

ELECTRO-REFINING OF ALUMINIUM

K S SRINIVASAN, C O AUGUSTIN, K S DANDAPANI, A SELVAKESAVAN, G N KANNAN, S M SUKUMARAN, L K SRINIVASAN, P SUBRAMANIAN, T SELVIN DEVASAHAYAM, N RAJAGOPALAN, S SRIKANTAN, P S DESIKAN and K I VASU

Central Electrochemical Research Institute, Karaikudi-623 006

ABSTRACT

Bench scale cells of 200 A capacity have been designed and operated for electrorefining of aluminium, incorporating some improvements in the design. Factors to be studied are alloy composition, electrolyte composition, operating parameters like current density, interpolar gap, developing a suitable method of feeding the impure metal and removing the purified aluminium.

Key Words: Electrorefining, superpure aluminium, three layer electrolysis

INTRODUCTION

Aluminium produced commercially by Hall-Heroult's process is of purity 99.5 - 99.8% and is useful for various alloying purposes. Since a higher purity of aluminium confers some technological characteristics that are extremely useful in certain special applications just as in the production of light aluminium-magnesium alloys for use in aeronautics industry, in electronic industries for making capacitors and in providing contacts, refining of aluminium becomes necessary. The requirement of the superpure aluminium is small and at present the demand is met by import. Considering the strategic sector in which it finds application in aeronautics and space science, developing an indigenous technology was keenly felt.

The various metallic impurities present in the primary metal such as iron, copper, zinc, magnesium, silicon, are usually picked up in the various processing stages in primary aluminium production. The impurities could not be removed to the desired level by normal fluxing procedure—chemical reaction—since the total energies of formation for compounds of oxygen, fluorine and chlorine are found to be unfavourable. Physical methods e.g zone refining in which impurity content can be reduced to less than 10 ppm is hindered by low diffusion rates and has never led to industrial interest. The electrorefining wherein the pure metal is extracted leaving the impurities behind has received focus and is commercially practised in high-capacity cells (20 KA) all over the world.

Three-layer cell [1]

The well known Hoope's process is essentially a galvanic cell consisting of molten electrolyte containing Al^{3+} ions which separates two molten electrodes—impure metal alloyed with copper as the anode and superpure aluminium acting as the cathode. The impure aluminium is alloyed with 30 wt% copper to lower the liquidus temperature from 660° to 560°C and increase the density to about 3.0 so that it is made the bottom most anode layer of the three-layer process. All fluoride-high temperature electrolyte (Hoope's process) was subsequently replaced by low temperature chloride-fluoride electrolyte (Pechiney process). Several modifications of cell design have been reported [2,3].

Theoretical considerations of the electrorefining process

Thermodynamic consideration will show that for extracting one gram atom of aluminium from alloy and transferring it to the molten superpure aluminium layer, 0.005 volts only is required as per the following equation:

$$E = \frac{-R}{3 \times 98500} \ln 0.85 = .005V$$

where 0.85 is the activity of aluminium in copper-aluminium alloy. This works out to nearly 0.015 kwh/kg of pure aluminium for isothermal transfer from alloy to the cathode. But in practice commercial cells operate at about 5.5V resulting in an energy consumption of 18 kwh/kg of superpure aluminium. Major portion of the excess energy is used for overcoming the ohmic resistance of the bath and is gainfully used in maintaining the thermal balance of the cell.

Criteria for bath selection

On an analogy with the primary electrowinning bath, fluoride baths have been recommended for the following reasons. Since the free energy for formation of fluorides are far more negative than the chlorides and are stable, e.g. ΔG at 1000° K for AlF_3 is -194 kcal and for $AlCl_3$ -92 kcal, only those fluorides of metal, whose free energy is more negative than that of AlF_3 can be used. But a quite wide choice amongst the fluorides of sodium, barium, calcium and magnesium exists, since these elements will not contaminate the pure aluminium product when there is sufficient aluminium concentration in the bath. A judicious mixture of the fluorides of alkali and alkaline earth metals has hence to be selected taking into consideration the other physico-chemical properties like primary crystallisation temperature, density, viscosity and volatility. In general aluminium fluoride is introduced into the cell as such or as cryolite. Magnesium, if present in the alloy, will enter into the flux and get deposited whereas Fe, Si, Mn, Ti, Zn, V, Ga and Cu will be retained in the aluminium-copper alloy so long as the alloy contains sufficient aluminium concentration and bath contains fluoride ions to fix the extracted aluminium from the alloy. Electrolysis of pure molten cryolite containing barium chloride will result in formation of aluminium in small amounts due to breakdown of AlF_6 complex, and barium at the cathode. Sodium will not be formed since sodium is bound to AlF_6 groups. When excess fluoride ions in the form of NaF/AlF_3 are added, barium ion will be surrounded by them to yield the stabler BaF_2 . Under these conditions electrolysis will produce only aluminium at the cathode and no barium will be deposited.

Based on these considerations, the following baths are commercially used. [4]

(i) *AIAG (German process)*: 48 wt% AlF_3 , 18% NaF , 18% BaF_2 , 16% CaF_2 (Temp. 740-750°C)

(ii) *Hoope's process*: 25-30% NaF, 30-38% AlF_3 , 30-38% BaF_2 , 0.5-3% Al_2O_3 (Temp. 1000°C)

(iii) *Pechiney process*: 23 wt% AlF_3 , 17% NaF, 60% BaCl_2 (Temp. 750°C)

EXPERIMENTAL

Laboratory scale experiments were undertaken to study the three layer refining process with a view to optimise some of the critical parameters before a commercial or semicommercial scale refining cell could be developed. These include, the choice of the bath, behaviour of the alloy system, materials of construction, faradaic efficiency, interelectrode gap and of course the refining efficiencies.

The experimental cell was designed to operate around 200 Amps. The cell system generally adopted is given Fig. 1, even though certain minor modifications were made in each experiment. One of the main deviations

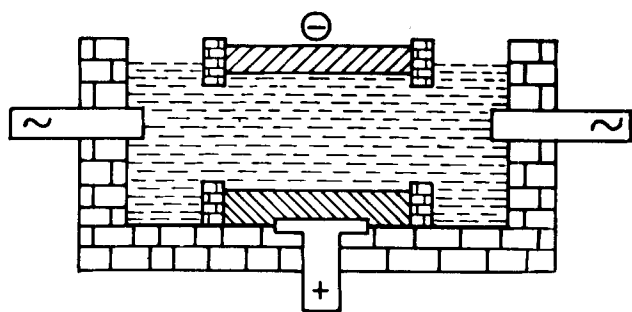


Fig. 1 . 3 Layer Cell (Lab Scale) 200 A. without feeding arrangement

which had to be made from the conventional large scale cell of Hoopes type is with respect to the heating arrangements for keeping the bath molten in such a small cell. At 500 Amps under normal operating voltage condition of 7-8 volts the heat energy available is around 15 kW, which is hardly enough to keep the alloy as well as electrolyte molten. In view of the fact that this is a refractory cell, external heating arrangement was also not possible. Hence the required additional heat was supplied through auxiliary AC (low voltage-higher current) sources using the electrolyte itself as the resistor. These heat reservoirs were accommodated at the two ends of the rectangular cell and communication with the main cell was established through the electrolyte itself. Refractory partitions were employed to keep apart the heating chamber and electrolyser. Magnesite bricks were employed both for the cell walls and the partitions.

TABLE I Operating data of the refining cell
Anode: Alloy of impure Al with 30% copper

Sl.No.	Current (A)	Cell voltage (V)	Duration of electrolysis (Hrs)	Bath composition Wt%	Metal collected (Kg)	Current efficiency (%)
1	250	13-14	84	$\text{BaCl}_2 = 60$ $\text{NaF} = 17$ $\text{AlF}_3 = 23$	2.65	38
2	200	14	70	$\text{BaCl}_2 = 55$ $\text{NaF} = 17$ $\text{AlF}_3 = 23$ $\text{NaCl} = 5$	4.75	99
3	150	9	112	-do-	5.5	97

The two main problems which had to be encountered during the operation of this laboratory cell are the proper heat distribution and giving contacts to the liquid metal electrodes. In the initial experiments, a chloride-fluoride bath containing 23% AlF_3 , 17% NaF and 60% BaCl_2 which melted at a temperature of about 750°C was employed. Unlike the arrangement shown in Fig.1, a single heating chamber was used in the initial design. It was found that in view of the high melting point and lack of fluidity of the bath, the heat distribution was not proper. As the temperature at the heating chamber was raised, there was more of local heating resulting in the vapourisation of the bath. To overcome this problem, two modifications were effected—the first being the introduction of the second heating chamber as shown in Fig.1 and secondly the use of a modified bath containing 5% of sodium chloride in addition to the above mentioned components, namely, aluminium fluoride, sodium fluoride and barium chloride. The introduction of sodium chloride helped to lower the melting point by about 40°C and also to improve the fluidity of the bath.

For passing the DC current into the cell, graphite leads were used. For anode a circular graphite disc was embedded at the bottom of the cell over which the molten anode alloy was kept. This arrangement was satisfactory. For cathode, the liquid metal floating at the top acted as cathode. The electrical leads with graphite presented some problems, due to the poor wettability of molten aluminium with graphite and due to air oxidation of the graphite at the air liquid interface. The initial arrangements with vertical lead plunged into the molten aluminium, as described in the literature for large scale cells, did not work properly. Consequently a fully submerged graphite plate was employed as cathode lead in later experiments. Here also sufficiently large amounts of liquid cathode metal pool had to be kept to overcome the surface tension effects between graphite and aluminium and ensure proper contacts.

The cell was initially started by melting the electrolyte first with the auxiliary AC, adding the anode alloy (pre-alloyed) in solid form slowly and finally adding top layer cathode metal. It could thus be seen that until the DC is switched on, the molten alloy anode would be in contact with the molten electrolyte resulting in the possibility of chemical dissolution of some copper in the electrolyte. This perhaps invariably resulted in some copper contamination in the refined metal at least in the initial stages. A pre-electrolysis step to remove initial copper in these electrolytes was also tried but the efficacy of this step could not be confirmed.

Electrical conductor grade aluminium was used as starting material both for anode and cathode. The extent of refining on the cathode layer was monitored by analysing the impurities using AAS periodically during the experiments. Based on the capacity of the cell and the quantities of cathode metal used, one could expect the attainment of superpurity grade if the cell could operate continuously for 15 days. However the experiments reported in this paper were restricted to the maximum of five days only, since the method of introducing the impure metal into the small cell could not yet be perfected and therefore conducted on a batch basis.

RESULTS AND DISCUSSION

Table I gives the operating characteristics of the cell during three of the most successful experiments which were subjected to a number of modifications each time. Some of the general conclusions which could be drawn during these short runs are as follows.

Electrolyte

A new electrolyte incorporating the sodium chloride over the conventional bath appears to be superior in the sense it was relatively more fluid and hence easily controllable with respect to the heat distribution or vapourisation less thereby lessening the need for frequent replenishment of the bath. The smooth performance of the cell is also reflected in the attainment of higher current efficiencies.

The interelectrode distance and cell voltage

Interelectrode distance of 8-10 cms was maintained in these experiments giving a cell voltage of 10 to 12 volts. Even though the interelectrode distance could be kept lower still, this was not attempted due to the fear of copper contamination in cathode metal due to the physical mixing. Also part of the energy needed to keep the electrolyte molten could be furnished by DC if the voltage could be kept relatively high.

Current efficiency

Good faradaic efficiencies were realised during the experiments. A maximum of 90-97% was realised in two batch runs. The overall current efficiency was computed by weighing the quantities of metal removed and also the metal which remained at the termination of each run.

Refining efficiency

Table II shows typical data of refining of various elements during the experiments. It could be seen that all elements except copper get reduced steadily which indicated that if the electrolysis had continued, the requirements of superpurity aluminium could be met. But in the case of copper, there was an increase in the impurity level which could be attributed to chemical dissolution of copper during power interruptions and also to some extent the mixing of anode and cathode metal. However it was found

that after an initial increase, the copper content maintained steady level in the cathode metal which indicated that the continuance of the electrolysis upto 15 days might yield superpurity aluminium.

TABLE II : Analytical report

Element	Starting metal %	End metal %	Superpurity aluminium %
Zn	0.007	0.002	0.0006
Fe	0.430	0.050	0.0003
Mn	0.005	0.002	—
Mg	0.020	0.003	0.0007
Cu	0.010	0.020	0.0004

CONCLUSIONS

Small scale experiments conducted so far on three layer refining were helpful in establishing that a modified electrolyte incorporating 5% sodium chloride in the chloride-fluoride bath was helpful. The experiments were also helpful to develop suitable method for giving electrical contacts in the cell and also towards the choice of construction materials for the three layer system. A suitable method for introducing the impure metal into the cell has yet to be devised to enable the continuous run which only could yield the completely refined metal of superpurity grade.

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