

The electrodeposition of aluminium from molten aluminium chloride/sodium chloride

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The electrodeposition of aluminium from an $\text{AlCl}_3/\text{NaCl}$ melt (80 wt % purified AlCl_3 , 20 wt % NaCl at 175°C) has been studied and conditions established for the production of good quality electroplate on steel. To obtain a coherent, dendrite-free plate at current densities up to 16 mA/cm^2 , the presence of not less than about 0.07 wt % hydrogen chloride was found to be essential. Under these conditions the current efficiency was 85%. Continued plating resulted in a progressive increase in current efficiency up to practically 100% and a progressive deterioration in plate quality. Addition of more HCl at this stage restored the original conditions.

These observations explain inconsistencies in previously reported values for current efficiency and maximum current density.

The mechanism of the action of HCl was not established but it is suggested that it may have an action akin to chemical polishing by dissolving off the high spots on the already deposited aluminium. Alternatively, the electrolytic reduction of hydrogen preferentially on active sites may block these off and so prevent the build-up of aluminium dendrites.

1. Introduction

The work done on the electrodeposition of aluminium from the binary molten salt system aluminium chloride/sodium chloride is quite extensive.

In 1952 Collins [1] described a method for the electroplating of steel from a fused salt bath and found satisfactory plating could be obtained with a mixture of aluminium chloride (80 wt % Flux Grade) and sodium chloride (20 wt %) at a temperature of 180°C and using an aluminium anode. He employed a current density of about 16 mA/cm^2 .

Midorikawa [2, 3] has made a valuable contribution to the understanding of this system. His investigations have been mainly with a view to refining aluminium but his findings are applicable to electroplating. He has examined the state of aluminium deposited in the electrolysis of $\text{AlCl}_3/\text{NaCl}$ on changing the cathode

material (Pb, Zn, Cu, Fe, Al and C), the composition of the electrolyte and the bath temperature. He found that a flat, compact and fine aluminium deposit was most easily obtained with a lead cathode. It was found that the aluminium was satisfactorily fine and the current efficiency about 90% when the current density was adjusted between 1.0 and 3.0 mA/cm^2 at a bath temperature of about 160°C . He also found that if iron was present to more than 0.001% in the bath the current efficiency was lowered and the deposited aluminium crystals rough. In the electrolytic refining of aluminium in a mixture of $\text{AlCl}_3/\text{NaCl}/\text{KCl}$ Midorikawa found that the occurrence of rough crystals could be prevented by superimposing a.c. (60 to 500 Hz) on the direct current. He also found that if 0.001% to 0.01% of PbCl_2 is added to the melt when using a lead cathode the occurrence of needle-like crystals of aluminium is prevented.

More recently Miyate [4] carried out an extensive study on the effect of current density on the state of the resultant electroplate. He made use of a melt of the eutectic composition at a temperature of 175°C and varied the current density through the range 4.0 to 40.0 mA/cm² and found that a satisfactory smooth plate was obtained at a current density of 20 mA/cm² with a current efficiency of 85%.

Mohan and Balachandra [5] have described a method of electroplating steel wire with aluminium from the aluminium chloride/sodium chloride bath. They too, found the optimum conditions to be AlCl₃ (80 wt %) NaCl (20 wt %) at 180°C, and that the addition of small amounts (approximately 4 wt %) of BaCl₂ · 2H₂O improved performance by reducing volatilization. Similar general conclusions to those of the above-mentioned investigators have been arrived at by Smith [6] and Good [7].

It is clear from the above that although a large amount of work has been carried out on the electroplating from this molten salt mixture there are a number of inconsistencies in the conclusions reached. In particular there appears to be no agreement as to the most suitable current density or the current efficiency obtained. What has been established is that a bath of the eutectic composition at a temperature of about 175°C with a pure aluminium anode is the most suitable system for the electroplating of aluminium.

The irregularities relating to the current efficiency and current density, point to the possibility of impurities being present in the melts which have been studied. The object, therefore, of the work to be described below was to attempt to establish conditions for obtaining consistently good electroplates of aluminium on steel, in relation to the current density and the purity of the molten salts.

Preliminary studies on electroplating using the conditions established by Collins (i.e., AlCl₃ 80%, NaCl 20%, temperature 180°C and current density 16 mA/cm²) indicated that with commercial grade (or flux grade) aluminium chloride a tolerable electroplate free of dendrites could be obtained but frequently the surface was rough and the general appearance poor. It would seem that this was due mainly to insoluble foreign

material present in the commercial grade aluminium chloride.

In an attempt to improve on the plate produced by Collins's conditions it was decided to carefully purify the aluminium chloride by a process developed to enable the rapid production of 100 g quantities of this material [8].

Electroplating with the purified melt brought to light a rather surprising fact: that under these conditions only dendrites of aluminium could be produced unless the current density was lowered to 1.0 mA/cm² or less. At current densities of less than 1.0 mA/cm² it was possible to produce a smooth electroplate but of course it required a considerable time to deposit a reasonably thick plate.

It was decided to make up an electrolyte which had just been carefully purified, add to it the impurities known to be present in commercial grade aluminium chloride and determine the state of the deposited aluminium when electroplating at a cathode current density of 8 mA/cm².

It was thought that, of the impurities present, ferric chloride and/or some of the products of hydrolysis of aluminium chloride (i.e., HCl and Al₂O₃) would be most likely to alter the electrolysis process and thus the effect of these was first determined.

It is readily seen how ferric chloride and hydrogen chloride will enter into the electrolysis process and warrant an investigation into their effect on the dendritic threshold current density. It was, however, decided to take account also of the effect of alumina, generated by hydrolysis of aluminium chloride since sufficiently small particles, such as these, could be held in suspension and thus be co-deposited and possibly mask active sites where dendrites would otherwise grow.

2. Apparatus

The apparatus used in this work has been described elsewhere [9]. It was developed to carry out measurements of conductivity over a range of compositions and temperatures and was, in fact, more elaborate than was needed for the present work. Essentially it consisted of a Pyrex glass vessel to contain the melt which was

heated by an oil bath. The upper part of the vessel was maintained by means of heating tape, at a temperature somewhat above that of the melt in order to reduce convection and evaporation loss of AlCl₃. Provision was made for maintaining an atmosphere of dry nitrogen above the melt and for introducing the electrodes without risk of contamination by grease from the ground glass joints. The electrodes used consisted of 60 mm lengths of 4.8 mm diameter rod drilled and tapped at one end to enable the lead to be connected. The anode was of 99.99% aluminium. The cathode was generally mild steel but some experiments with copper and platinum gave the same results. The distance between anode and cathode varied from about 20 mm to 40 mm in different sets of apparatus.

3. Materials

Analytical grade sodium chloride was used without further purification other than drying at 550°C for 6 h and cooling in a desiccator.

Aluminium chloride of commercial quality was purified by sublimation from an AlCl₃/NaCl melt after addition of aluminium and, if necessary, sodium to reduce the ferric chloride present [8].

4. Experimental procedure

Initially electrodeposition was carried out at a cathode current density of 8 mA/cm² in a bath of approximately the eutectic composition (20 wt % NaCl) at a temperature of 175°C.

A standard specimen was freshly prepared for each electrodeposition and this involved, first, mechanically polishing the electrode in a lathe with a number of grades of silicon carbide paper (grades 280, 400, 500 and 600) and finally with alumina (5 μ), producing a highly polished surface. The specimen was then washed with distilled water, dried and cleaned with acetone. The electrode was then mounted as described above and immersed in the electrolyte to a depth which exposed an area of 5.5 cm² for electrodeposition.

The electrolysis cell was then connected to the appropriate electrical circuit and electrodeposition at an effective current density of 8 mA/cm²

carried out for a period of 60 min. The electrode was then removed, washed with distilled water, dried and the state of the plate examined.

5. Results

5.1. Addition of impurities

In the manner described above electrolytes with the following combinations of added impurities were first examined.

- (i) Ferric chloride and products of hydrolysis (HCl + Al₂O₃)
- (ii) Ferric chloride
- (iii) Products of hydrolysis.

Products of hydrolysis were introduced by exposing the aluminium chloride to the atmosphere, for approximately 5 min. The components were then melted down in the cell.

For each set of conditions three specimens were plated.

- (i) With ferric chloride and products of hydrolysis added.

The first specimen plated was covered by a fairly rough crystalline deposit. The second specimen showed some improvement but the deposit was still fairly rough. The third specimen showed a marked improvement, having a smooth compact plate.

- (ii) With ferric chloride added.

The aluminium deposited from the bath containing ferric chloride as an impurity showed no improvement on that obtained from the pure electrolyte. Each specimen examined was covered with a dark rough deposit.

- (iii) With products of hydrolysis.

The aluminium deposited from the bath containing products of hydrolysis showed a remarkable improvement over that obtained from the pure electrolyte. Each specimen studied was covered by a smooth compact matte deposit which on wiping with one of the commercial metal polishes produced a highly reflecting mirror finish. The improvement achieved is clearly indicated in Fig. 1. The specimen on the left is produced by a bath containing

products of hydrolysis while that on the right is one produced from a bath containing no added impurities.

The results of experiments on the addition of impurities to the electrolyte clearly indicate that the presence of products of hydrolysis of aluminium chloride suppresses the formation of a dendritic deposit and encourages the formation of a smooth compact electroplate. Having established this fact, a set of experiments was planned to establish which of either Al_2O_3 or HCl was responsible for the observed results.

The first of these was to add to a pure electrolyte about 1% of dry alumina of a fine grain size and determine the effect, if any, on the state of the deposited aluminium.

The second was to bubble dry hydrogen chloride gas into a pure electrolyte and determine the effect, if any, on the state of the deposited aluminium.

(iv) With alumina added.

Fine grain alumina (0.05μ) which had been dried for 4 h at 550°C was added, with the sodium chloride, to the purified aluminium chloride.

The process of electrolysis was again carried out on three specimens as described above. All three specimens were covered by a rough dendritic deposit after electrolysis had been carried out for 60 min.

(v) With hydrogen chloride added.

Hydrogen chloride gas was drawn from a small cylinder and passed into the melt through a fine jet via a concentrated sulphuric acid gas wash-bottle. The process of electrolysis was carried out on three specimens. All three specimens examined were covered by a smooth compact electroplate. A fourth specimen was electroplated at an increased current density of 16 mA/cm^2 and again a smooth compact deposit was obtained. It was noted that slight gassing occurred at the cathode due to the production of hydrogen by the reduction of hydrogen chloride.

From the observations described above it would appear that the presence of hydrogen chloride dissolved in the melt is effective in preventing the production of a rough dendritic

deposit. Thus if, to a purified electrolyte, hydrogen chloride is introduced, either by bubbling the gas into the melt or by exposing the purified aluminium chloride to the atmosphere for a short time (to achieve *partial* hydrolysis) steel may be readily and satisfactorily electroplated with aluminium at a current density of 16 mA/cm^2 .

In order to confirm that dissolved hydrogen chloride is the effective species and to attempt to relate the observations made here with those of previous workers, a series of experiments was carried out.

5.2. Extended electrodeposition

An electrolyte was made up, with products of hydrolysis introduced into it in the manner described above, and a series of six specimens electroplated in turn, for a period of 60 min at a current density of 16 mA/cm^2 .

The results of one such run are indicated in Fig. 2. Moving from left to right, the first three specimens are covered with a satisfactory plate. Specimen four shows some dulling of the deposit at the foot and specimens five and six show a progressively roughening deposit. The seventh specimen (extreme right) is that achieved by subsequently bubbling hydrogen chloride into the melt or by adding to it a few grams of aluminium chloride which has been exposed to the atmosphere for a short time.

This process of 'recharging' a bath which had ceased to produce satisfactory electroplates could be repeated several times and could always be achieved by either bubbling hydrogen chloride gas into the melt or adding to it partially hydrated aluminium chloride. For convenience, in practice, the latter procedure was generally adopted.

5.3. Current efficiency

During the experiments above, the current efficiency was determined for electrodes 1, 4, 6 and 7. The results obtained are as follows:

Electrode No.	Current efficiency (%)	State of plate
1	80.1	Satisfactory
4	84.3	Satisfactory/fair
6	99.6	Rough deposit
7	83.8	Satisfactory



Fig. 1. Specimens plated with (left) and without (right) products of hydrolysis present in the melt.

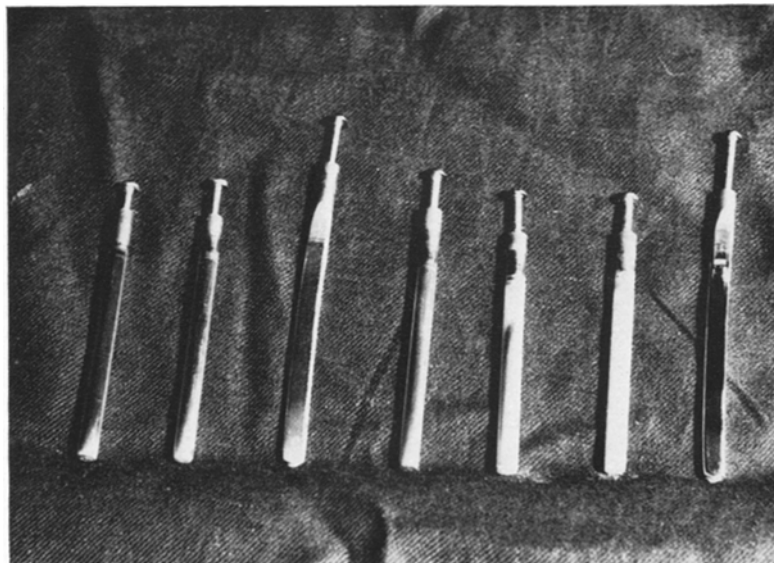


Fig. 2. Continued electrodeposition showing (left to right) progressive deterioration and (extreme right) regeneration of plate quality.

It is clear from these observations that when a satisfactory plate is obtained the current efficiency is considerably less than 100% and when a rough deposit is produced that the theoretical value of 100% is closely approached.

An auxiliary reaction involving the reduction of hydrogen chloride would readily explain the observed results. The reduction could either be direct electrolytic reduction or reduction by reaction with already deposited aluminium.

The observed current efficiency figures can also give information relating to the weight per cent of hydrogen chloride present in the melt. Such a figure is clearly difficult to determine accurately. The vigorous reaction which takes place between water and anhydrous aluminium chloride means that it is impossible to determine how much hydrogen chloride has been introduced when a known weight of water or hydrated aluminium chloride (AlCl₃·6H₂O) has been added. An approximate figure may be obtained from the current efficiency figures. From the data above it is clear that at a current efficiency of 80% sufficient hydrogen chloride is present to produce a satisfactory electroplate while at a current efficiency of 99% almost all the hydrogen chloride has been removed and a poor deposit results.

If an average current efficiency of 85% is assumed for the electrodeposition of specimens one to six then the weight of hydrogen chloride removed from the melt can be calculated. The figure arrived at for the weight per cent of hydrogen chloride in the melt, necessary to produce a satisfactory deposit is approximately 0.07%.

5.4. Current density

Having established a means of readily depositing aluminium on steel at a higher current density it is clearly worthwhile to determine the dendritic growth threshold current density for the system containing dissolved hydrogen chloride.

To do this several specimens were electroplated at increasing current densities with the following results. (See next column).

It is clear that a satisfactory plate may be obtained at a current density in the region of 16 mA/cm². In this region deposition may be

Current density	State of plate
8 mA/cm ²	Satisfactory
16 mA/cm ²	Satisfactory
20 mA/cm ²	Generally satisfactory but occasionally specimen had slight roughness.
25 mA/cm ²	Deposit tended to be rough.

carried out with no danger of a dendritic deposit. The dendritic growth threshold current density for the system is in the region of 20–25 mA/cm².

6. Discussion

From the information collected there would seem to be no doubt that dissolved hydrogen chloride is effective in producing a satisfactory plate.

By establishing that hydrogen chloride, dissolved in the melt, is effective in producing a smooth compact corrosion-resistant deposit of aluminium it has been possible to indicate conditions capable of providing an electroplate which (as far as one can determine from a study of the literature) is superior to any previously obtained.

With the evidence available it is difficult to describe the precise action of hydrogen chloride in greater detail. It is however possible that its action is simply to remove aluminium from high spots where a crystal growth of a dendritic nature could continue, by converting it to aluminium chloride with the liberation of hydrogen. Another possible mechanism would be that potentially dendritic crystals, which project further into the electrolyte than crystals of a smaller size, provide a site more favourable for the electrolytic reduction of hydrogen ions introduced by way of the hydrogen chloride thus blocking off these sites to the further deposition of aluminium. If either of these two processes were continued throughout the period of electrolysis the net effect would be a refining of crystal size producing the smooth compact plate observed.

7. Summary

The conditions which have been established for electroplating are as follows:

1. Composition of electrolyte

Pure anhydrous aluminium chloride (free of Fe) 80 wt %
 Analytical grade sodium chloride 20 wt %

To this is added a small amount of moisture which will result in approximately 0.07 wt % hydrogen chloride dissolved in the melt. As hydrogen chloride is removed from the melt it must be replenished to maintain the required concentration.

2. Bath temperature 175°C.

3. Current density 16 mA/cm².

These conditions consistently produce electroplates of a high quality and show a marked improvement on those obtained by the conditions established by Collins. The data obtained from current efficiency and current density enable the inconsistencies in the literature in this area to be explained in a convincing manner.

From the investigations described above, the dendritic growth threshold current density (D.G.T.C.D.), the current efficiency and the state of the deposited aluminium may be linked as follows:

State of electrolyte	D.G.T.C.D. mA/cm ²	Current efficiency (%)
Pure (no added moisture)	1	100
0.07% of HCl (added moisture)	20	80

As the hydrogen chloride concentration (from added moisture) increased from 0.0 to 0.07% so the dendritic growth threshold current density increases from 1 to 20 mA/cm² and the current efficiency decreases from 100 to 80%.

If we consider the work of Collins, the fact that flux grade aluminium chloride was used

means that hydrogen chloride, produced from partial hydrolysis, would have been present in his melts, resulting in the recommended current density 16 mA/cm² and the observed current efficiency figure of about 80%.

Midorikawa has observed current efficiencies in excess of 90% and recommends a current density of 1.0–3.0 mA/cm². It would, therefore, appear that only a very small percentage of hydrogen chloride (0.07%) had been present.

Miyata observed current efficiencies of about 85% and recommends a current density of about 20 mA/cm² which would suggest that hydrogen chloride was present in his melts to the extent of about 0.07%.

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