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THE PERFORMANCE OF ALUMINIUM ELECTROLYSIS IN CRYOLITE BASED ELECTROLYTES CONTAINING LiF, KF AND MgF_2

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Abstract

The effects of LiF and MgF_2 addition to the electrolyte on current efficiency were investigated during aluminium electrolysis using base $NaF-AlF_3-Al_2O_3-CaF_2$ system at 980°C in laboratory scale. The electrolysis was performed with a cryolite ratio of 2.5 and with 4% Al_2O_3 and 5% CaF_2. The duration of each electrolysis experiment was 4 h with a graphite anode and a cathodic current density of 0.85 Acm^{-2}. Additions of LiF up to 5 wt% were found to improve the current efficiency. Additions of MgF_2 had a positive effect on current efficiency. The effects of KF and LiF on the cathode process were studied using the same system. The alkali metals concentration including K, Na and Li in deposited aluminium were analyzed as a function of the cathodic current density. Results are presented from a study of the influence of electrolyte composition and cathodic current density on current efficiency and cathode process.

Introduction

Aluminium is the most abundant metallic element in the earth's crust. The Hall-Héroult process is the only method by which aluminium is produced industrially today. Liquid aluminium is produced by the electrolytic reduction of alumina dissolved in an electrolyte mainly containing cryolite. The $Na_3AlF_6-Al_2O_3-AlF_3$ system is the main electrolyte during aluminium electrolysis. The overall cell reaction may be written:

$$Al_2O_3\,(diss) + 3/2\,C\,(s) = 2Al\,(l) + 3/2\,CO_2\,(g) \qquad (1)$$

Most of the changes in electrolyte chemistry have aimed at better cell operation by using additives that improve the physicochemical properties of the electrolyte [1]. Besides the main components (Na_3AlF_6, AlF_3, Al_2O_3), the electrolyte may contain some additives such as CaF_2, LiF and MgF_2.

Current efficiency is one of the main parameters describing the performance of the cell. It is defined as the ratio of the actual metal produced and the theoretical amount that should be formed according to Faraday's first law. The main reason for the loss in current efficiency is that the metal has a small, but significant solubility in the bath. The rate of the back reaction is controlled by diffusion of dissolved metals through the diffusion layer near the cathode. The dissolved metal may react with the CO_2 that is formed on the anode, and it can be written as follows:

$$Al\,(diss) + 3/2\,CO_2\,(g) = Al_2O_3\,(diss) + 3/2\,CO\,(s) \qquad (2)$$

The solubility of aluminium in cryolite-based melts is of the order of 0.03 to 0.06 wt% Al for electrolytes of industrial relevance. Dissolved metal is a decisive factor for current efficiency in the industrial process, and a proper understanding of the $Na_3AlF_6-Al_2O_3-AlF_3$ system is therefore of considerable importance.

Lithium fluoride is very effective in lowering the liquidus temperature and in increasing the electrical conductivity of the electrolyte. There are many papers about lithium-modified electrolytes that have improved the operational results of industrial cells [2-4]. Previously the effects of lithium fluoride and potassium fluoride on the current efficiency in a laboratory cell were studied [5]. Magnesium fluoride has been shown to have a positive effect on current efficiency in laboratory study [6, 7] and industrial cells [8]. It is present in the electrolyte of some aluminium smelters, sometimes in connection with the use of lithium-containing melts.

The alkali metals are not reduced at the cathode because they are less noble than aluminium. However, it has been found that some reduction of these metals does take place as an equilibrium concentration of lithium, magnesium, and calcium in the aluminium metal pool in cells is established relative to the concentration of these metals present in the cryolite based electrolyte. Measurements indicate that the amount of dissolved sodium is much greater than that of dissolved aluminium measured as wt% Al [1]. Sodium is produced at the bath–metal interface due to the chemical reaction occurring when reaching thermodynamic equilibrium and sodium partitioning into the two phases based upon equilibrium constant for the following reaction [9]:

$$Al + 3NaF = 3Na + AlF_3 \qquad (3)$$

When LiF and KF are added to the melts, it is expected that they would behave similarly to NaF, according to

$$Al + 3MF = 3M + AlF_3 \qquad (4)$$

where M is either Li or K

Experimental

The cell design for the laboratory experiments is shown in Fig.1. The cell design used for the experiments was developed by Solli et al [7, 10], specially designed for determination of CE as a function of isolated variable parameters in the Hall-Héroult process. The anode was designed to give enhanced and reproducible bubble induced electrolyte convection, while the wettable cathode substrate gave a well defined cathode area, and thus a uniform current density.

The chemicals used were cryolite (Na_3AlF_6, natural hand-picked), AlF_3 (sublimed), Al_2O_3 (calcined), LiF, KF and CaF_2 of high purity. A graphite anode was immersed about 4 cm into the

electrolyte and placed about 4 cm above the steel cathode. Standard experimental conditions were Na_3AlF_6-Al_2O_3 (sat) with excess AlF_3 corresponding to a molar ratio of NaF/AlF_3 (CR) of 2.5 and 5 wt% CaF_2 at 980℃ and a constant current density of 0.85 A/cm^2. The duration of each electrolysis experiment was 4 h. The influence of additions of LiF and MgF_2 on the current efficiency was studied. The current efficiency was calculated from the ratio of metal produced and the theoretical amount given by Faraday's law of electrolysis.

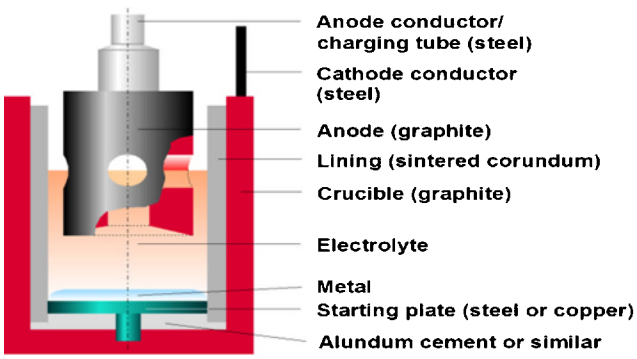


Figure 1. The cell design for laboratory study

The contents of sodium, lithium, potassium in aluminium pad at different current densities with additives of LiF and KF were determined using the same cell. Sampling of metal was performed every 1 hour at different current density with additions of LiF and KF during electrolysis. Metal samples were dissolved and analyzed by ICP-MS.

Results and discussion

Current efficiency

Current efficiencies were obtained at different additions of magnesium fluoride in Figure 2. Current efficiencies with additions of MgF_2 were obtained ranging from 92.5% to 93.5%. Current efficiencies were found to increase with increasing addition of MgF_2. It should be noted that higher MgF_2 gives a high density and reduces the metal solubility in the electrolyte. High density is good for preventing mixing and maintaining good separation between metal and electrolyte. It may also affect the rate of dissolution of alumina.

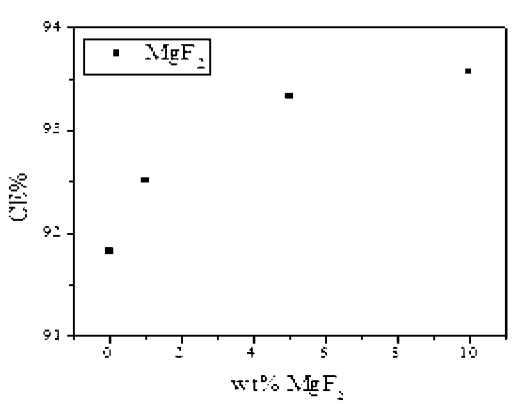


Figure 2. Current efficiency for aluminium deposition as a function of addition of MgF_2

The effects of different additions on the current efficiency are shown in Figure 3. 5% LiF and 5% MgF_2 additions were found to increase current efficiency compare to the others with additions of LiF and MgF_2. It is higher than 5% MgF_2 addition.

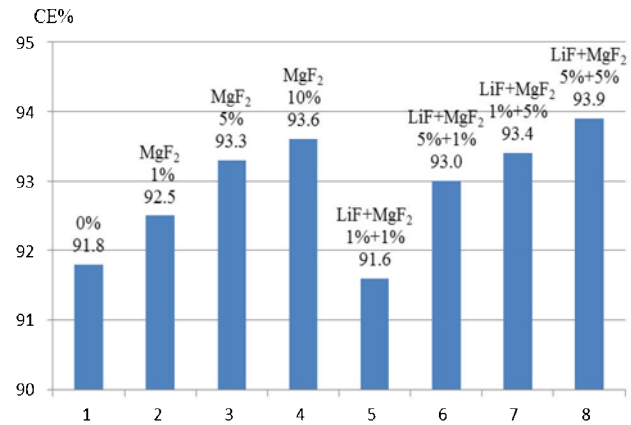
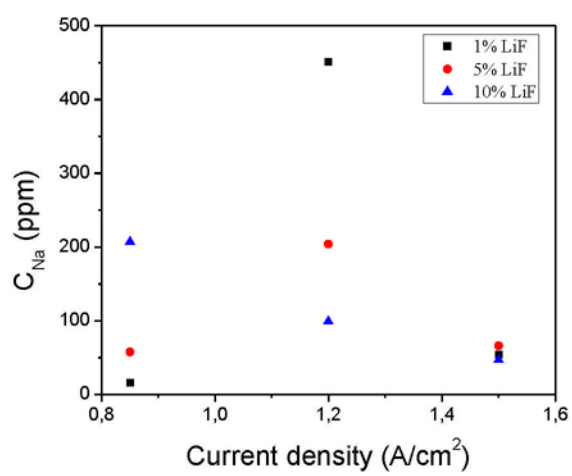


Figure 3. Current efficiency as a function of additions of LiF and MgF_2

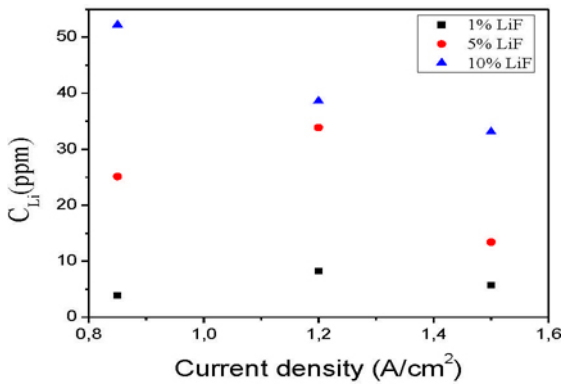
The main purpose of using additives is to modify the composition of the electrolyte to improve its physico-chemical properties of the electrolyte, in order to increasing current efficiency and to reduce the energy consumption. However, there is no optimum electrolyte composition for a given aluminium electrolysis cell. Because the price of lithium fluoride has so far limited a widespread use in the aluminium industry, the combined addition of LiF and MgF_2 represents a more economic alternative to achieve improvement in current efficiency.

Cathode process

Samples were taken at different current densities every 1 hour during electrolysis with different additions of LiF and KF. The contents of sodium, lithium, potassium in aluminium were obtained at different current densities with different additives as shown in Figures 4-6.



(a) Na



(b) Li

Figure 4. The contents of Na and Li in aluminium at different current densities with additions of LiF.

Figure 4 shows that the contents of sodium and lithium in aluminium vary with current density at different LiF additions. The rate of chemical and electrochemical reactions taking place at the aluminium/melt interface at the temperatures of electrolysis is high because of high current density [11]. Thus, the sodium and lithium contents in aluminium are related to the composition of the melt at the aluminium/melt interface by the reaction

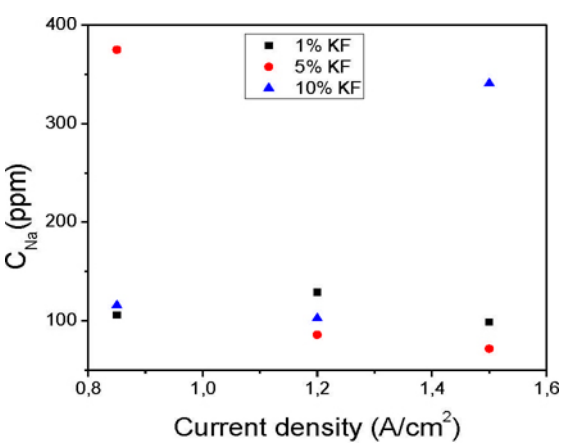
$$\text{Li (in Al)} + \text{NaF} = \text{Na (in Al)} + \text{LiF}$$

The equilibrium content of sodium and lithium in aluminium can be described by the following reactions [12]

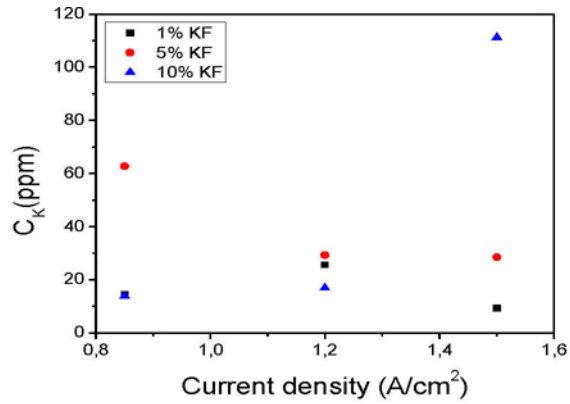
$$4\ \text{NaF} + \text{Al} = 3\ \text{Na (in Al)} + \text{NaAlF}_4$$

$$3\ \text{LiF} + \text{NaF} + \text{Al} = 3\ \text{Li (in Al)} + \text{NaAlF}_4$$

The contents of sodium in aluminium tend to be close when the current density is 1.5 A/cm^2. It should be noted that low sodium contents might be due to strong stirring at the high current density increasing in laboratory study. The contents of lithium in aluminium increase with increasing additions of LiF.



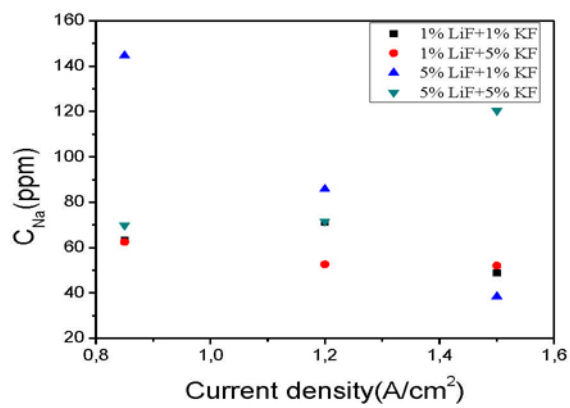
(a) Na



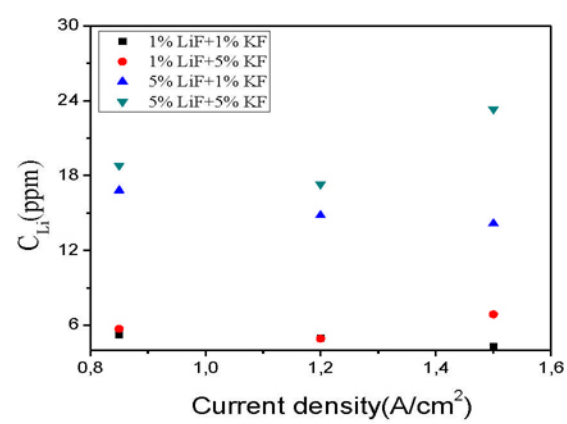
(b) K

Figure 5. The contents of Na and K in aluminium at different current densities with additions of KF.

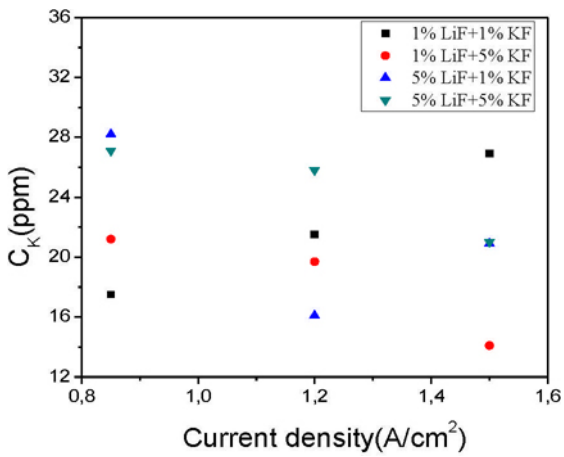
Figure 5 shows that the contents of sodium and potassium in aluminium vary at a small range with different additions KF. Some points are very high in the figure, which is probably due to sampling problems. KF has a smaller effect on the contents of sodium and potassium in aluminium.



(a) Na



(b) Li



(c) K

Figure 6. The contents of Na, Li and K in aluminium at different current densities with additions of LiF and KF.

Figure 6 shows that the contents of sodium and lithium in aluminium vary slightly with current density increasing at 1% LiF additions together with different KF additions. The contents of sodium in aluminium increase with current density increasing. It was found to vary differently with the others additions of LiF and KF. The contents of potassium in aluminium vary between 14-28 ppm with increasing current density.

Conclusions

The current efficiency for aluminium deposition was investigated in molten NaF-AlF_3 (CR=2.5) -CaF_2 (5 wt%)-Al_2O_3 (sat) at 980℃ and 0.85 A/cm^2. MgF_2 has a positive effect on current efficiency. 5% LiF and 5% MgF_2 additions were found to increase the current efficiency compared to the other additions of LiF and MgF_2.

The behaviour of LiF and KF on the cathode process is different. The contents of sodium in aluminium tend to be low when the current density is 1.5 A/cm^2 with additions of LiF. The contents of lithium in aluminium increase with increasing additions of LiF. Additions of KF have a smaller effect on the contents of sodium and potassium in aluminium.

Acknowledgments

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References

1. J. Thonstad, P. Fellner, G.M. Haarberg, J. Hives, H. Kvande, and A. Sterten, *Aluminium electrolysis: fundamentals of the Hall-Héroult process*, Düsseldorf: Aluminium-Verlag. 2001.

2. B. Langon and P. Varin, Light Metals 1986, p. 10-12, 14.

3. E.W. Dewing, Metallurgical Transactions B-Process Metallurgy, p. 177-182 (1991).

4. A.T. Tabereaux, T.R. Alcom, and L. Trembley, Light Metals 1993, p. 221-226.

5. G.M. Haarberg and P. Cui, Light Metals 2014, p. 749-752.

6. K. Grjotheim, *Aluminium electrolysis: fundamentals of the Hall-Héroult process*, Düsseldorf: Aluminium-Verlag. XI,443 s. 1982.

7. P.A. Solli, T. Eggen, E. Skybakmoen, and A. Sterten, Journal of Applied Electrochemistry, p. 939-946 (1997).

8. Fiona J. Stevens, W. Zhang, Mark P. Taylor, and J.J.J. Chen, Light Metals 1992, p. 541-547.

9. A.T. Tabereaux and R.D. Peterson, *Chapter 2.5 - Aluminum Production*, in *Treatise on Process Metallurgy*, S. Seetharaman, Editor. 2014, Elsevier: Boston. p. 839-917.

10. P.A. Solli, T. Eggen, S. Rolseth, E. Skybakmoen, and A. Sterten, Journal of Applied Electrochemistry, p. 1019-1025 (1996).

11. A. Kisza, J. Thonstad, and T. Eidet, Journal of the Electrochemical Society, p. 1840-1847 (1996).

12. V. Danielik, P. Fellner, and J. Thonstad, Journal of Applied Electrochemistry, p. 1265-1268 (1998).