

Electrodeposition of aluminium containing alloys from molten fluoride electrolytes containing metal oxides

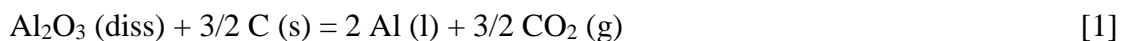
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Aluminium is produced by the Hall-Heroult process by electrowinning in a molten fluoride electrolyte with dissolved alumina at ~955 °C. Several metallic impurities typically end up in the produced metal due to the fact that most metals are more noble than aluminium. Such co-deposition of metals may be utilized to form aluminium alloys. Another advantage is that many metal oxides are readily soluble in molten cryolite based electrolytes. The more noble metals will deposit at the limiting current density. The alloy composition is essentially determined by the bath concentration of the dissolved cations of the alloying element. Therefore it is possible to produce alloys of certain compositions by controlled addition of metal oxides. Interesting candidate alloying elements are silicon, iron, titanium and manganese but also exotic elements such as scandium are possible. Electrochemical studies were carried out in laboratory experiments and the behaviour of dissolved metal oxides was studied in industrial cells. High current efficiencies for the codeposition of the alloying elements Si, Fe, Ti and Mn were confirmed. Significant savings for producing alloys by this method are expected.

Introduction

Aluminium is produced by electrolysis in molten NaF-AlF₃-Al₂O₃ at ~955 °C, where dissolved alumina is reduced to liquid aluminium at the cathode and CO₂ is evolved at consumable carbon anodes. The current efficiency with respect to aluminium can be as high as 96 % in modern Hall-Heroult cells. The total cell reaction is:



More than 60 million tons aluminium were produced by this process globally in 2019 (1). China is the dominating country but also India, Canada, Russia and countries in the Middle East have significant production of primary aluminium.

Drawbacks of the process are related to high specific electric energy consumption (~13 kWh/kg Al), low energy efficiency (~50 %) and emissions of CO₂ due to consumption of carbon anodes and generation of electricity. Another challenge is to eliminate the emissions of PFC gases (CF₄ and C₂F₆) that are formed during so-called anode effect due to depletion of dissolved alumina.

Today various aluminium based alloys are made by adding pure alloying elements to the produced liquid aluminium before casting. The most common alloying elements of commercial alloys are silicon, copper, zinc, magnesium, iron, and manganese. More exotic elements are titanium and scandium which may give attractive properties. Many of these elements can be co-deposited during electrolysis since aluminium is a reactive metal with a high deposition potential. Another interesting feature is that most metal oxides are readily soluble in the molten fluoride electrolyte used in the Hall-Heroult process.

Metallic impurities that are more noble than aluminium tend to deposit at the liquid aluminium cathode in the industrial process (2). It has been shown (3, 4) that cations of such impurities are reduced at the cathode at the limiting current density (i_{lim}) which is given by the following equation:

$$i_{lim} = nFkc^o \quad [2]$$

where k is the mass transfer coefficient and c^o is the concentration of the dissolved impurity element species in the bulk of the electrolyte. Studies of impurities in industrial cells have been carried out by analyses of samples of electrolyte and metal as a function of time after additions of known amounts of compounds containing impurities. The concentration of the impurity species under investigation versus time after addition can be expressed as follows (4)

$$c = c_o \exp\left(-\frac{A}{V}kt\right) \quad [3]$$

where A is the area of the active cathode and V is the volume of the electrolyte. By knowing the latter quantities, the mass transfer coefficient can be determined. Typical values have been reported to be in the range from 10^{-5} - 10^{-6} m/s (3, 4), iron giving slightly higher values than silicon and titanium. However, such mass transfer coefficients will depend more on design, technology and operation of industrial cells. High convection of electrolyte and metal pad or unstable cells will cause higher values.

Experimental

Laboratory experiments were carried out in a standard furnace under argon atmosphere. A tungsten wire (2.0 mm \varnothing) was used as working electrode, while the counter electrode was made of platinum or carbon. A wire of platinum served as a quasi reference electrode. In experiments with dissolved alumina an aluminium reference electrode was used, where liquid aluminium was placed inside an alumina tube with a slot for electrolyte contact and a tungsten wire. High purity and dried chemicals of NaF, AlF₃, Al₂O₃, SiO₂, Fe₂O₃, TiO₂ and Mn₂O₃ were used. The electrolyte was contained in a platinum or a sintered alumina crucible. Electrochemical studies and electrolysis experiments were performed. Recent experiments were carried out by adding minority elements throughout the course of electrolysis to maintain constant conditions.

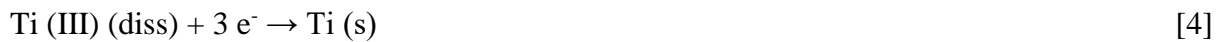
Other experiments were carried out in industrial aluminium producing cells. Known amounts of metal oxides were added and samples were taken for analysis from electrolyte (bath) and metal before and at certain intervals for up to 24 h.

Results and discussion

Laboratory experiments

Fig. 1 shows cyclic voltammograms in pure molten cryolite saturated with alumina at 1020 °C recorded using a tungsten electrode. J and K represent deposition and oxidation of Al, while L is the anodic potential limit due to oxidation of tungsten. The considerable background current before Al deposition is due to the formation of dissolved Al as well as dissolved Na. The formation of an alloy of Al-W may also contribute to some cathodic current. Co-deposition of iron, silicon, manganese and titanium take place within the potential window where alumina is thermodynamically stable.

The electrochemical behaviour of dissolved titanium species was studied by cyclic voltammetry in molten cryolite with dissolved TiO₂ (5). The results suggested that titanium is reduced in two steps according to the following scheme:



These results are in agreement with reports from other studies in fluoride melts where titanium is deposited from Ti (III) because Ti (II) species are unstable (6).

Industrial experiments

It was found that all the studied minority elements, iron, silicon, manganese and titanium, were efficiently reduced at the cathode. Of special interest is manganese, where it was found that essentially all the added manganese was found to end up in the metal regardless of the compound that was added to the electrolyte; Mn₂O₃, MnO₂ or MnO. Figure 2 shows the concentration of manganese in the electrolyte and metal as a function of time before and after addition of Mn₂O₃. For the other elements about 90 % of the metal containing additions were found to be co-depositing on the cathode. One reason for the loss may be poor dissolution or inefficiency due to the presence of species of different oxidation states. However, it was found that Fe (II) may not be oxidized to Fe (III) at the anode under normal electrolysis conditions.

Figure 3 shows a plot of the data for manganese after addition of Mn₂O₃ according to equation [3]. The good linear fit suggests that manganese is reduced at the cathode at diffusion controlled conditions. Similar results were obtained for the other elements. Figure 4 shows concentration of silicon and titanium in the bath as a function of time before and after adding SiO₂ and TiO₂.

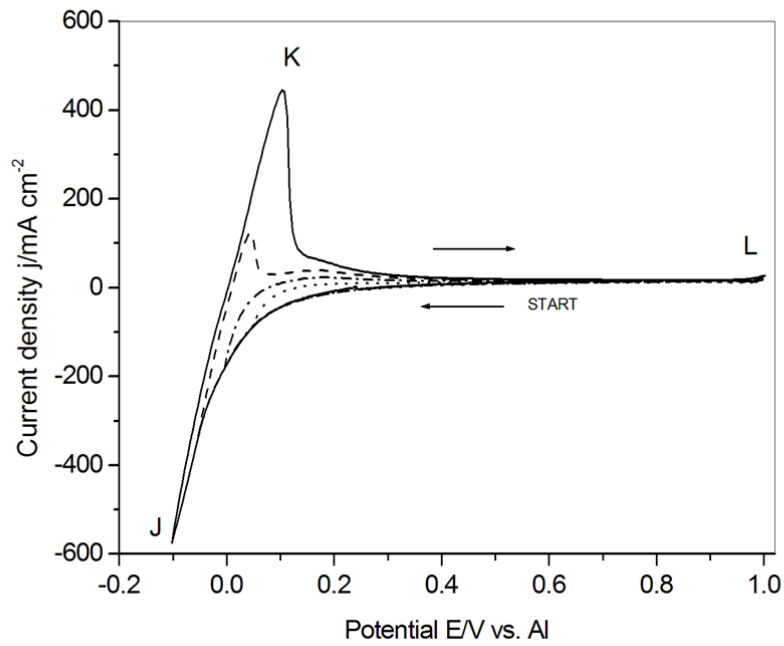


Figure 1. Voltammograms recorded on a tungsten working electrode in molten cryolite (Na_3AlF_6) saturated with Al_2O_3 at 1020°C . Sweep rate 0.1 V s^{-1} .

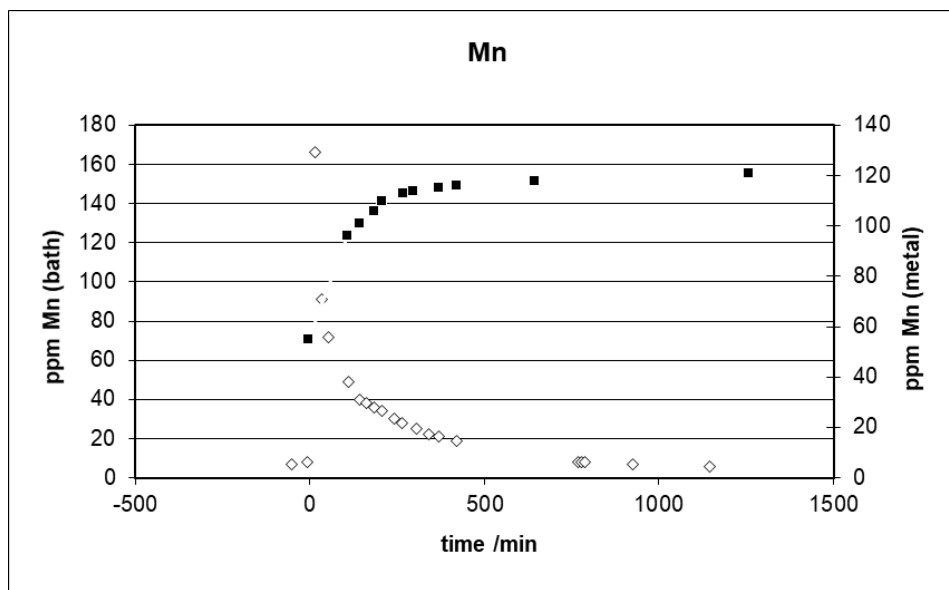


Figure 2. Concentration of manganese in bath and metal as a function of time before and after addition of Mn_2O_3 . The addition was made at $t = 0$.

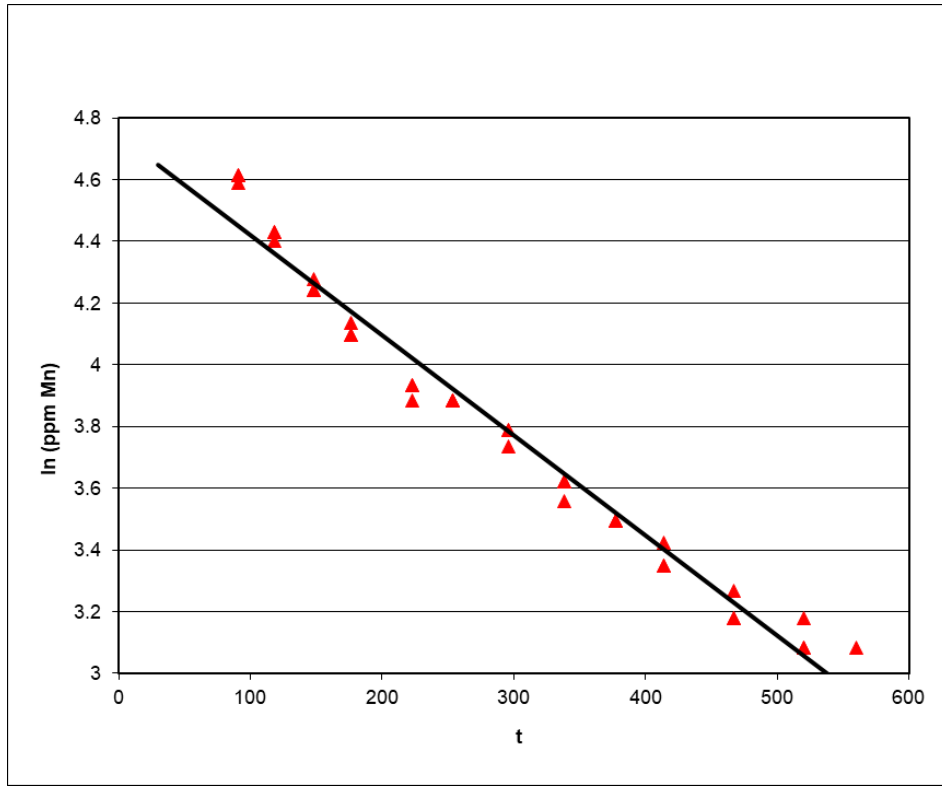


Figure 3. Plot of log concentration of manganese in the bath as a function of time after addition of Mn_2O_3 . The solid line is a linear fit of the data.

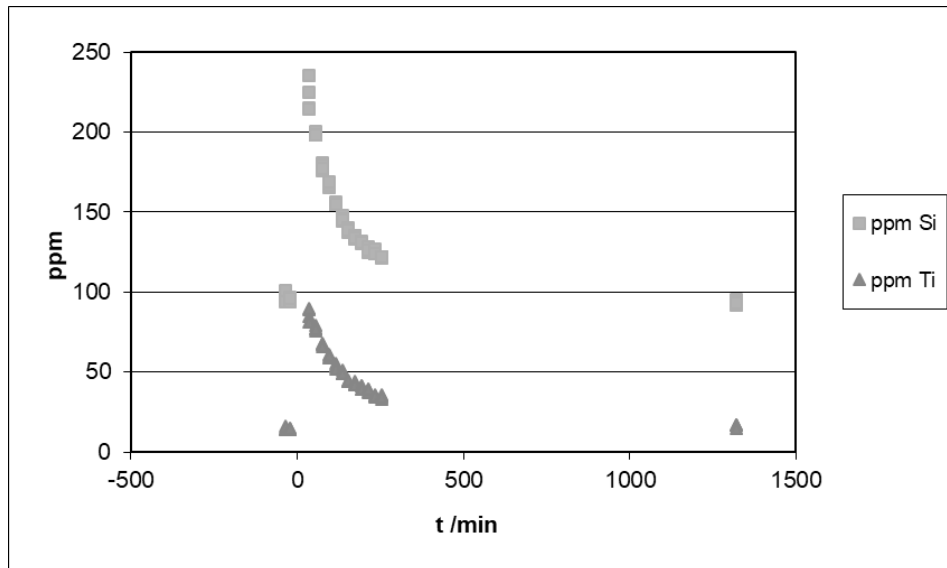


Figure 4. Concentration of silicon and titanium in the bath as a function of time before and after adding SiO_2 and TiO_2 . The addition was made at $t = 0$.

From plots like shown in Figure 3 and using equation [2], the mass transfer coefficient was found to be of the order of $1 \cdot 10^{-5}$ m/s for all the investigated metals. This is in agreement with literature (3, 4).

Ongoing laboratory experiments are focussing on investigating the conditions where the concentration of dissolved metal oxides is kept constant by additions throughout the electrolysis. Quantitative results are not available because electrolyte and metal samples have not yet been analysed. Preliminary results indicate that electrolysis time, concentration of dissolved metal oxides and electrolysis temperature or superheat may influence the dissolution of the metal oxides and affect the content of the alloying element.

It is expected that successful co-deposition of alloying elements may give big savings compared to the current practice. New valuable such as $TiAl_3$ may be produced by controlled co-deposition. Another benefit by using co-deposition is the possibility to use inexpensive raw materials containing impurities which can be utilized for producing alloys.

Conclusions

Laboratory studies of the electrochemical behaviour of candidate alloying elements with aluminium were carried out for iron, silicon, manganese and titanium. These elements can be reduced from their dissolved metal oxides in molten cryolite-alumina based electrolytes.

Experiments were also carried out in industrial aluminium cells. Large quantities (kg) of metal oxides were added to the electrolyte during electrolysis, and samples of electrolyte and produced metal were taken and analysed as a function of time after addition. The results suggested all these metals were co-depositing with liquid aluminium at their limiting current density. The apparent current efficiency for metal co-deposition was estimated to be of the order of 90 % for iron, silicon and titanium and close to 100 % for manganese.

Significant savings for implementing this method for producing aluminium based alloys are expected.

Acknowledgements

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