



Direct Production of Al-Mn Alloys During the Electrodeposition of Aluminum in a Laboratory Cell

Omar Awayssa, Geir Martin Haarberg, Gudrun Saevarsdottir, and Rauan Meirbekova

Abstract

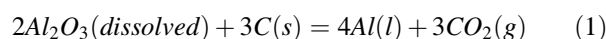
This study reports the direct production of aluminum–manganese alloys during the electrodeposition of aluminum in cryolitic melts. For the purpose of measuring current efficiency, experiments were conducted in a laboratory cell. The temperature was changed between 960 and 980 °C at a cryolite ratio (CR) of 2.2 and a cathodic current density (CCD) of 0.9 A/cm². Up to 3.0 weight percent of manganese was present. Mn₂O₃ was used as a method of manganese addition. To track the dissolution of manganese during electrolysis, bath samples were routinely taken, and ICP-MS was examined. Al-Mn alloy electrodeposition current efficiency was estimated to be in the region of above 90%. Estimates of aluminum's current efficiency were made. The metal deposits' hardened surfaces were essentially flat, but some were deformed.

Keywords

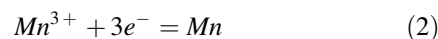
Aluminum–manganese alloys • Current efficiency • Aluminium electrodeposition

Introduction

According to the overall electrochemical reaction described by [1], liquid aluminum (Al) is produced in the Hall–Héroult process by electrolytic reduction of alumina (Al₂O₃) dissolved in an electrolyte including cryolite (Na₃AlF₆) at 960–970 °C:



The 3xxx family of aluminium alloys' main alloying component is manganese (Mn). The alloy has a greater corrosion resistance and is significantly stronger than commercially available pure aluminium when a small amount of Mn (up to 1.5 wt%) is added to Al. Due to advancements in its mechanical characteristics, the alloy has become suitable for widespread usage in applications requiring good workability and moderate strength [2, 3]. Manganese dissolves in molten aluminium extremely slowly, and this is greatly influenced by the particle size of the manganese that has been introduced [4]. When powdered manganese is introduced to molten aluminium, some of it may float to the surface and create a hard crust, which indicates that part of it may have undergone oxidation [4]. The possibility to produce aluminum–manganese alloys right in cryolitic melts has been reported [5] such that by incorporating MnO, MnO₂, or their mixes with alumina in a cryolite-based electrolyte, it has been claimed that the produced alloys contained up to 10 weight percent Mn. As opposed to Al₁₂Mn, which is more likely to develop at a manganese level of 7.7 at. % at T ~ 511 °C, an Al₆Mn phase is more likely to form with a manganese value of 14.3 at. % at ~ T 658 °C [6]. When Mn₂O₃ is utilized as a precursor for manganese, the reduction process will proceed as follows:



Current efficiency measures may be used to assess the utilization of supplied electrical current used to deposit

O. Awayssa (✉)

Department of Chemical and Petroleum Engineering,
UAEU, 15551 Al Ain, United Arab Emirates
e-mail: Omar.awayssa@uaeu.ac.ae

G. M. Haarberg · G. Saevarsdottir
Department of Materials Science and Engineering,
NTNU, Sem Sælands Vei 12, NO-7491 Trondheim, Norway

G. Saevarsdottir
School of Science and Engineering, Reykjavik University,
Menntavegi 1, 101, Reykjavik, Iceland

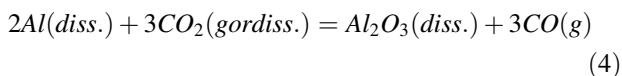
R. Meirbekova
Tæknisetur, Árleynir 8, 112 Reykjavík, Iceland

aluminium which may be estimated by metal weight gain relating the actual produced aluminum to the aluminum that would theoretically be produced based on Faraday's law. Then CE% may be written as

$$CE\% = \frac{W_{actual}}{W_{theoretical}} \times 100 = \frac{W_{actual}}{MIt/zF} \times 100 \quad (3)$$

where W_{actual} is the actual mass of metal produced whereas $W_{theoretical}$ 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 A, z is the number of electrons transferred, and F is the Faraday constant of 96,487 C/mol.

In practical terms, it is impossible to acquire the amount of aluminium predicted by Faraday's law. In the electrolyte, aluminum always dissolves to some extent. The metal is thus transferred to a location near the cathode outside the diffusion layer where it is oxidized by CO_2 . During the back reaction, alumina is produced and carbon monoxide is released, as per the following:



At the cathode, dissolved impurity species that are more noble than aluminium will undergo reduction [8]. The decrease in current efficiency for aluminum reduction is caused by the current utilized to co-deposit such contaminants as Mn. The alloy's average current efficiency may be estimated using

$$CE_{alloy}\% = \frac{W_{alloy}}{W_{alloy.theoretical}} \times 100 \quad (5)$$

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

$$W_{alloy.theoretical} = \frac{M_{alloy}It}{z_{alloy}F} \quad (6)$$

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-Mn alloy according to the so-called electrochemical equivalent given by

$$W_{equiv.} = \frac{\left[\frac{M_{Al}}{z_{Al}}\right] \cdot \left[\frac{M_{Mn}}{z_{Mn}}\right]}{\left(x_{Al} \frac{M_{Mn}}{z_{Mn}}\right) + \left(x_{Mn} \frac{M_{Al}}{z_{Al}}\right)} \quad (7)$$

Thus CE % for the alloy can be given by

$$CE\%_{alloy} = \frac{W_{alloy}}{W_{equiv.} \frac{It}{F}} \times 100 \quad (8)$$

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

This investigation presents findings from a study into the electrochemical deposition of an aluminum-manganese alloy during aluminium reduction in fluoride-based melts in a laboratory cell using industry standards. It is examined how the presence of Mn affects the current efficiency relative to Al, the current efficiency for the alloy, and the texture of the deposit's surface once it has hardened.

Experimental

Experiments were carried out in a laboratory cell originally designed by Solli et al. [7] for current efficiency measurements during electrodeposition. The laboratory cell is schematically illustrated in Fig. 1. 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 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 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. By that, the gas bubbles would have less effect on the diffusion layer and thus the current efficiency would not be significantly affected by increased convection.

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 as a result an even current distribution. A steel pin of 21.0 mm 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 after cementing the bottom of the crucible with a layer of cast alumina cement of 7.0 mm thickness. These two layers should prevent loss of the deposit and minimize chances of aluminium carbide (Al_4C_3) formation. The electrolyte constituents as shown in Table 1 were transferred into the crucible after being dried at 200 °C for 24 h. 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 up 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

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

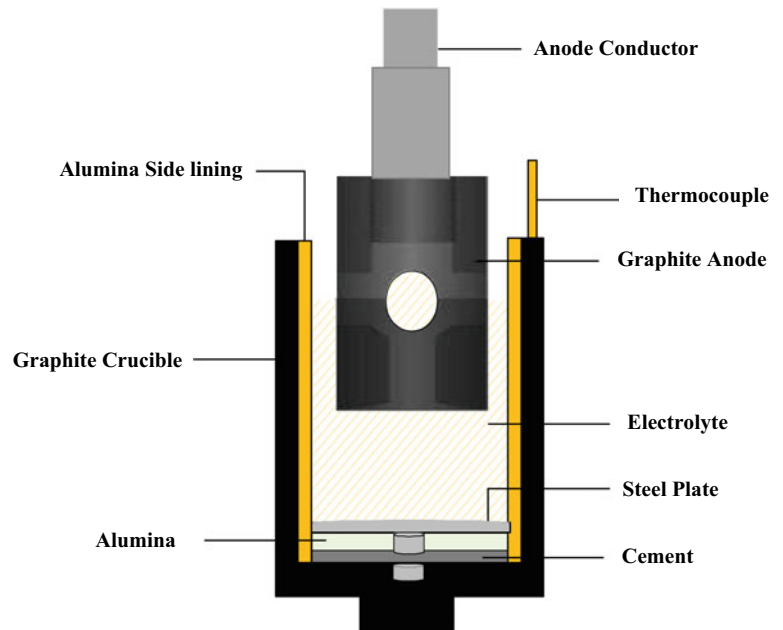


Table 1 Electrolyte components

Chemicals	Pre-treatment	Quality/supplier
AlF ₃	Sublimed at 1090 °C for 24h	Industrial grade, Alcoa-Norway
NaF	Dried at 200 °C for 24 h	99.5%, Merck-Germany
CaF ₂	Dried at 200 °C for 24 h	Precipitated pure, Merck-Germany
Al ₂ O ₃	Dried at 200 °C for 24 h	Anhydrous (γ -alumina), Merck-Germany
Mn ₂ O ₃	Dried at 200 °C for 24 h	325 Mesh powder, 98%, Alfa Aesar-Germany

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 was varied from 13.0 to 28.0 °C, being calculated from an equation in [10]. The cathodic current density (CCD) was kept at 0.9 A/cm² for all runs. A cryolite ratio (CR) of 2.2 was used for all runs. The standard electrolyte was 12.0 wt. % AlF₃, 5.0 wt. % CaF₂, 4.0 wt.% Al₂O₃, and balance of NaF-AlF₃-based cryolite. Manganese (III) oxide was initially admixed with the bath constituents prior to electrolysis. Three concentrations were considered based on Mn content which were 1 wt. % Mn, 2 wt. % Mn, and 3 wt. % Mn.

The bath was sampled regularly at constant intervals using quartz tubes while keeping the same position of the sampling in the bath for all runs. The collected metal samples were subjected to mechanical and chemical post-treatments, the latter by 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, HNO₃, and HF. The solutions were digested and agitated to ensure a complete dissolution. ICP-MS was conducted for samples afterwards to determine the Mn content in the bath.

Results and Discussion

Manganese Addition

Mn₂O₃ was admixed into the bath before melting. Three concentrations were considered: 1.0 wt. % Mn, 2.0 wt. % Mn, and 3.0 wt.% Mn. Temperatures were 965 °C, 970 °C, 975 °C, and 980 °C.

Bath Analysis

Baths for experiments conducted at 965 °C and an initial content of Mn added 1 wt.% and 3 wt. % were analysed for Mn content. As seen in Fig. 2, around 45 % of Mn dissolved depleted during the first half of the experiment (120 min) at 965 °C whereas 21% depleted at 980 °C.

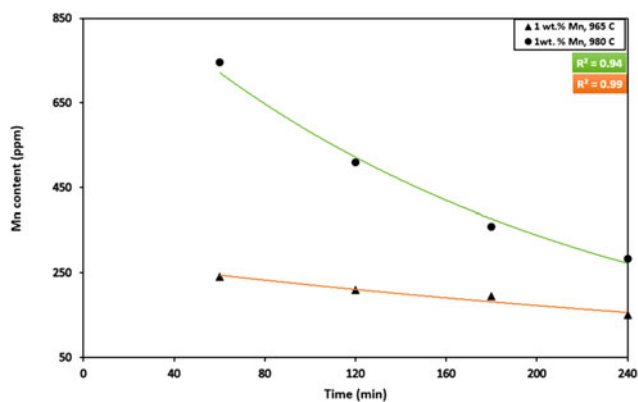


Fig. 2 Decay of Mn in the bath at 1 wt. % content at 965 °C and 980 °C

The electrodeposition in a laboratory cell may be considered a semi-batch process where the rate of depletion of Mn in the bath at any time may be expressed in the form of

$$c = c_0 \exp\left(-\frac{A}{V}kt\right) \quad (9)$$

where c_0 is the initial concentration of the impurity species prior to addition, A is the active surface area of the cathode, V is the electrolyte volume, k is the mass transfer coefficient, and t is the time at which the sample has been taken out of the cell.

Electrodeposits Analysis

According to the results, regardless of the operating temperature, a rise in the starting concentration of Mn caused an increase in the metal's Mn content to be seen. The ultimate amounts of Mn in the metal at starting bath concentrations of 1.0 wt% and 2.0 wt% Mn were approximately 8.0 wt% and 13.0 wt%, respectively, independent of the operating temperature, suggesting that the latter may have had less of an impact on the solubility of manganese in the bath.

Cell Performance

Current Efficiency for Aluminium

When examining the impact of Mn in the deposit on CE, blank tests would be a useful point of comparison. Based on the net weight of aluminium present in the solidified deposit, current efficiency for aluminium is calculated. That indicates that the weight of the co-deposited manganese will be subtracted from the overall weight of the deposit after cleaning. An overview of the actual current efficiency for all

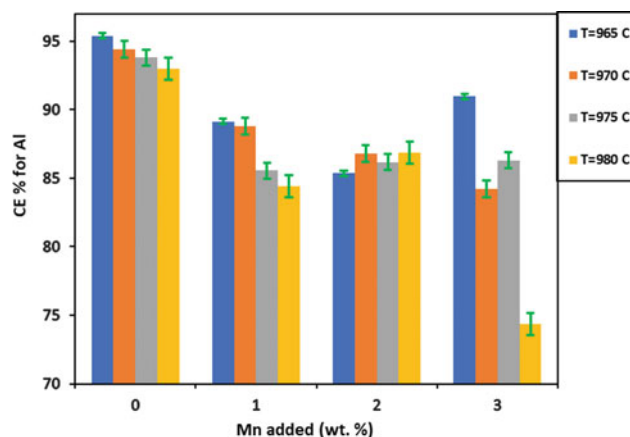


Fig. 3 Summary of actual CE % for Al at different temperatures and Mn contents initially added to the bath

temperatures at various initial Mn contents supplied to the bath is shown in Figure 3. The highest current efficiency of Al was attained at 965 °C and 3.0 wt% Mn originally added to the bath, whereas the lowest was at the same Mn concentration at 980 °C.

Current Efficiency for Al-Mn Alloys

Equations (5–8) were used to estimate the average current efficiencies of Al–Mn alloys. According to each element's proportion in the alloy, the average current efficiency serves as a representation of the current efficiency of the alloy as a whole. Figure 4 provides the actual current efficiency for aluminium and the average current efficiency of aluminum–manganese alloys.

The values obtained for Al-Mn current efficiency were comparable to those for blank tests under the same scenarios, which may imply the viability of the approach suggested.

Electrodeposits Shape

The solidified deposits' surfaces of all blank tests were flat as depicted in Fig. 5. The solidified deposits' surfaces were flat when experiments were carried out under the additions of 1 wt. % Mn and 2 wt. % Mn at 965 °C, 970 °C, 975 °C, and 980 °C. However, the deposits' surfaces of runs at 3 wt. % Mn at 970 °C and 980 °C were deformed as seen in Fig. 6.

It is worth mentioning that the shape of the electrodeposit is related to the current distribution during the electrolysis. Flat surfaces assure even current distribution, and thus reliable current efficiency measurements. Similar behavior has been reported in similar experiments but with different alloying element additions [8–10].

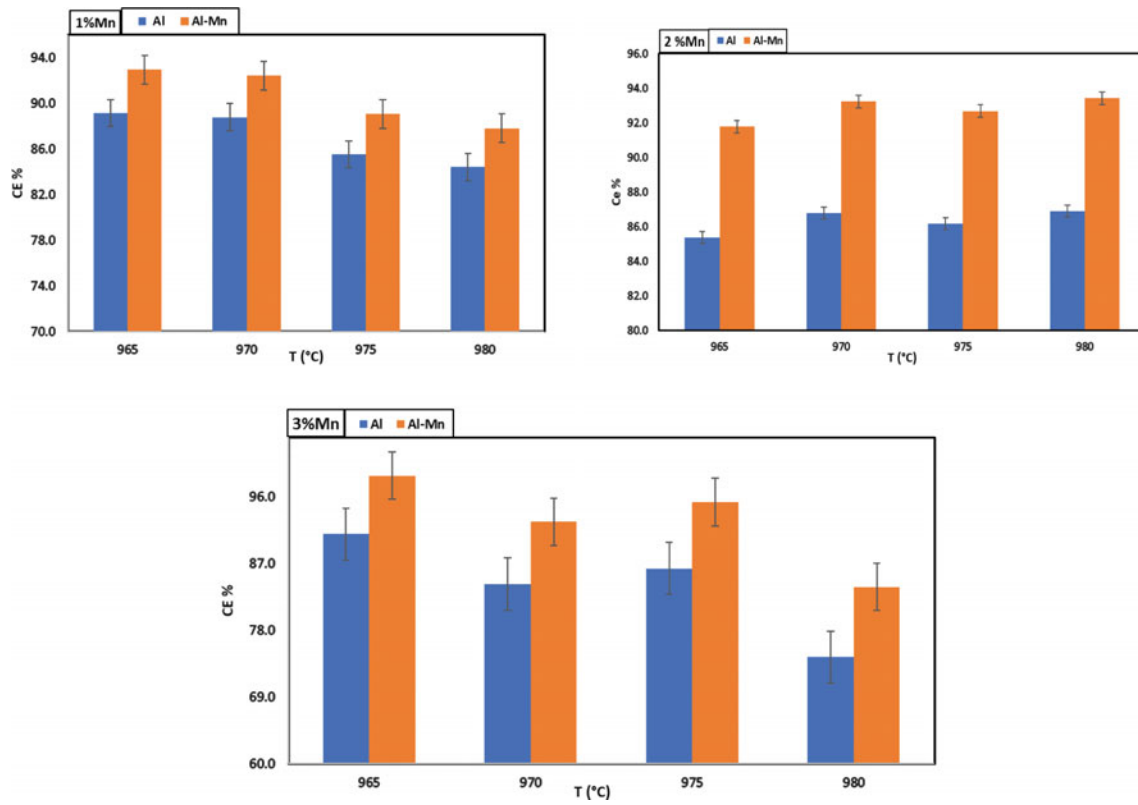


Fig. 4 Actual CE% for Al and average CE % for Al-Mn at initial added Mn

Fig. 5 Blank tests using NaF-AlF₃ cryolite with no alumina feeding at CR = 2.2, CCD = 0.9 A/cm², t = 4 h, (left) T = 965 °C, (right) T = 980 °C



Fig. 6 Deposits using NaF-AlF₃ cryolite with no alumina feeding at 3 wt. % Mn, CR = 2.2, CCD = 0.9 A/cm², t = 4 h, (left) T = 970 °C, (right), T = 980 °C



Conclusions

In a laboratory cell designed for studies of the aluminum current efficiency, the co-deposition of manganese to yield Al-Mn alloys was investigated. ICP-MS analysis suggests that regardless of the operating temperature, increasing the initial concentration of manganese precursor supplied to the bath brings about an increase in the amount of Mn in the metal.

The average current efficiencies of Al-Mn alloys have a difference of up to 9% in comparison to those estimated for the actual deposition of Al which implies that this path is quite efficient to produce such alloys.

All of the blank tests' hardened deposits had flat surfaces, which indicated even current distribution. For the majority of runs at various Mn contents and operating temperatures, the co-deposition of Mn had little impact on the surface morphology of the solidified deposits. High Mn₂O₃ concentration correlates to 3.0 wt% Mn that was added to the bath at 970 °C and 980 °C, resulting in the deformation of the deposits' surfaces.

Acknowledgements Financial support from Start-up Fund number 12N132-UAEU and NTNU is greatly acknowledged.

References

1. Grjotheim K, Kvande H (1993) Introduction to Aluminium Electrolysis : understanding the Hall-Héroult process, 2nd ed., Düsseldorf: Aluminium-Verlag.
2. Davis J (2001) Alloying: Understanding the Basics, *ASM International*.351–416.
3. Davis J (1998) Aluminum and Aluminum Alloys, Metals Handbook Desk Edition, 2nd ed., *ASM International*. 417–505.
4. Kline J, Yeh W, Preston U (1975) Method of adding manganese to aluminium. *USA Patent 3,865,583*.
5. King W (1976) Aluminium-Manganese Alloy. *USA Patent 3,951,764*.
6. Solli P, Eggen T, Rolseth S, Skybakmoen E (1996) Design and performance of a laboratory cell for determination of current efficiency in the electrowinning of aluminum. *Journal of Applied Electrochemistry*.1019–1025.
7. Solheim A, Rolseth S, Skybakmoen E, Støen L, Sterten Å, Støre T (1996) Liquidus Temperatures for Primary Crystallization of Cryolite in Molten Salt Systems of Interest for Aluminum Electrolysis. *Metall. Mater. Trans. B*. vol. 27B,739-744.
8. Awayssa O, Meirbekova R, Saevarsdottir G, Audunsson G, Haarberg G M (2020) Current efficiency for direct production of an aluminum–titanium alloy by electrolysis in a laboratory cell. In: Tomsett A. (eds) Light Metals. The Minerals, Metals & Materials Series. Springer, Cham.
9. Awayssa O, Saevarsdottir G, Meirbekova R, Haarberg G M (2021) Electrochemical Production of Al-Si Alloys in Cryolitic Melts in a Laboratory Cell. *Journal of The Electrochemical Society*, 168 046506
10. Awayssa O, Saevarsdottir G, Meirbekova R, Haarberg G M (2021) Electrodeposition of aluminium-titanium alloys from molten fluoride-oxide electrolytes. *Journal of The Electrochemistry Communications*, 123 106919.