

The electrodeposition of aluminium on brass from a molten aluminium chloride–sodium chloride bath

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The electrodeposition of aluminium on brass (63/37) from a dry $\text{AlCl}_3/\text{NaCl}$ melt (80 wt.% purified AlCl_3 , 20 wt.% NaCl) using static as well as rotating cathodes and a variety of conditions has been studied. The current efficiency of the process is very high and the electrodeposits are smooth, fine grained and silver white in appearance. Although at lower temperatures, there is a tendency for flakes to be formed locally these are easily removed and do not affect the overall quality of the electroplate.

1. Introduction

The electrodeposition of aluminium from fused salt baths based on AlCl_3 and NaCl has been studied in some detail [1–8]. However, there has been very little work with brass substrates, an important construction alloy often requiring a durable bright surface. We report the results of such a study, using the fused salt bath AlCl_3 80 wt.% and NaCl 20 wt.% and brass substrates in the present communication. The effects of the following variables on the quality of the plate: (a) speed of rotation of the substrate; (b) current density; (c) duration of electrolysis; and (d) bath temperature have been examined. For a better understanding of the deposition process, a pure and dry bath has been preferred in place of the impure or moist bath used in most of the previous investigations.

2. Experimental

Aluminium chloride (anhydrous, BDH) was purified by sublimation from an $\text{AlCl}_3/\text{NaCl}$ melt containing 5–10 wt.% of sodium chloride to which some aluminium powder had been added. Two repeated sublimations yielded perfectly white and glossy crystals of AlCl_3 . The all-glass sublimation apparatus used for purifying aluminium chloride is shown in Fig. 1. Sodium chloride used for the bath was of BDH 'AnalaR' grade, dried at about 500°C for 6 h before use.

The electrolysis cell, shown in Fig. 2, consisted of a glass beaker with an aluminium cover. The anode was made from an aluminium sheet of 0.5 mm thickness and 99.5% purity. The design of the anode was similar to that used by Capuano and Davenport [9] for electrodeposition of aluminium from organic baths; its height, diameter and the inner area being 4.5 cm, 4.2 cm and 52.86 cm^2 respectively. The cathode was a polished and cleaned brass (63/37) rod of 5 mm in diameter and 12 cm in length and could be rotated at different speeds, when desired, by means of an adaptor and a spring cord driven by a suitable motor and pulley arrangement. The whole set-up was housed inside a dry box with the provision for circulation of dry nitrogen gas from a cylinder.

A mixture of aluminium chloride and sodium chloride of the desired composition was prepared by weight and was thoroughly powdered and mixed inside a dry box. An appropriate amount ($\sim 150\text{ g}$) of this mixture was taken in the experimental cell and was heated to bring it to the molten state and then to the required temperature while the central opening of the cover was closed by means of a well-fitting aluminium stopper (shown in Fig. 2b). The temperature of the electrolytic bath was maintained within $\pm 2^\circ\text{C}$ of the required temperature, and the cover at a slightly higher temperature than that of the bath by regulating currents in the heating mantle (surrounding the lower part of the electrolytic cell and serving as the main heat source) and in the heating coil provided below

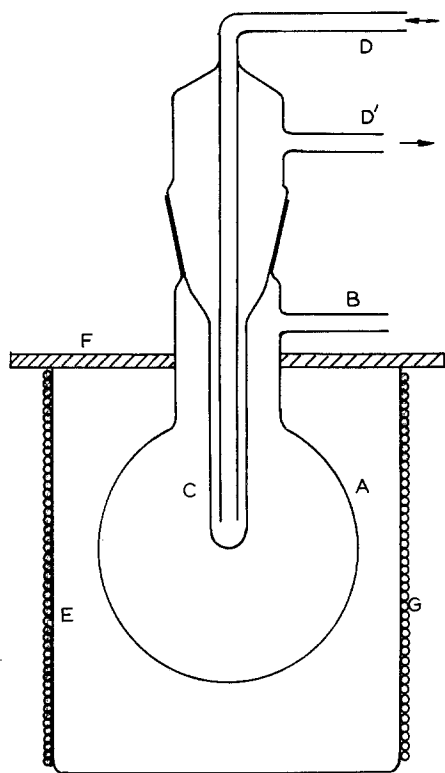


Fig. 1. All-glass sublimation apparatus for purifying aluminium chloride. A—flask; B—side tube; C—cold finger; D, D'—water inlet and outlet respectively; E—aluminium vessel; F—asbestos cover and G—asbestos rope for insulation.

the aluminium cover of the cell.

The hot aluminium cover effectively minimized the loss of volatile aluminium chloride from the bath. However, to ensure that the composition of the bath did not change appreciably, a fresh bath was used every 25–30 runs.

Each specimen cathode was, first of all, mounted on an aluminium sleeve, and was then introduced into the bath after removing the stopper from the cover so that about 5 cm of the rod dipped inside the bath. Electrolysis was started after 5 min of the insertion of the cathode in order to allow thermal equilibrium. On completion of the plating the plated sample was washed thoroughly with water and dried. The first few plated samples were rejected as these were mainly used to pre-electrolyse the bath to remove any possible impurities. Under identical plating conditions duplicate specimens of the cathode were plated, of which one specimen was used for the determination of current efficiency, and the other, for examination of the quality of the electroplate.

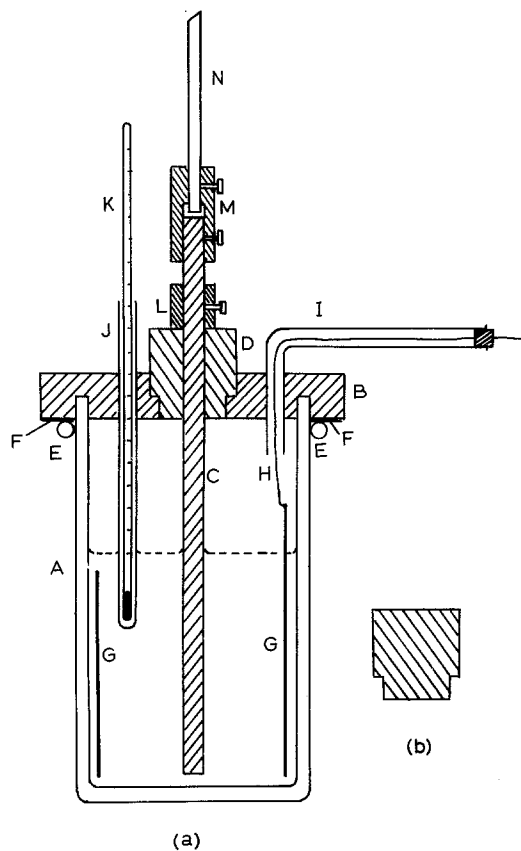


Fig. 2. Electrolysis cell. A—glass vessel; B—aluminium cover; C—cathode; D—aluminium sleeve; E—heating coil; F—mica ring; G—anode; H—anode lead; I—glass tube; J—thermometer pocket; K—thermometer; L—brass bush; M—adapter and N—spring cord—cathode lead.

One difficulty encountered during the electrolysis was the occasional appearance of random flake deposits on a few points of the cathode surface, although the overall plating on the substrate was excellent throughout. These flakes fell out of the samples when washed with water. However specimens having flakes at more than 2–3 points were discarded.

Surface roughness of plated specimens was measured in a type QA profilometer amplimeter (Micrometrical Manufacturing Company, Michigan, USA). The RMS roughness value obtained in terms of microinches were converted into micrometers (μm). Photomicrograph of the polished and etched cross-sectional view of the aluminium deposit was obtained using a Vickers projection microscope (Cooke Troughton and Simms, UK). Debye-Scherrer photographs for X-ray analysis of the electroplates were taken with the help of a

Table 1. Electrodeposition under various speeds of rotation of the cathode. Bath temperature = $175 \pm 2^\circ \text{C}$

Run No.	Rotation of Cathode (rev min ⁻¹)	Cathode c.d. (mA cm ⁻²)	Time (min)	Surface roughness (μm)	Current efficiency (%)
1	0	18.0	30	0.36	98.0
2	86	17.6	30	0.36	90.3
3	112	17.7	30	0.28	95.9
4	148	18.0	30	0.33	86.5
5	220	18.1	30	0.33	96.9

Philips (Holland) Debye-Scherrer camera of diameter 11.46 cm. Specimens for X-ray diffraction were prepared by dissolving out the inner brass substrate of the plated rod with concentrated nitric acid. Electron microprobe analysis of the electroplate was carried out in a Map II microprobe analyser of Russian make.

Cathodic current efficiency was determined from the weight loss of the plated specimen on stripping in a 0.5% sodium hydroxide solution. Trial runs showed that the loss of zinc from the brass treated in such a solution was negligible, and the weight loss of the cathode due to stripping was in close agreement with the weight of aluminium estimated quantitatively in the stripping solution.

3. Results and discussion

Results of experimental runs of electrodeposition carried out under varying conditions are summarized in Tables 1-4.

Speed of rotation of the substrate, cathodic current density (c.d.) and duration of electrolysis,

within the ranges tried (Tables 1-3), did not apparently affect the quality of the electroplate and in all cases the deposits were very good. The fact that good electroplates could be obtained with a c.d. as high as 53 mA cm^{-2} is significant since this is in contrast with the earlier experience of Howie and Macmillan [8] relating to electrodeposition of aluminium on mild steel in which the dendrite growth threshold c.d. was of the order of 1 mA cm^{-2} in dry bath and 20 mA cm^{-2} in a bath containing about 0.07% HCl.

The cathodic current efficiency of the deposition process was high throughout, approaching 100%, except when flakes were formed. The frequency of occasional flake deposits was found to be slightly more with rotating substrates and prolonged electrolysis. The relatively lower values of current efficiency obtained in some cases were most probably due to the detachment of such flakes either during rotation of the cathode or its subsequent washing.

Variation of bath temperature from 135 to 195°C did not affect the overall quality of the

Table 2. Electrodeposition of aluminium under varying current densities under static and rotating conditions. Bath temperature = $175 \pm 2^\circ \text{C}$

Run No.	Current density (mA cm ⁻²)	Rotation of cathode (rev min ⁻¹)	Time (min)	Surface roughness (μm)	Current efficiency (%)
1	6.05	0	90	0.31	95.3
2	18.0	0	30	0.36	98.0
3	30.0	0	18	0.28	88.5
4	41.7	0	13	0.31	100.0
5	52.8	0	10	0.25	87.9
6	6.07	112	90	0.25	101.1
7	17.7	112	30	0.28	95.9
8	30.0	112	18	0.33	96.8
9	41.6	112	13	0.28	95.2
10	52.8	112	10	0.28	89.9

Table 3. Effect of the duration of electrolysis on aluminium deposition under static and rotating conditions. Bath temperature = $175 \pm 2^\circ \text{C}$

Run No.	Time (min)	Current density (mA cm^{-2})	Rotation of cathode (rev min^{-1})	Surface roughness (μm)	Current efficiency (%)
1	9	30.6	0	0.31	100.0
2	18	30.0	0	0.28	88.5
3	36	30.2	0	0.33	92.6
4	9	30.8	112	0.33	88.7
5	18	29.9	112	0.33	96.8
6	36	30.1	112	0.31	87.3

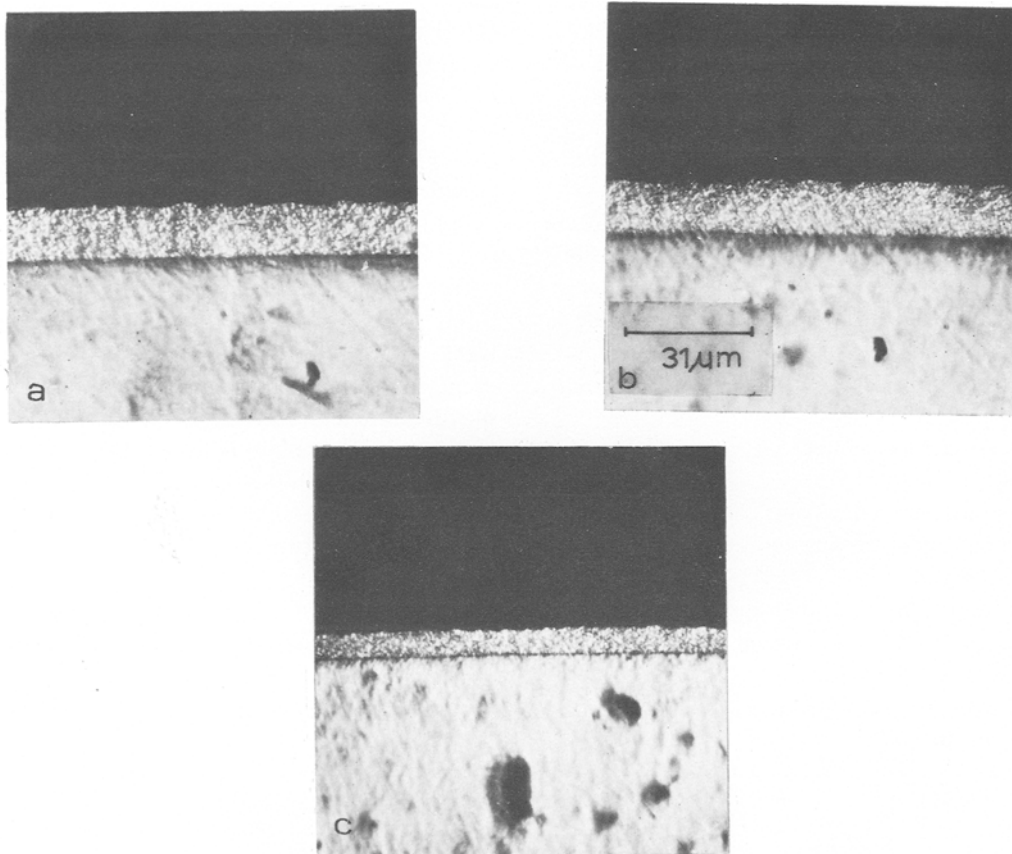


Fig. 3. Photomicrographs (cross-sectional view) of aluminium deposits obtained: (a) from a bath at 175°C with a rotating cathode; speed of rotation: 220 rev min^{-1} ; c.d.: 18.1 mA cm^{-2} ; duration of electrolysis: 30 min; (b) from a bath at 175°C with a stationary cathode; c.d.: 6.05 mA cm^{-2} ; duration of electrolysis: 90 min; (c) from a bath at 175°C with a rotating cathode; speed of rotation: 112 rev min^{-1} ; c.d.: 30.8 mA cm^{-2} ; duration of electrolysis: 90 min; (c)

plate, as in all cases, satisfactory deposits were obtained, but it had a pronounced effect on the appearance of local flake deposits. Probability of appearance of flake deposits was more at lower

temperatures than at higher ones, and on the layer of the electrode in contact with the surface of the molten electrolyte than on layers below this level. The situation was more or less the same with the

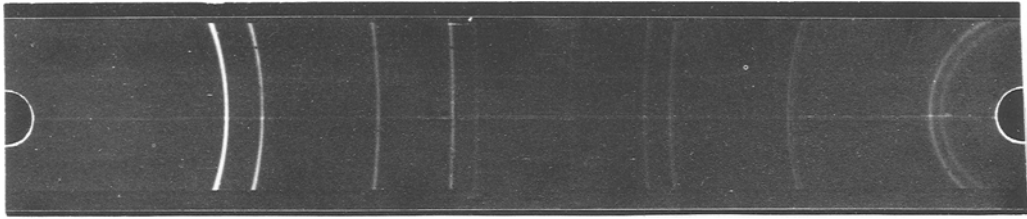


Fig. 4. Debye-Scherrer X-ray diffraction photograph of electrodeposited aluminium film obtained in run 4 Table 5.

Table 4. Effect of varying bath temperature on aluminium deposition under static and rotating conditions

Run No.	Temperature (° C)	Rotation of cathode (rev min ⁻¹)	Current density (mA cm ⁻²)	Time (min)	Surface roughness (μm)	Current efficiency (%)
1	195	0	18.1	30	0.31	99.6
2	175	0	18.1	30	0.25	98.3
3	155	0	18.0	30	0.31	83.2
4	135	0	18.7	30	0.28	76.9
5	195	112	18.0	30	0.31	100.4
6	175	112	18.1	30	0.31	94.8
7	155	112	18.3	30	0.28	78.1
8	135	112	18.7	30	0.28	70.0

Table 5. Lattice parameters of aluminium film deposited under various conditions. Bath temperature = 175 ± 2° C

Run No.	Rotation of cathode (rev min ⁻¹)	Cathode current (mA cm ⁻²)	Time (min)	Lattice parameter (Å)
1	112	53.0	5	4.0504
2	0	6.07	45	4.0496
3	112	6.07	45	4.0496
4	0	53.0	5	4.0490

Table 6. Impurities found in electroplated aluminium; c.d. = 18 mA cm⁻²; time = 30 min

Run No.	Bath temperature (° C)	Percentage (by weight) of			
		Cu	Zn	Si	Fe
1	135	0.859	0.438	trace	nil
2	155	0.933	0.464	trace	nil
3	175	0.940	0.478	trace	nil
4	195	0.954	0.444	trace	nil

static as well as the rotating electrodes. The current efficiency was consequently lower at lower bath temperature than at higher temperature as can be seen from Table 4.

In all cases, the electroplate obtained was silver white in appearance, shining, smooth and aestheti-

cally quite appealing even in the unpolished state. The surface roughness (RMS value) as measured by the profilometer was in the range of 0.25–0.36 μm which was almost similar to that of polished brass substrate (0.28–0.33 μm) used.

Adherence of the aluminium electroplate to the

brass substrate was tested qualitatively. Attempts to separate a small portion of the plating from the surface with the help of a sharp knife always failed, indicating the adhesion between aluminium and brass to be very good.

The cross-sectional view of aluminium deposits under a microscope revealed these to be uniform, compact and fine grained in all cases. The photomicrographs of a few typical samples are shown in Fig. 3.

Debye-Scherrer X-ray diffraction photographs of the deposits were analysed for the lattice parameters of the deposited aluminium crystals. A typical diffraction pattern is shown in Fig. 4. The results obtained in some selected specimens are given in Table 5 which indicate that the lattice parameter remains unaffected under different conditions of plating and agree very well with the standard value [10] of 4.0495 Å found for pure aluminium fcc lattice. Thus the electrodeposited aluminium appears to be structurally similar to pure aluminium.

The findings of the electron microprobe analysis of the surface of the aluminium electroplated at different bath temperatures are given in Table 6. Analysis was made for Fe, Si, Cu and Zn as these are the expected impurities originating from the bath or the substrate.

The results show that despite all precautions taken to purify AlCl_3 , it still contained a trace of silicon possibly in the form of SiCl_4 and was ultimately deposited along with aluminium. The presence of copper and zinc clearly shows that there was some diffusion of these elements from the brass to aluminium layer.

4. Conclusions

From the information collected here, it is clear that brass is an ideal substrate for electrodepositing aluminium from the molten bath containing aluminium chloride and sodium chloride. Unlike the requirement in the case of steel [8] the presence

of HCl in the bath is not necessary to obtain a satisfactory plating, and barring the appearance of few washable flakes, there is no evidence of any dendritic crystal growth under any of the conditions tried. White, shining, smooth, compact and very adherent deposits can be obtained under widely varying conditions with current efficiencies of the order of 90% or more. The aluminium deposited, although not absolutely pure due to co-deposition of silicon from the bath and diffusion of copper and zinc from the substrate to the electroplate, has the same crystalline form as the pure aluminium with no change in the lattice parameter.

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