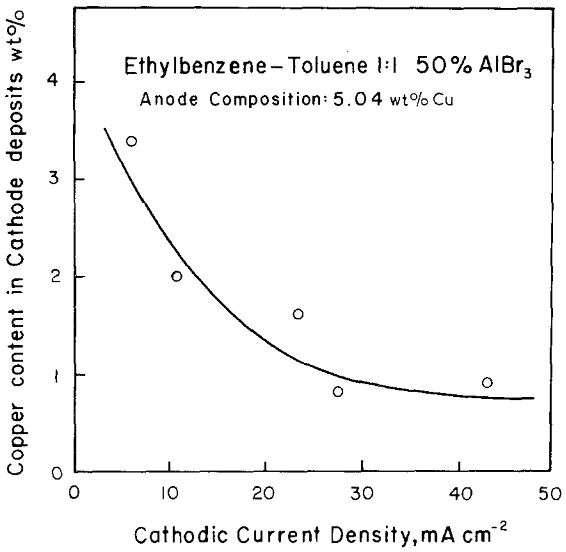

Fig. 3. Copper content of cathode deposits as a function of cathode current density, constant anode composition (5·04 wt% Cu).

increasing current density. In the case of the alloy anodes, however, the drop appears to be somewhat more serious.

5. Discussion

5.1. *Quality of deposit*

Figs. 5a and b are scanning electron micrographs (x 800 magnification) of the outer surfaces of pure aluminium and aluminium–2·5 wt% copper coatings, both 0·025 mm in thickness. The more uniform and less porous structure of the alloy plate is readily apparent. In general the alloy coatings were somewhat brighter than their pure aluminium counterparts. Like pure aluminium, the alloy platings adhered well to the substrate and they were anodized without difficulty.

5.2. *Efficiency of transferring copper from anode to cathode*

An interesting result of the experiments was that only about half of the copper in the anode was actually plated on the cathode (Fig. 2). This means that over the experimental period either (i) copper ions were building up in the solution or (ii) copper

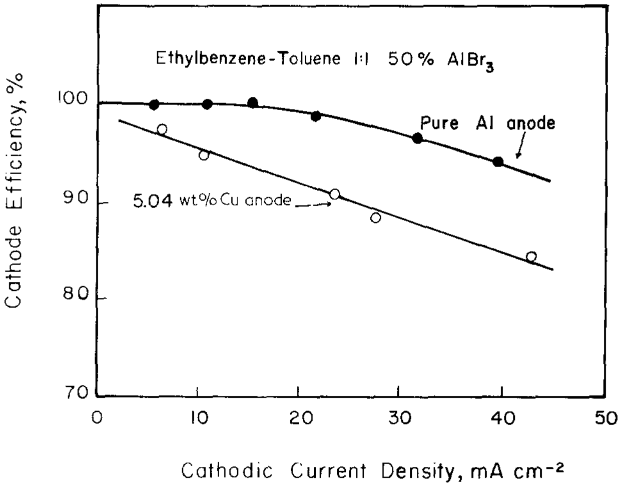

Fig. 4. Cathode current efficiency as influenced by cathode current density when plating pure aluminium •; and aluminium–copper alloys (5·04 wt% Cu anodes) ○. The efficiencies are based on trivalent aluminium ions and monovalent copper ions.

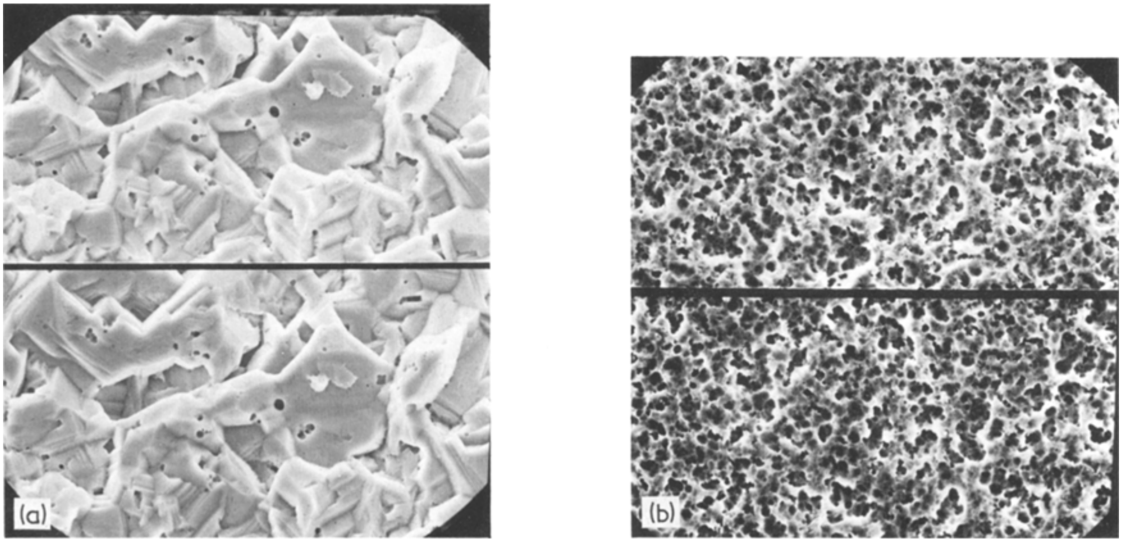

Fig. 5. Stereoscopic electron probe photomicrographs of 0·025 mm electrodeposits of (a) pure aluminium and (b) an Al–Cu alloy (2·5 wt% Cu). Both deposits were plated at a current density of 10 mA cm^{-2}. Magnification, × 800.

was being precipitated. Inspection of the cell and contents after completion of the test programme showed that the latter was the case, i.e. significant quantities of copper bromide were found in the glass wool filter of the cell. A small amount of metallic copper was also detected as a cementation product on the anodes whenever they were left in the solution without passing current.

5.3. *Copper content of cathode deposit as influenced by current density*

As is demonstrated by Fig. 3, the copper contents of cathode deposits decrease with increasing cathode current density. Since copper ions should plate preferentially to aluminium ions if they reach the cathode (i.e. copper is more noble than aluminium, Table 1), this result indicates that the ratio of Cu:Al ions reaching the cathode decreases with increasing current density.

These observations indicate that copper ions are in such low concentration in the electrolyte that they cannot diffuse rapidly to the cathode surface; the net results being that at high current density:

(a) Copper ions are depleted at the cathode surface.

(b) The concentration of copper in the deposit is low.

Chemical analysis of the electrolyte (Section 2.1) showed that its copper content is only in the order of 1–2 mM as compared to an aluminium concentration of 4M. This supports the view that the high current densities of the study greatly exceed the limiting current density of the dissolved copper ions.

5.4. *Cathode current efficiencies*

A preliminary study of copper dissolution from pure copper anodes (10 mA cm^{-2}) indicated that the rate of dissolution was commensurate with the formation of a univalent ion. Other workers [2, 8] are in agreement with this observation. Thus the cathode efficiencies presented in Fig. 4 are based on univalent copper ions and trivalent aluminium ions.

The less than 100% cathode current efficiencies obtained experimentally (concurrent with 100% anode efficiencies) are thought to be due to:

(a) precipitation of a portion of the electrolytically dissolved anode copper; and

(b) reduction of non-metallic species at the cathode.

The latter may be intrinsic to the electrolyte (cathodic reduction of hydrogen ions or HBr) or it may occur as a consequence of metal precipitation, possibly by the following sequence of reactions:

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{+}_{(\text{anodic dissolution})} + e^{-} \qquad (1)$$

$$\mathrm{Cu}^{+} + \mathrm{HBr} \rightarrow \mathrm{CuBr}_{(\text{precipitate})} + \mathrm{H}^{+} \qquad (2)$$

$$\mathrm{H}^{+} + e^{-} \rightarrow 1/2\ \mathrm{H}_{2(\text{cathodic reduction})}. \qquad (3)$$

Even under the highest current densities of this investigation, Reactions 1–3 could only account for for a 5% loss of current efficiency (i.e., copper dissolution represents only a small fraction of the total metallic dissolution) which is much smaller than that noted in Fig. 4. It appears, therefore, that copper ions somehow tend to promote the reduction of non-metallic species at the cathode.

6. Conclusions

The following conclusions were reached:

(a) Aluminium–copper alloys have been plated on steel from Al–Cu alloy anodes and alkyl benzene electrolytes.

(b) The resulting coatings are bright, adherent and readily anodizeable. They are less porous than their pure aluminium counterparts.

(c) Simultaneous addition of aluminium and copper ions to the system is readily accomplished by using Al–Cu alloys as anodes. Appropriate choice of anode composition can be used to obtain a cathode deposit of specified composition.

(d) The solubility of copper in alkyl benzene electrolytes in only 1–2 mM with the copper likely to be present as $\mathrm{Cu}^{+} \cdot (\text{organic}) \cdot \mathrm{AlBr}_4^{-}$ complexes. The low copper solubility leads to small limiting diffusion current for copper and it accounts for the observation that the efficiency of anode-to-cathode copper transfer decreases with increasing current density.

(e) Potential differences between aluminium and other metals are ten to thirty times less in alkyl benzene electrolytes than in aqueous electrolytes. This indicates that alkyl benzene electrolytes should be useful for plating alloys other than aluminium–copper.

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