



Full Communication

Electrodeposition of aluminium-titanium alloys from molten fluoride-oxide electrolytes

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ABSTRACT

This study reports the direct production of an aluminium-titanium alloy during aluminium electrolysis in fluoride-based melts. Experiments were conducted in a laboratory cell dedicated to current efficiency measurements. The temperature was varied from 960 to 980 °C at a cathodic current density (CCD) of 0.9 A/cm² and a cryolite ratio (CR) of 2.2. The titanium content was up to 1.0 wt%. Titanium was added in the form of a TiO₂ precursor. Bath samples were collected regularly and analyzed with ICP-MS to observe the decay of titanium during electrolysis. The current efficiency for electrodeposition of Al-Ti alloys was estimated to be at least around 90%. The surface of the solidified metal deposits was mostly flat, but some deposits were partially deformed.

1. Introduction

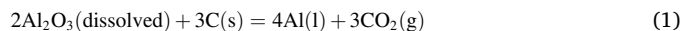
Titanium has good mechanical properties, including good corrosion resistance, a high strength to weight ratio, and stiffness. It is used in various fields such as the aerospace industry as well as in biomedical applications when alloyed with aluminium [1,2]. However, titanium's strong affinity towards elements like O, N, S, and C makes its extraction costly due to the high energy requirements [3,4].

Attempts to produce Ti alloys using the Hall-Heroult process have been reported. The solubility of titania in cryolite based electrolytes has been a subject of research as the idea of co-depositing of titanium during the primary production of aluminium has been suggested by many researchers [5–8]. Al-2%Ti has been successfully produced by the addition of titania into the electrolyte. It is worth mentioning that traces of titanium of the order of 10 to 100 ppm do exist in commercial aluminium [9], being 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 [10–17]. It is also added in the cast house to form the desired alloy compositions.

The current method of producing aluminium-titanium alloys is via admixing pure titanium metal with primary molten aluminium prior to

casting [18]. Melt mixing has several drawbacks, such as the high cost of pure titanium metal, the significant energy requirements, and the possibility of serious segregation [19]. These drawbacks could be remedied through an in situ electrochemical reduction of titania in fluoride-based melts, which has long been a subject of research [20,21]. A recent publication from the authors of the present paper reports the formation of an alloy with up to Al-2.0% Ti with an enhancement in the current efficiency for Al in the range 6.0–8.0% in alumina tests due to the co-deposition of titanium [19].

Liquid aluminium is produced in the Hall-Heroult process by the electrolytic reduction of alumina (Al₂O₃) dissolved in an electrolyte based on cryolite (Na₃AlF₆) at 960–970 °C. The overall electrochemical reaction representing the deposition process is as follows [22]:



TiO₂ dissolves readily in this electrolyte and will co-deposit with the aluminium as it has a lower decomposition potential. Electrochemical investigations [23,24,25] of Ti (IV) in fluoride-based electrolytes suggested a two-step reduction mechanism, with Ti (III) as a stable intermediate:



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The potential difference between the deposition reactions for aluminium and titanium was estimated to be 0.3 V, which is very close to the difference between the standard decomposition potentials of alumina and titania (0.33 V) [5]. Such results suggest the likelihood of forming an Al-Ti alloy on the cathode.

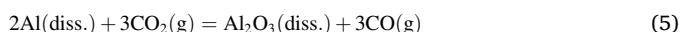
It is likely that $TiAl_3$ is formed as illustrated in the phase diagram of the Ti-Al system published in the literature [26], according to the operating conditions of the Hall-Heroult process.

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

$$CE\% = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100 = \frac{W_{\text{actual}}}{MI/nF} \times 100 \quad (4)$$

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

In practice, the amount of aluminium calculated based on Faraday's law can never be obtained as there is always a certain amount of aluminium that dissolves in the electrolyte. As a result, the metal is transported outside the diffusion layer close to the cathode where it gets oxidized by CO_2 . CO is released and alumina is produced in the so-called back reaction which can be expressed as:



Dissolved impurity species of metals more noble than aluminum tend to get reduced on the cathode [27]. The current used to co-deposit metals such as Ti represents a loss in the current efficiency of the electrolysis process. In a study where titania was added as a precursor in a 250-kA prebaked anode industrial cell, the average fraction of co-depositing titanium was estimated to be 0.9 [24]. The issues related to the polyvalent species were less challenging as liquid Al-Ti alloy was deposited [24].

The average current efficiency of the alloy can be calculated according to:

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

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

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

where M_{alloy} is the average molecular mass of the alloy and z_{alloy} is the average charge 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:

$$W_{\text{equiv.}} = \frac{\begin{bmatrix} M_{Al} \\ z_{Al} \end{bmatrix} \begin{bmatrix} M_{Ti} \\ z_{Ti} \end{bmatrix}}{\left(x_{Al} \frac{M_{Ti}}{z_{Ti}}\right) + \left(x_{Ti} \frac{M_{Al}}{z_{Al}}\right)} \quad (8)$$

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_{Al} , M_{Ti} , z_{Al} , z_{Ti} , x_{Al} , and x_{Ti} are the molecular masses of Al and Ti, their charges, and their mass fractions, respectively.

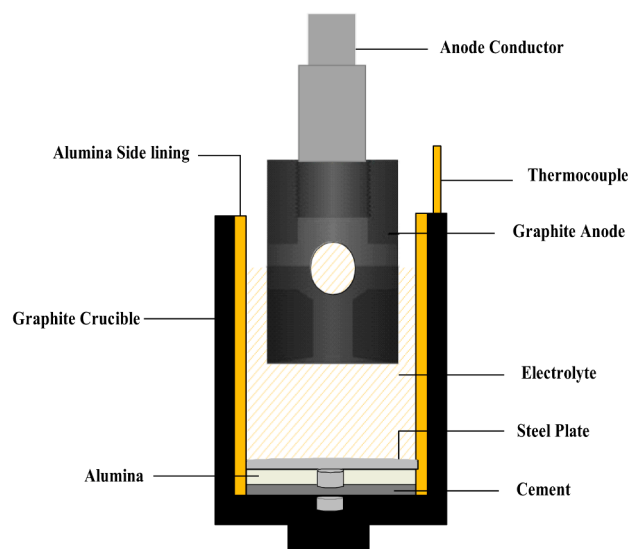


Fig. 1. The design of the CE laboratory cell used in this work.

Table 1
Electrolyte Constituents.

Chemicals	Pre-treatment	Quality/Supplier
AlF_3	Sublimed at 1090 °C for 24hrs	Industrial grade, Alcoa, Norway
NaF	Dried at 200 °C for 24 hrs	99.5%, Merck, Germany
CaF_2	Dried at 200 °C for 24 hrs	Precipitated pure, Merck, Germany
Al_2O_3	Dried at 200 °C for 24 hrs	Anhydrous (γ -alumina), Merck, Germany
TiO_2	Dried at 200 °C for 24 hrs	Rutile, 99.8% (metal basis) Alfa Aesar, Germany

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 surface shape of the deposit are discussed.

2. Experimental

Experiments were carried out in a laboratory cell originally designed by Solli et al. [28] for current efficiency measurements during electro-deposition. The laboratory cell is schematically illustrated in Fig. 1. A graphite crucible with a cylindrical sintered alumina side lining, about 10 cm in height, containing anode, cathode, and electrolyte was used. The anode is cylindrical with a central vertical hole passing through it with an inward inclination angle of 10° as well as horizontal holes penetrating the anode. This design provides good convection within the bath, with anode gas bubbles passing 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. In this way, the gas bubbles should have less effect on the diffusion layer and thus the current efficiency should not be significantly affected by increased convection.

The liquid aluminium metal product wets a steel plate resting on the bottom of the graphite crucible which acts as a cathode, ensuring an almost flat deposit surface and as a result an even current distribution. A steel pin 21.0 mm in height is placed in a 4.0 mm deep hole at the center of the bottom of the graphite crucible to make contact with the steel cathode plate. The latter is placed on top of a layer of alumina powder

Table 2
CE of alumina tests in Fig. 2 and Fig. 3 with some statistical analysis.

Temperature (°C)	CE %	CE % Mean	Standard Deviation (SD)	Standard Error (SE)
965	95.8	95.5	0.2	0.1
	95.4			
	95.4			
970	95.1	94.5	0.6	0.3
	94.6			
	93.9			
975	93.8	93.8	0.7	0.4
	94.5			
	93.2			
980	93.8	93.0	0.9	0.5
	93.1			
	92.0			

after cementing the bottom of the crucible with a layer of cast alumina cement 7.0 mm thick. These two layers should prevent loss of the deposit and minimize the possibility of aluminium carbide (Al_4C_3) formation. The electrolyte constituents listed in Table 1 were transferred into the crucible after being dried at 200 °C for 24 hrs. The cell was then placed in a Pythagoras tube inside a vertical furnace. Two copper lids with greased rubber O-rings were used to seal the two ends of the furnace, making it gas tight. The anode was placed in the bath and held by a steel

current collector. The furnace was continuously flushed with argon gas during the experiment in order to prevent air burning of cell components. The temperature was recorded during electrolysis using a thermocouple made of Pt/Pt10Rh placed inside a lateral slot of the crucible.

A DC power supply was used to supply the current. The operating temperature was varied from 965 to 980 °C with a fixed electrolysis duration of 4 h. The corresponding superheat varied from 13.0 to 28.0 °C, the liquidus temperature being calculated from an equation in [29]. The cathodic current density (CCD) was kept at 0.9 A/cm² for all runs as was the cryolite ratio (CR) (2.2). The standard electrolyte was: 12.0 wt% AlF_3 , 5.0 wt% CaF_2 , 4.0 wt% Al_2O_3 , and the balance was NaF- AlF_3 based cryolite. Titanium (IV) oxide was initially admixed with the bath constituents prior to electrolysis. Three concentrations were considered, based on Ti content: 0.2 wt% Ti, 0.6 wt% Ti, and 1.0 wt% Ti.

The bath was sampled regularly at constant intervals using quartz tubes, keeping the same sampling position in the bath for all runs. The collected metal samples were subjected to mechanical and chemical post-treatments, the latter using aluminium chloride hexahydrate solution for 30–40 min. Bath samples were crushed into fine powder and dissolved in a mixture of strong acids including HCl, HNO_3 , and HF. The solutions were digested and agitated to ensure complete dissolution. ICP-MS was conducted on the samples afterwards to determine the Ti content in the bath.

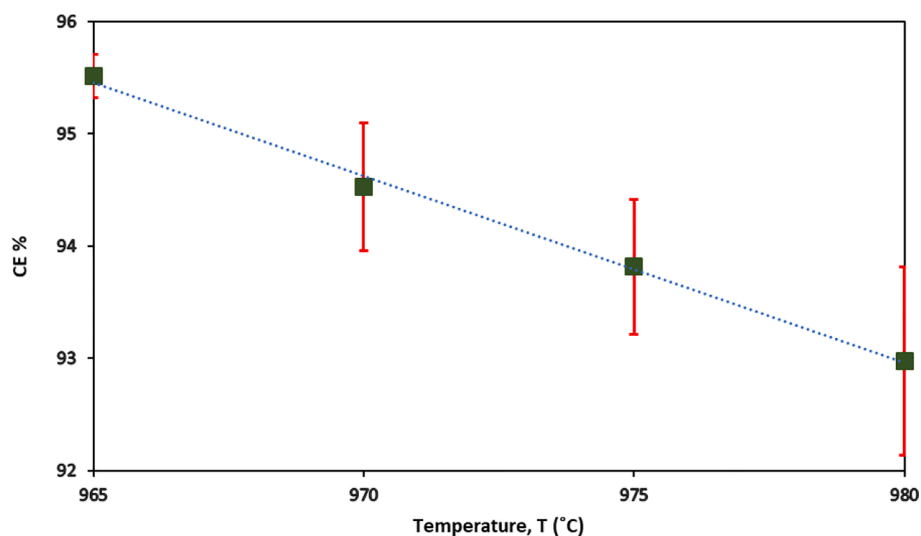


Fig. 2. Average values of CE for alumina tests carried out at different temperatures, CR = 2.2, without alumina feeding, 0.9 A/cm², and electrolysis time 4 h. Error bars are based on the standard error of the mean values from Table 2. The dotted line is based on the least squares regression. $CE = 256 \pm 7.0 - (0.2 \pm 0.0) T$.

Table 3
Experimental conditions and results for the actual co-deposition of Ti.

Run #	Temp. (C)	Initial Ti content added to the bath (wt. %)	Apparent CE % for electrolysis	Conversion % of Ti at actual co-deposition	Deposit Ti content (wt. %)	Average CE% of Al-Ti	CE % for Al
1	965	0.2	90.4	98.9	2.1	90.0	88.6
2		0.6	94.5	87.3	5.2	93.3	89.6
3		1.0	106.8	75.7	6.7	–	99.7
4	970	0.2	91.0	83.0	1.7	90.6	89.4
5		0.6	94.0	78.6	4.7	92.9	89.6
6		1.0	103.6	74.3	6.8	–	96.6
7	975	0.2	92.0	67.1	1.4	91.7	90.7
8		0.6	93.3	69.9	4.2	92.3	89.4
9		1.0	97.4	72.8	7.1	95.6	90.5
10	980	0.2	91.0	51.1	1.1	90.7	90.0
11		0.6	92.9	61.2	3.7	92.0	89.4
12		1.0	95.5	71.4	7.1	93.8	88.8

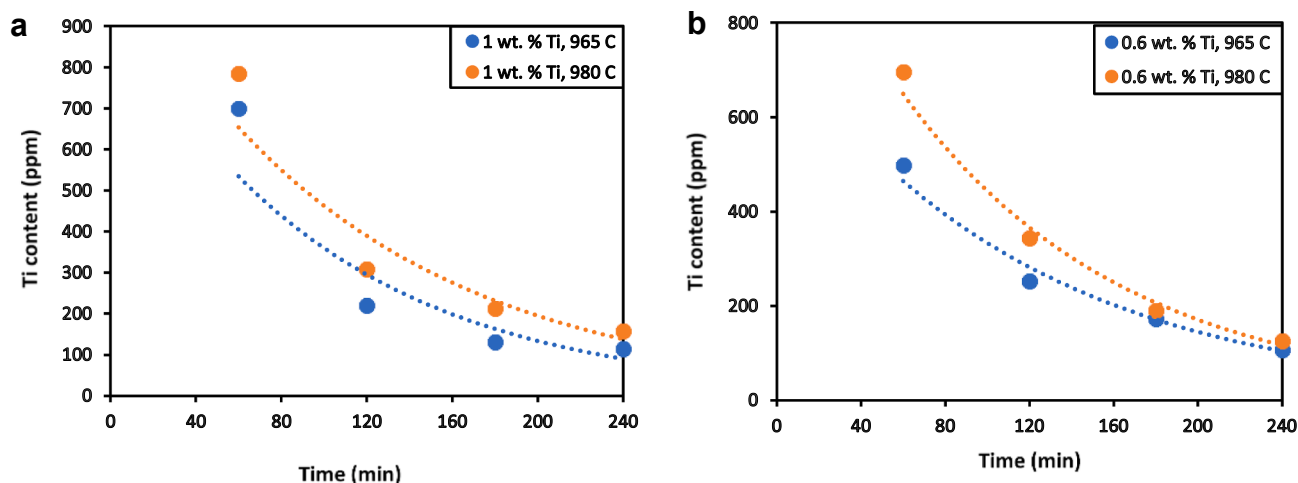


Fig. 3. Decay of Ti in the bath: (a) (left) at 1.0 wt% Ti initially added as titania (b) (right) at 0.6 wt% Ti initially added as titania. Temperatures for both concentrations are 965 °C and 980 °C.

3. Results and discussion

3.1. Cell performance

3.1.1. Alumina tests

Three alumina tests were carried out without addition of TiO_2 at 965 °C, 970 °C, 975 °C, and 980 °C. The values of the current efficiency for aluminium deposition are presented in Table 2.

The trendline constructed in Fig. 2 based on the least squares regression yielded an increase in the current efficiency of 0.2% for every 1.0 °C reduction in the operating temperature. This agrees with reports which suggest that an enhancement of 1% in current efficiency was recorded upon decreasing the operating temperature by 5 °C [29]. Alumina tests can be considered as benchmarks to check the effect of adding alloying elements on the current efficiency for electrolysis.

3.2. Ti addition

TiO_2 was admixed into the bath before melting. Three concentrations were considered: 1.0 wt% Ti, 0.6 wt% Ti, and 0.2 wt% Ti. The temperatures considered for each concentration were 965 °C, 970 °C, 975 °C, and 980 °C. The conditions for each experiment are summarized in Table 3.

3.2.1. Bath analysis

Baths for experiments 2, 3, 11, and 12 (see Table 3) were analyzed for Ti content. As seen in Fig. 3(a), starting with 1 wt% Ti, around 30.0% of Ti was depleted during the first half of the experiment (120 min) at 965 °C whereas 34.0% was depleted at 980 °C. Starting with 0.6 wt% Ti, around 38.0% of Ti was depleted during the first half of the experiment (120 min) at 965 °C whereas 30.0% was depleted at 980 °C, as shown in Fig. 3(b).

3.2.2. Solidified deposit analysis

ICP-MS analysis was carried out for the deposits. Table 3 shows the content of Ti in the metal at different temperatures and the initial Ti content added to the bath. The results suggest that there is an increase in the content of Ti in the metal upon increasing the initial concentration, regardless of the operating temperature, which is in good agreement with results from a previous study [19]. The material balance of experiments analyzed for their baths as well as their deposits was at least 95%. Interestingly, the results shown in Table 3 suggest that the metal content of Ti at 965 °C and 970 °C is quite similar when the same initial Ti content is added. The pattern also applies for 975 °C and 980 °C.

When 1.0 wt% Ti is initially added to the bath, the final content of Ti in the metal was around 7.0 wt%, regardless of the operating temperature, which may imply less effect of the latter on the solubility of Ti in the bath.

3.3. Current efficiency for Al–Ti alloys

The average current efficiencies of the Al–Ti alloys were estimated using Eqs. (6)–(9). The average current efficiency for the alloy is a representation of the current efficiency of each element based on its content in the alloy. Fig. 4(a), 4(b), and 4(c) show the actual current efficiency for aluminium and the average current efficiency for the aluminium–titanium alloys. The results in Fig. 4(a) show a difference of 1% between the CE for Al–Ti and the CE for Al. A difference in the range from 2 to 3% was estimated for the results in Fig. 4(b), and a difference in the range of 5% for the results in Fig. 4(c). The average current efficiencies for Al–Ti alloy at 965 °C and 970 °C when a relatively high Ti content (1.0 wt%) was initially added to the bath were higher than 100%. This can be explained by the possibility that some of the bath precipitated within the deposit prior to solidification due to lower superheat at these operating temperatures. This might have contributed to the increase in the weight of the solidified deposit, which implies higher current efficiencies for Al and Al–Ti alloys.

3.3.1. Calculating the current efficiency for an Al–Ti alloy: A numerical example

For run 12 from Table 3, the weight of the produced alloy (W_{alloy}) was experimentally found to be 38.28 g. The mass fraction of Ti (x_{Ti}) was determined by ICP-MS for this metallic alloy to be 0.071. Thus, the mass fraction of Al (x_{Al}) is 0.929. The charges transferred during the electrodeposition of Al (z_{Al}) and Ti (z_{Ti}) are 3 and 4 equivalent/mol respectively. The molar masses of Al (M_{Al}) and Ti (M_{Ti}) are 26.98 g/mol and 47.87 g/mol, respectively. Faraday's constant is 96,487C/mol. The current applied to the process which corresponds to a current density of 0.9 A/cm² is 29.86 A. The electrolysis time is 4 h (14440 s). Substituting in Eq. (8) gives:

$$W_{\text{equiv.}} = \frac{\left[\frac{47.87}{4} \right] \left[\frac{26.98}{3} \right]}{\left(0.071 \times \frac{26.98}{3} \right) + \left((1 - 0.071) \times \frac{47.87}{4} \right)} = 9.154 \text{ g/equivalent}$$

Substituting in Eq. (9) yields:

$$\text{CE}_{\text{alloy}}\% = \frac{38.28}{9.154 \times \frac{29.86 \times 14400}{96487}} \times 100 = 93.838\% \text{ (rounded to 93.8\%)}$$

As seen in Table 3, the co-deposited titanium content was in the range 1–7 wt%. The ratio of the titanium found in the metal to the

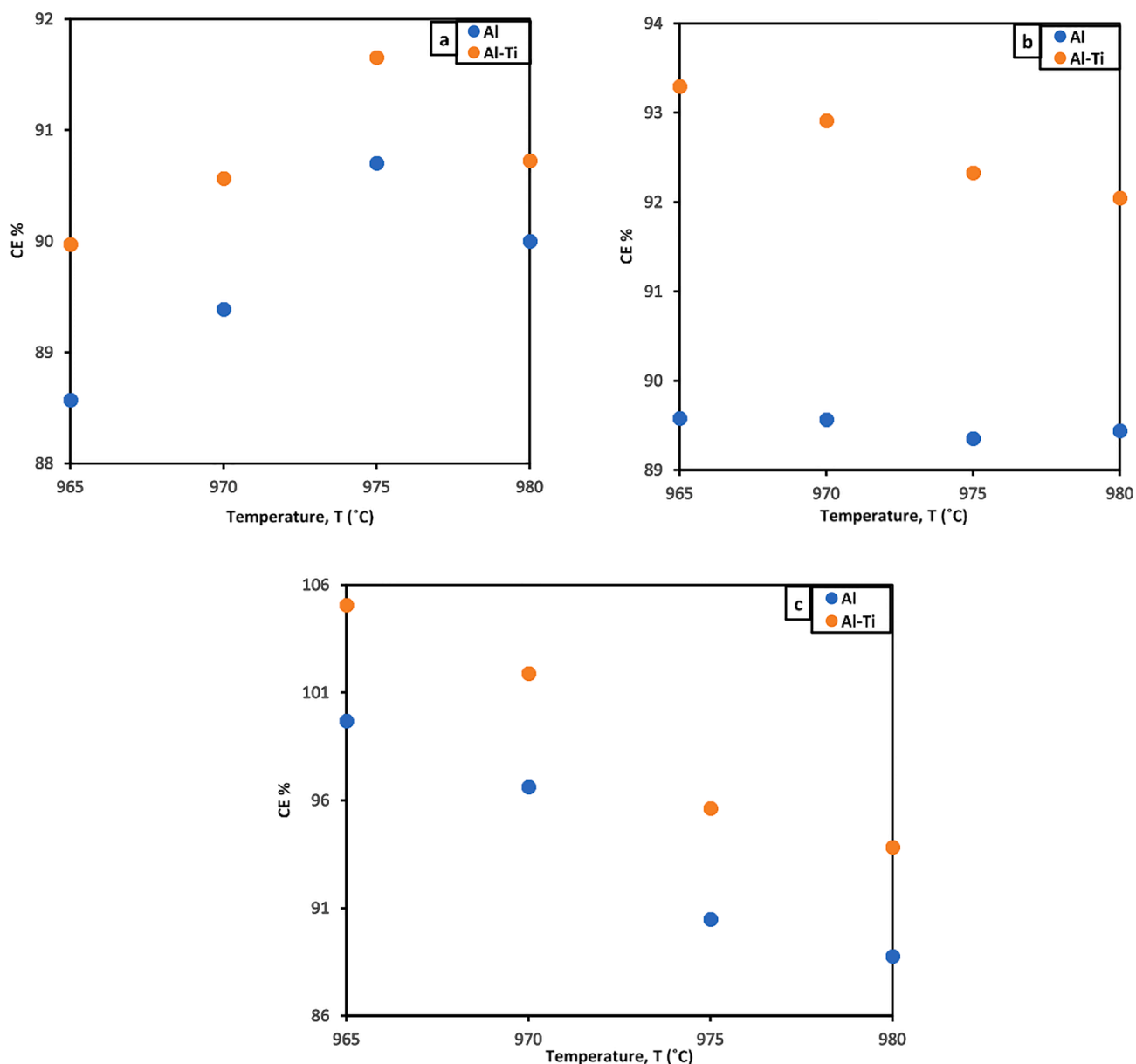


Fig. 4. Actual CE% for Al and average CE % for Al-Ti with different initial concentrations of added titania, corresponding to the following content of Ti: (a) 0.2 wt%, (b) 0.6 wt%, (c) 1.0 wt%.

titanium initially added to the bath in the form of titania is referred to as conversion. The results shown in Table 3 suggest that almost all the 0.2 wt% Ti initially added to the bath at 965 °C has ended up in the metal. It can also be seen that when 0.2 wt% Ti was initially added, a reduction of about 3% in the conversion was estimated for every 1 °C increase in the operating temperature. The reduction in the conversion of Ti was estimated to be 1.7% and 0.3% for 0.6 wt% Ti and 1.0 wt% Ti, respectively, for every 1 °C increase in the operating temperature. It can also be seen that at 965 °C and 970 °C the higher the initial content of titanium added in the form of titania, the lower the conversion. However, the opposite trend is observed at 975 °C and 980 °C. This may be explained by the fact that the solubility of titania increases at higher temperatures and thus more titania would be removed (reduced). It has been reported that the solubility of TiO_2 in alumina-saturated cryolitic melts is 1.9 wt% Ti and 2.0 wt% Ti at 975 °C and 980 °C, respectively [30].

The apparent current efficiencies of the experiments are also shown in Table 3. Apparent current efficiency here is defined as the percentage ratio of the total weight of the solidified deposit assuming that

everything is aluminium, and the value calculated based on reduction of aluminium according to Faraday's law. As seen from Table 3, the apparent current efficiencies are no more than 2% higher than the average current efficiencies for the alloys, which are very much comparable. This may indicate the feasibility of the proposed process.

3.4. Current efficiency for Al

Alumina tests provide a good reference when looking at the effect of the presence of Ti in the deposit on CE. The current efficiency of Al is based on the net weight of Al found in the deposit. That implies the deduction of the weight of the co-deposited titanium from the total weight of the deposit after cleaning. If all the Ti initially added ended up in the deposit, an enhancement in the CE of Al would be recorded at 2.0% and 0.3% at 965 °C and 970 °C, respectively, for an initial 1.0 wt% Ti content added in the bath. The enhancement in the current efficiency could be attributed to the fact that co-deposition of titanium lowered the activity of aluminium in the metal deposit, and thus lowered the

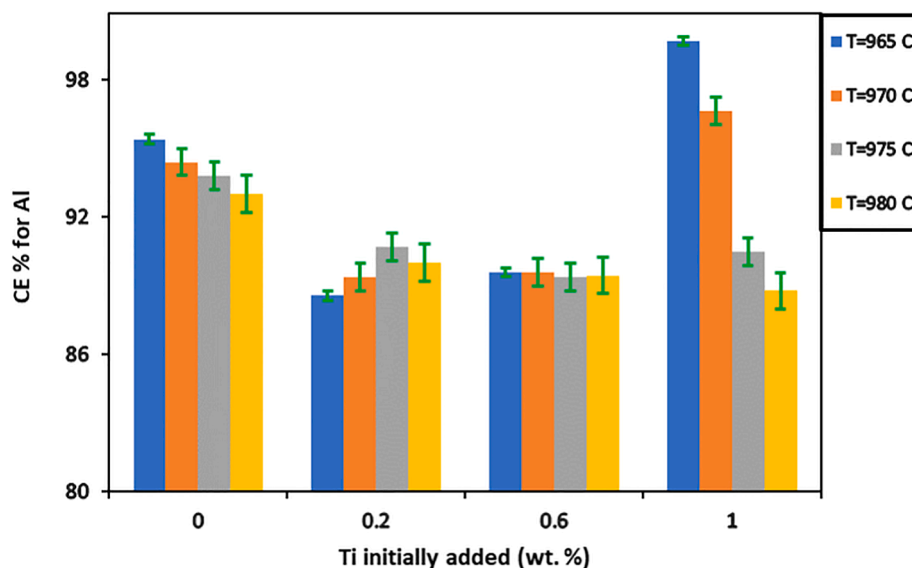


Fig. 5. Summary of actual CE % for Al at different temperatures and with different Ti content initially added to the bath. Current efficiencies of the blank tests are based on average values from Table 2. Error bars are based on the standard errors from Table 2.

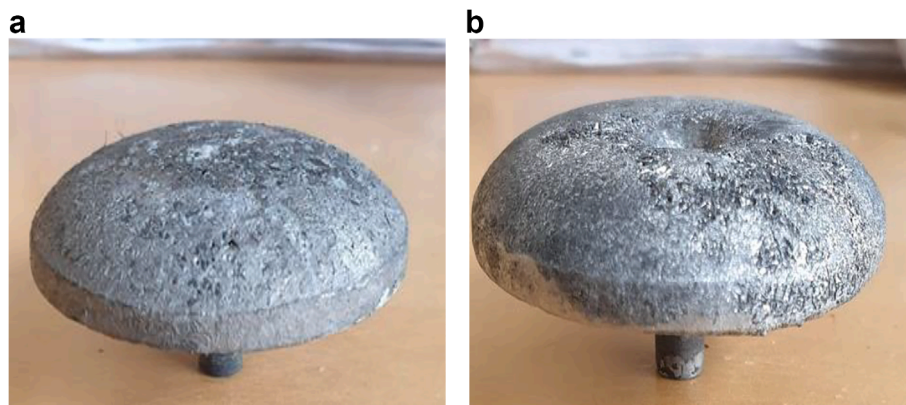


Fig. 6. Alumina tests using NaF-AlF₃ cryolite with no alumina feeding at CR = 2.2, CCD = 0.9 A/cm², t = 4 h, (a) (left) T = 965 °C, (b) (right) T = 980 °C.

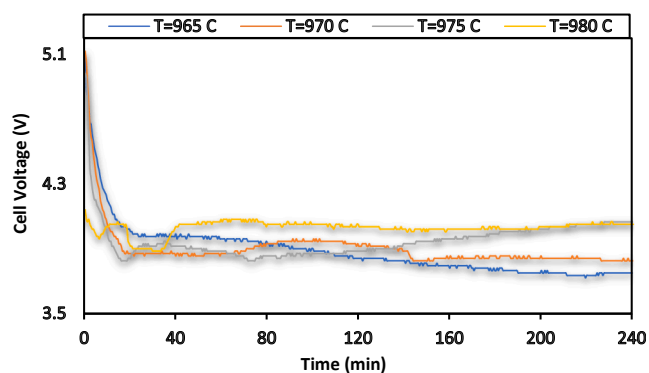


Fig. 7. Cell voltage behavior of alumina tests at using NaF-AlF₃ cryolite with no alumina feeding, CR = 2.2, CCD = 0.9 A/cm² at different temperatures.

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.

Fig. 5 shows a summary of the actual current efficiencies for aluminium for all temperatures when different initial amounts of Ti are

added to the bath. The maximum current efficiency for Al obtained was 99.7% at 965 °C with 1.0 wt% Ti initially added to the bath, while the lowest was 88.6% at the same temperature but with 0.2 wt% Ti. The high value of the CE for Al at 965 with 1 wt% Ti initially admixed with the bath may be attributed either to the co-deposition of titanium, as mentioned previously, or the existence of some bath precipitation due to the relatively low superheat at 965 °C and 970 °C. A reduction in the CE for Al due to the co-deposition of titanium, with respect to the average current efficiency for Al in the corresponding alumina tests, was estimated to be in the range 3% to 7% under the different conditions considered in Fig. 5.

4. Current distribution and cell voltage behavior

The surfaces of the solidified deposits in all alumina tests were flat. Samples from experiments run at 965 and 980 °C are shown in Fig. 6, indicating even current distributions. Fig. 7 illustrates similar and stable cell voltage behavior for the alumina tests, with minimum fluctuations.

The surfaces of the solidified deposits obtained in runs 3 and 6 (see Table 3) were partially deformed. Areas around the flat parts included some solidified bath, as seen in Fig. 8(a) and Fig. 8(b). The solidified

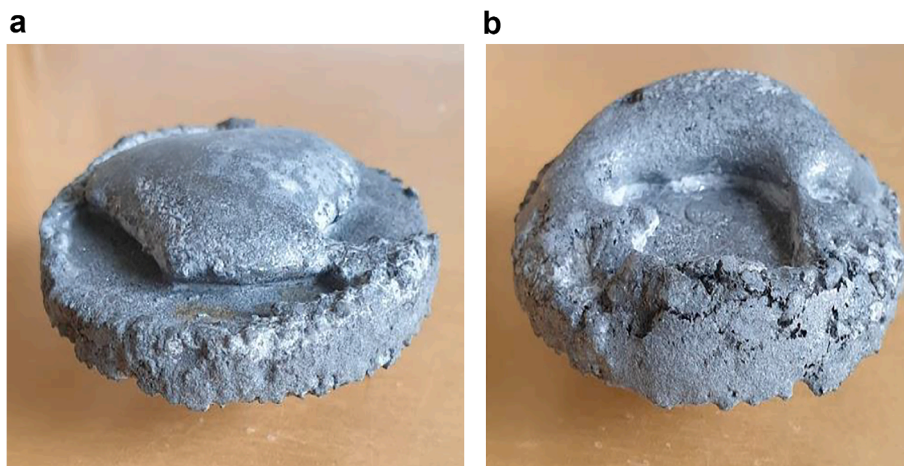


Fig. 8. Deposits using NaF-AlF₃ cryolite with no alumina feeding at 1.0 wt% Ti, CR = 2.2, CCD = 0.9 A/cm², t = 4 h, (a) T = 965 °C (b) T = 970 °C.

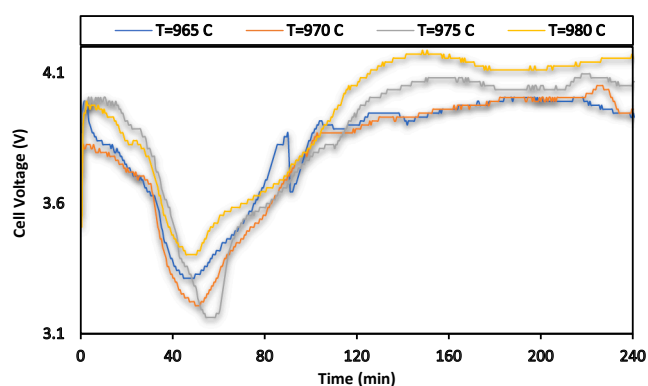


Fig. 9. Cell voltage behavior with an initial Ti content of 1.0 wt% at different temperatures using NaF-AlF₃ cryolite with no alumina feeding, CR = 2.2, CCD = 0.9 A/cm².

deposits from runs 9 and 12 were flat. Runs 3, 6, 9, and 12 showed a similar cell voltage behavior with drops of around 600 mV in the first hour of electrolysis, as shown in Fig. 9.

For a titanium content of 0.6 wt%, the surfaces of the solidified deposits were flat. The cell voltage behavior of such runs was similar and

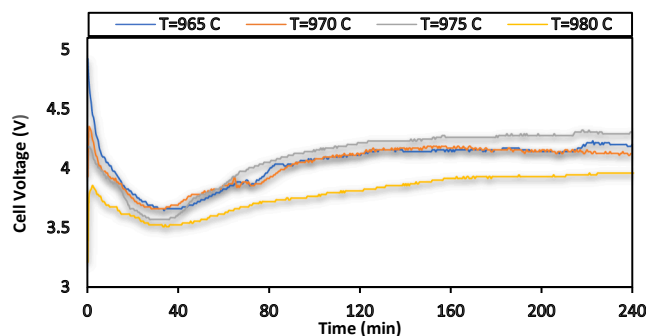


Fig. 10. Cell voltage behavior with an initial Ti content of 0.6 wt% at different temperatures using NaF-AlF₃ cryolite with no alumina feeding, CR = 2.2, CCD = 0.9 A/cm².

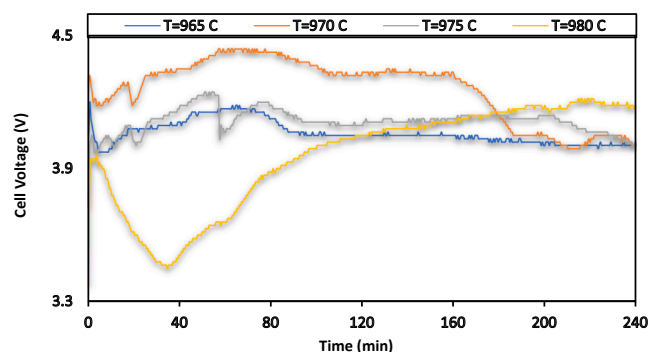


Fig. 11. Cell voltage behavior for an initial Ti content of 0.2 wt% at different temperatures using NaF-AlF₃ cryolite with no alumina feeding, CR = 2.2, CCD = 0.9 A/cm².

stable as seen in Fig. 10. Drops in the cell potential of 1400 mV, 800 mV, 600 mV, and 300 mV over the first 40 min of the electrolysis of runs 2, 5, 8, and 11, respectively, were recorded. It seems the lower the operating temperature (more co-deposited Ti) the higher the drop in the cell voltage recorded.

At a low titanium content of 0.2 wt%, the surfaces of the deposits were flat. The cell voltage behavior of these tests showed low fluctuations except for that carried out at 980 °C as seen in Fig. 11.

5. Conclusions

Alumina tests showed an enhancement of 1% in current efficiency for aluminium deposition when the operating temperature was lowered by 5 °C due to the decrease in the solubility of metal in the bath, which agrees with literature data.

Co-deposition of titanium to produce Al-Ti alloys was studied in a laboratory cell dedicated to aluminium current efficiency measurements. Results from ICP-MS suggest that there is an increase in the content of Ti in the metal upon increasing the initial concentration of added TiO₂, regardless of the operating temperature. The material balance of experiments analyzed for their baths as well as their deposits was at least 95%. Results suggest that the metal content of Ti is quite similar for the same initial Ti content added as TiO₂ at all operating temperatures tested in this work. When a relatively high Ti content was initially

added to the bath, the final content of Ti in the metal was around 7 wt% regardless of the operating temperature, which may imply less effect of the latter on the solubility of titania in the bath.

The average current efficiencies of Al–Ti alloys have a difference of up to 5% compared to those estimated for the actual deposition of Al, which implies that this path is quite efficient for producing such alloys. When a relatively low initial concentration of Ti was added to the bath at 965 °C, all the Ti ended up in the metal. A reduction of about 3% and 2% in the conversion was estimated for every 1 °C increase in the operating temperature when 0.2 wt% Ti and 0.6 wt% Ti were added to the bath, respectively.

The surfaces of the solidified deposit produced by all alumina tests were flat, indicating an even current distribution, which was demonstrated in the cell voltage behavior with minimum fluctuations. The addition of titanium as TiO₂ did not affect the shape of the deposit surface for most of the runs with different Ti contents and operating temperatures. At a high Ti content of 1 wt% at relatively low operating temperatures (965 °C 970 °C), the solidified deposit surfaces were partially deformed.

CRedit authorship contribution statement

Omar Awayssa: Methodology, Investigation, Validation, Writing - original draft. **Gudrun Saevarsdottir:** Supervision, Writing - review & editing. **Rauan Meirbekova:** Supervision, Writing - review & editing. **Geir Martin Haarberg:** Conceptualization, Supervision, Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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