

# Direct production of aluminum titanium alloys in aluminum reduction cells, a laboratory test

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## Abstract

Aluminum smelters produce pure aluminum in reduction cells by the Hall Héroult process, but supply a variety of alloys to their customers. The alloys are produced in the cast house, as desired alloying elements are added to the primary aluminum from the potroom before casting. In this paper the concept of producing titanium master alloys directly in the aluminum reduction cells is discussed, by feeding titanium oxide to the electrolyte, along with the alumina raw material. The results in this paper are obtained by running electrolysis experiments in a laboratory cell, and the current efficiency for the alloy deposition is estimated. Results for aluminum-silicon and aluminum-manganese alloys are reported in a different paper.

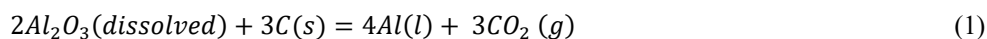
Keywords: Aluminum, electrolysis, current efficiency, titanium

## Introduction

Titanium has excellent properties such as good corrosion resistance, high strength to weight ratio, and stiffness. It is used in various applications like aerospace as well as in biomedical industry when alloyed with aluminium [1, 2].

Primary production of titanium by the Kroll process is very costly because it is energy and labor intensive with low productivity [3, 4]. Attempts to produce Al-Ti alloys in the Hall-Heroult process have been reported [5–7]. Al-2% Ti has been successfully produced by the addition of titania into the electrolyte. It is worth mentioning that traces of titanium of magnitude of 10 to 100 ppm is common in commercial aluminium [8]. It is introduced through the raw materials; alumina and tiny amounts present through pitch and anode materials. Titanium is used effectively as a grain refiner in many aluminium alloys in concentrations of up to 0.2 wt. % resulting in improved microstructure and mechanical properties [8,9]. The current method of producing aluminium-titanium alloys is by mixing pure titanium metal with primary molten aluminium prior to casting [10]. Melt mixing has several drawbacks such as the high cost of pure titanium metal, the significant energy requirement, and the possibility of serious segregation [11]. These drawbacks can be remedied through an in-situ electrochemical reduction of titania in fluoride-based melts which has been a subject of research for a long time [12, 13].

Liquid aluminium is produced in the Hall–Heroult process by the electrolytic reduction of alumina ( $Al_2O_3$ ) dissolved in an electrolyte based on cryolite ( $Na_3AlF_6$ ) at 960–970 °C according to the overall electrochemical reaction representing the deposition process given by [14]:



$TiO_2$  dissolves readily in the electrolyte and titanium will co-deposit with the aluminum as it has a lower decomposition potential. Electrochemical investigations [15] of Ti (IV) in fluoride-based electrolytes suggested a two-step reduction mechanism, with Ti (III) as a stable intermediate, as follows:



The potential difference between the deposition reactions for aluminium and titanium has been estimated to be 0.3 V [15]. It is likely that  $TiAl_3$  may be formed as it is a stable alloy at high contents of Al according to the phase diagram of the Ti–Al system [16]. It has been shown in experiments in industrial cells that titanium will co-deposit

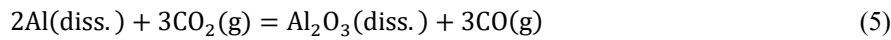
with aluminum at its limiting current density [17]. It was also found that about 90 % of the added titanium in the form of TiO<sub>2</sub> ended up in the produced metal [15].

The performance of a laboratory cell may be judged by current efficiency measurements. Current efficiency (CE) is a representation of how efficient the supplied electricity has been used to deposit aluminium. It can be estimated by metal weight gain relating the actual produced aluminium to the aluminium that would theoretically be produced based on Faraday's law. Then CE% may be written as:

$$CE\% = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100 = \frac{W_{\text{actual}}}{\frac{M_{\text{Al}}It}{nF}} \times 100 \quad (4)$$

where  $W_{\text{actual}}$  is the actual mass of metal produced whereas  $W_{\text{theoretical}}$  is the theoretical mass of metal produced according to Faraday's law.  $M$  is the molar mass of aluminum,  $I$  is the applied current intensity in Ampere,  $n$  is the number of electrons transferred, and  $F$  is the Faraday constant 96487 C/mol.

In practice, the amount of aluminum calculated based on Faraday's law can never be obtained. There is always a certain amount of aluminum that dissolves in the electrolyte. As a result, some dissolved metal will react with CO<sub>2</sub> produced at the anode in the so-called back reaction which can be expressed as:



The average current efficiency for an alloy such as Al-Ti can be calculated according to:

$$CE_{\text{alloy}}\% = \frac{W_{\text{alloy}}}{W_{\text{alloy,theoretical}}} \times 100 \quad (6)$$

where  $W_{\text{alloy}}$  is the total mass of metal produced experimentally whereas  $W_{\text{alloy,theoretical}}$  is the theoretical mass of the alloy produced. The theoretical mass of the produced alloy is given by Faraday's law as:

$$W_{\text{alloy,theoretical}} = \frac{M_{\text{alloy}}It}{n_{\text{alloy}}F} \quad (7)$$

where  $M_{\text{alloy}}$  is the average molecular mass of the alloy and  $n_{\text{alloy}}$  is the average number of electrons transferred for the deposition of the alloy. The two quantities may be estimated for the Al-Ti alloy, according to the so-called electrochemical equivalent given by:

$$W_{\text{equiv.}} = \frac{\left[\frac{M_{\text{Al}}}{n_{\text{Al}}}\right] \left[\frac{M_{\text{Ti}}}{n_{\text{Ti}}}\right]}{\left(x_{\text{Al}} \frac{M_{\text{Ti}}}{n_{\text{Ti}}}\right) + \left(x_{\text{Ti}} \frac{M_{\text{Al}}}{n_{\text{Al}}}\right)} \quad (8)$$

Thus CE % for the alloy can be given by:

$$CE\%_{\text{alloy}} = \frac{W_{\text{alloy}}}{W_{\text{equiv.}} \frac{It}{F}} \times 100 \quad (9)$$

where  $M_{\text{Al}}$ ,  $M_{\text{Ti}}$ ,  $n_{\text{Al}}$ ,  $n_{\text{Ti}}$ ,  $x_{\text{Al}}$ , and  $x_{\text{Ti}}$  are the molar masses of Al and Ti, their charges, and their mass fractions respectively.

The present work reports a study on the electrochemical reduction of an aluminium-titanium alloy during aluminium deposition in fluoride-based melts in a laboratory cell implementing industrial standards. The effect of the presence of Ti on the cell performance with respect to Al, the current efficiency for the produced alloy, and the deposit surface shape are discussed.

## Experimental

Carbon Experiments were carried out in a laboratory cell originally designed by Solli et al. [18] for current efficiency measurements during electrodeposition of liquid aluminum. The laboratory cell is schematically illustrated in Figure. A graphite crucible with cylindrical sintered alumina side lining of about 10 cm height containing anode, cathode, and electrolyte was used. The anode is cylindrical with a central vertical hole as well as horizontal holes penetrating the anode. This design provides good convection within the bath so that gas bubbles from the anode pass through the central vertical hole in the bottom allowing electrolyte to flow up and through the horizontal holes on the sides causing the electrolyte to circulate in a loop. Gas bubbles will then have less effect on the electrolyte convection near the cathode which otherwise may influence the current efficiency.

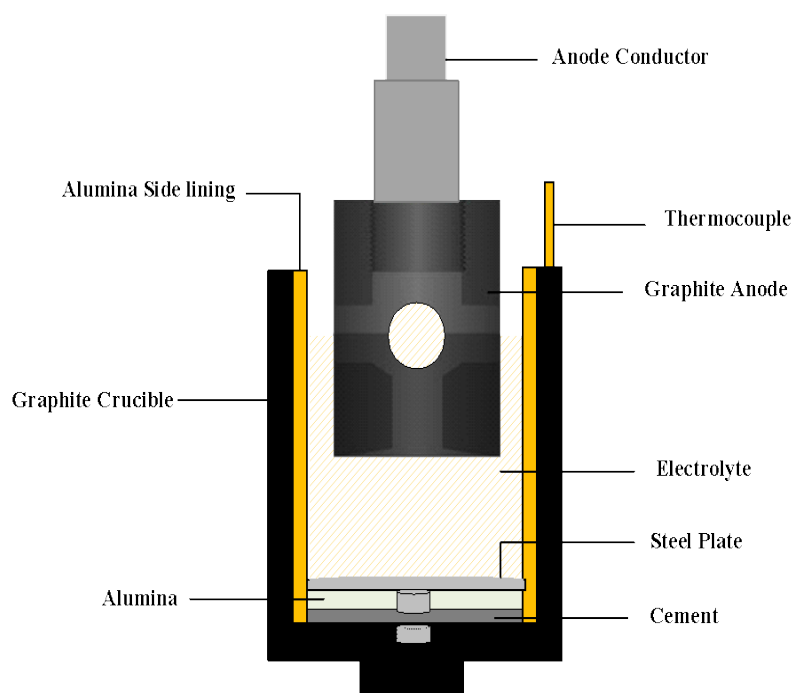


Fig. 1. Sketch of the laboratory cell.

The liquid aluminium metal product wets a steel plate resting on the bottom of the graphite crucible and acts as a cathode which ensures an almost flat deposit surface and an even current distribution.

The composition of the electrolyte is given in Table 1. The electrolyte components were dried at 200 °C for 24 hrs before being transferred to the crucible. The furnace was continuously flushed with argon gas during the experiment to prevent air burn of cell components.

Table 1. Electrolyte Components.

Chemicals	Pre-treatment	Quality/Supplier
AlF <sub>3</sub>	Sublimed at 1090°C for 24 h	Industrial grade, Alcoa- Norway
NaF	Dried at 200 °C for 24 h	99.5 %, Merck-Germany
CaF <sub>2</sub>	Dried at 200 °C for 24 h	Precipitated pure, Merck-Germany
Al <sub>2</sub> O <sub>3</sub>	Dried at 200 °C for 24 h	Anhydrous (γ-alumina), Merck-Germany
TiO <sub>2</sub>	Dried at 200 °C for 24 h	Rutile, 99.8% (metal basis) Alfa Aesar-Germany

Experiments were carried out by constant current for 4 h at temperatures from 965 – 980 °C. The corresponding superheat was varying from 13.0 – 28.0 °C. The cathodic current density (CCD) was kept at 0.9 A/cm<sup>2</sup> for all runs as well as the cryolite ratio (CR) of 2.2. The standard electrolyte was: 12.0 wt% AlF<sub>3</sub>, 5.0 wt% CaF<sub>2</sub>, 4.0 wt%

$\text{Al}_2\text{O}_3$ , and balance of  $\text{NaF}-\text{AlF}_3$  based cryolite. Titanium (IV) oxide was initially mixed with the bath constituents prior to electrolysis. Three concentrations, 0.2 wt% Ti, 0.6 wt% Ti, and 1.0 wt% Ti were used.

The bath was sampled regularly at constant intervals during electrolysis using quartz tubes. The collected metal samples were subjected to mechanical and chemical post-treatments, the latter by aluminium chloride hexahydrate solution for 30-40 minutes. Bath samples were crushed into fine powder and dissolved in a mixture of strong acids including HCl,  $\text{HNO}_3$ , and HF. The solutions were digested and agitated to ensure a complete dissolution. ICP-MS was conducted for samples to determine the Ti content in the bath.

## Results and Discussion

### Current efficiency for Al without addition of $\text{TiO}_2$

The Three blank tests were carried out with no addition of  $\text{TiO}_2$  at 965 °C, 970 °C, 975 °C, and 980 °C. The average current efficiency for aluminium deposition are given in Fig. 2.

The trendline in Fig. 2 are based on least square regression and yielded a decrease in the current efficiency of 0.2 % for each 1 °C increase in the operating temperature. It agrees with reports which suggest that the enhancement of 1 % in current efficiency was obtained by the decrease of 5 °C in the operating temperature [29]. Blank tests can be considered as benchmarks to check for the effect of the addition of alloying elements on the current efficiency for electrolysis.

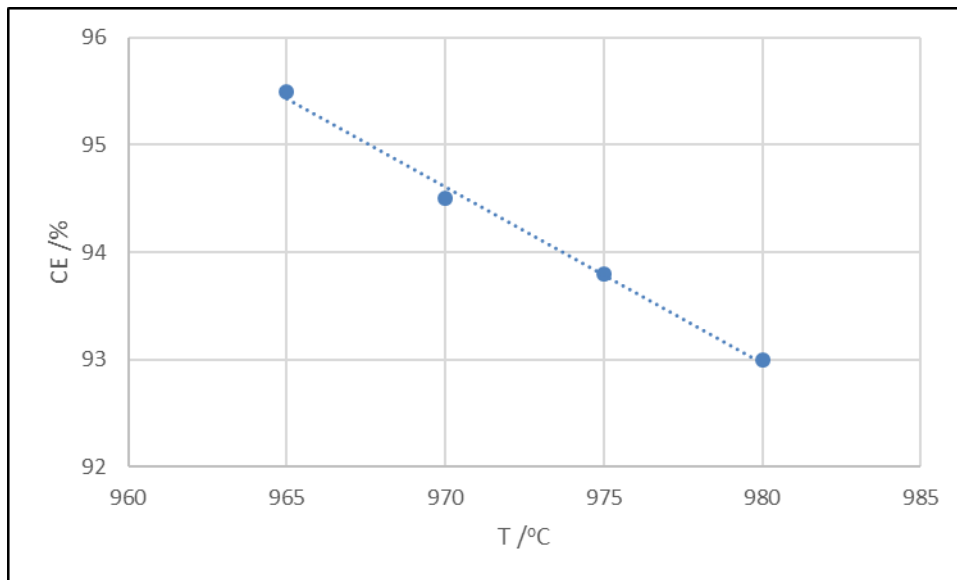


Fig. 2. Average values of CE of blank tests at different temperatures with a linear trendline. CR=2.2, no alumina feeding, 0.9 A/cm<sup>2</sup>, electrolysis time 4h.

### Titanium co-deposition and current efficiency after addition of $\text{TiO}_2$

The  $\text{TiO}_2$  was mixed with other bath components before melting. Three concentrations were considered: 1.0 wt. % Ti, 0.6 wt. % Ti, and 0.2 wt. % Ti. Temperatures were 965 °C, 970 °C, 975 °C, and 980 °C.

Electrolyte samples were analyzed for Ti content. As shown in Figure 3, around 30 % of Ti dissolved depleted during the first half of the experiment (120 min) at 965 °C whereas 34 % depleted at 980 °C.

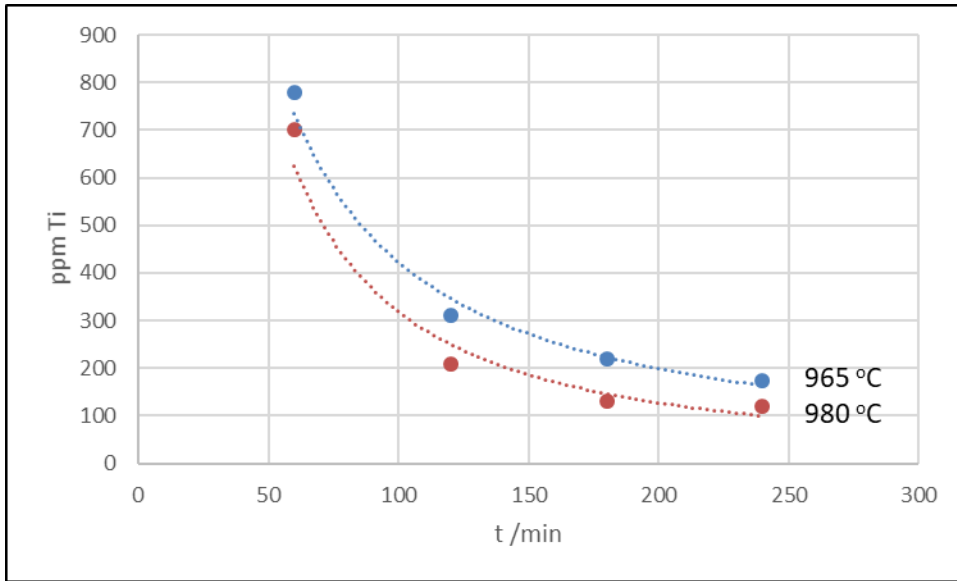


Fig. 3. Decay of Ti content in the bath during electrolysis. 1.0 wt% Ti added before electrolysis as  $\text{TiO}_2$ , 965 °C and 980 °C.

The average current efficiencies of Al–Ti alloys were estimated according to equations (7-10). The average current efficiency for the alloy is a representation of the current efficiency of each element based on its content in the alloy. The obtained average values for the current efficiency for Al–Ti alloys are shown in Fig. 4.

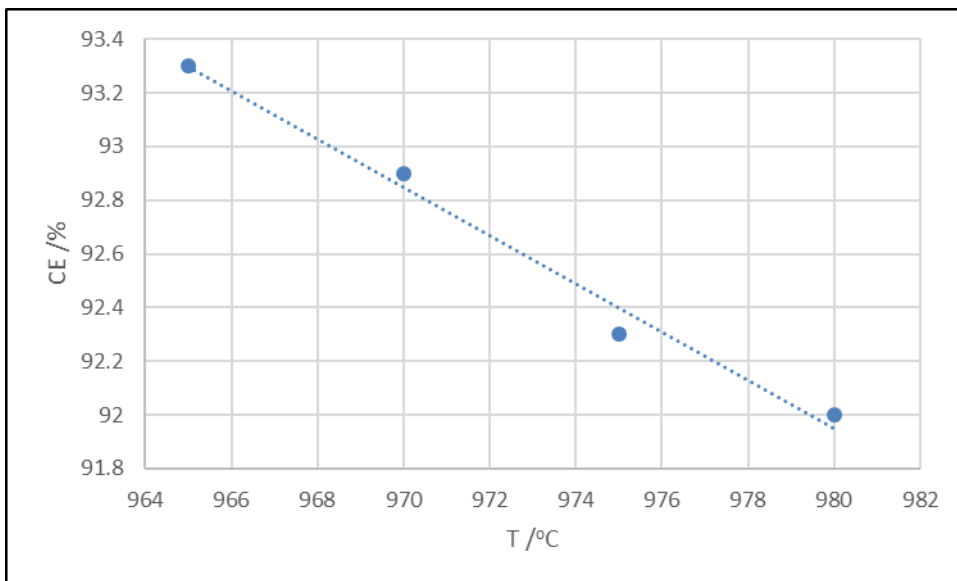


Figure 4. Average current efficiency for Al–Ti deposition as a function of temperature with a linear trendline. 0.6 wt% Ti added before electrolysis as  $\text{TiO}_2$ , 965 °C and 980 °C

It was found that the co-deposited titanium content was in the range from 1 – 7 wt. %. The ratio of titanium found in the metal and titanium initially added to the bath in the form of titania is referred to as the conversion. The results suggest that almost all the 0.2 wt% Ti initially added to the bath (in the form of  $\text{TiO}_2$ ) at 965 °C ended up in the metal. It was also observed that at 0.2 wt. % Ti initially added as  $\text{TiO}_2$  a reduction of about 3 % in the conversion was estimated for every 1 °C increase in the operating temperature. The decrease in the conversion of Ti was estimated to be 1.7 % and 0.3 % at 0.6 wt% Ti and 1.0 wt% Ti initially added to the bath as  $\text{TiO}_2$  respectively for every 1 °C increase in the operating temperature.

Blank tests are used as reference when looking at the effect of the presence of Ti in the deposit on the CE. Current efficiency for Al is based on the net weight of Al found in the deposit and taking into account the content of deposited Ti. If all Ti initially added would end up in the deposit, an increase in the CE of Al would be recorded at 2.0 % and 0.3 % at 965 °C and 970 °C respectively at initial Ti content of 1.0 wt% in the electrolyte. The increased current efficiency could be due to the fact that co-deposition of titanium lowered the activity of aluminium in the metal deposit and thus lowered the solubility of aluminium in the bath and reduced the rate of the back reaction which is the major factor for the loss in CE of Al. A decrease in the CE for Al, with respect to the average current efficiency for Al for corresponding blank tests, due to the co-deposition of titanium was estimated to be in the range from 3 % to 7 % at different conditions.

The shape of the solidified deposits after electrolysis experiments was examined visually. It was found that most of the experiments gave flat deposits with even thickness suggesting that homogeneous current distribution was achieved. Only experiments at the high Ti content of 1 wt% at 965 and 970 °C gave deformed deposits which may be due to precipitation of solid alumina or cryolite during electrolysis.

## Conclusions

Electrolysis experiments were carried out in a laboratory cell dedicated to aluminium current efficiency measurements. The current efficiency for aluminum deposition was found to decrease from 95.5 % to 93.0 % when the temperature changed from 960 – 980 °C due to the increased solubility of metal in the bath.

Co-deposition of titanium was observed after adding TiO<sub>2</sub> to the electrolyte before electrolysis. The content of Ti was found to vary from 1 – 7 wt% after adding 0.2, 0.6 and 1.0 wt% TiO<sub>2</sub>. The average current efficiencies of Al–Ti alloys were reduced by up to 5 % in comparison to those estimated for the actual deposition of Al which implies that this path is quite efficient to produce such alloys. More than 95 % of the added titanium as TiO<sub>2</sub> was found to end up in the deposited metal.

Solidified deposit surfaces of all blank tests were flat indicating even current distribution. At high TiO<sub>2</sub> content of 1 wt. % Ti with low superheat (13 °C and 18 °C) the solidified deposit surfaces were partially deformed.

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