

THE PERFORMANCE OF ALUMINIUM ELECTROLYSIS IN A LOW TEMPERATURE ELECTROLYTE SYSTEM

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Abstract

The electrolyte based on the molten KF-AlF₃-NaF system was investigated for low-temperature aluminium electrolysis in laboratory scale. The current efficiency for aluminium deposition was determined from the amount of aluminium deposited after 4 h at a cathodic current density of 0.85 A·cm⁻². The cryolite ratio of molar concentrations of alkali fluorides and aluminium fluoride $KR = (N_{KF} + N_{NaF}) / N_{AlF_3}$, was always retained constant, equal to 1.3 or 1.5. The cryolite-based melts contained 5 and 10 mass% NaF. The temperature was 750 °C for KR=1.3 and 800 °C for KR=1.5. Current efficiencies decreased with increasing content of NaF at cryolite ratios 1.3 and 1.5. The effect of NaF on the cathode process was studied. The contents of sodium and potassium in aluminium based on the KF-NaF-AlF₃ melts were determined as a function of the cathodic current density in the range from 0.5 to 1.2 A·cm⁻².

Introduction

Industrial production of aluminium is now exclusively based on the Hall-Héroult process. Producing aluminium by this process requires a large amount of energy and produces significant emissions of greenhouse and other harmful gases. In order to reduce harmful waste production and to improve other technological parameters for energy saving, the promising direction is the development of a new electrolyte having high electrical conductivity, high alumina solubility and the possibility to carry out the process at much lower temperature. The electrolyte may be regarded as the heart of the Hall-Héroult process. Most of the changes in electrolyte chemistry throughout the history of the process have aimed at better cell operation by using additives that improve the physicochemical properties of the electrolyte, in order to increase the current efficiency and to reduce the energy consumption of the process [1]. However, the radical decrease of operating temperature is difficult in the frame of the existing technology in which sodium cryolite is a basic component of the electrolyte.

In order to obtain essential decrease of the electrolyte liquidus temperature, the KF-AlF₃-based salts are attractive since the system has a eutectic point at 560 °C. The phase diagram of the KF-AlF₃ system [2, 3] shows that the system has a much wider low temperature liquid range than the NaF-AlF₃ system. Moreover, a KF-AlF₃-based system has higher alumina solubility compared with a NaF-AlF₃-based system. Meanwhile, a KF-AlF₃-based system contributes not only to decreasing the operating temperature but also to the possible application of inert anodes in the Hall-Héroult process [4]. No acceptable inert anode material has yet been found for long-term use in industrial aluminium electrolysis due to the high temperature environment of Al electrolysis cells.

In the KF-AlF₃ system, however, sodium, present as sodium fluoride in the electrolyte, is introduced to the electrolytic cell as an impurity in the alumina feed and can build up over time [5]. So, based on the KF-AlF₃ system, study of the NaF-KF-AlF₃ system is necessary.

Many studies have been performed on the physical and chemical properties and operating parameters in the NaF-KF-AlF₃-Al₂O₃ system. Some alumina solubility measurements have been published by Yan et al. [6] in KF-AlF₃-NaF systems. The liquidus temperature, electrical conductivity and alumina solubility in the KF-NaF-AlF₃ molten mixtures at the $[KF]/([KF]+[NaF])$ ratio ranging from 0 to 1 and at the fixed values of $([KF]+[NaF])/[AlF_3]$ ratio equal to 1.3, 1.5 and 1.7 have been measured by Apisarov [7]. Research by Wang et al. [8] suggested that electrolysis was more stable in the KF-NaF-AlF₃ (KF:NaF=1:1) electrolyte with CR=1.5 at 800 °C because high unstable fluctuating voltage (5.96-19.6 V) was observed in cells operated at 700 °C. Voltage fluctuation was explained by the formation of cathode encrustation. According to Zaikov [9, 10], increasing the CR to 1.5 and temperature to 800 °C, as well as modification of the bath composition, allowed for stable aluminium electrolysis in an NaF (12 wt%) - KF (30) - LiF (3) - AlF₃ (55) electrolyte. Sustained, stable operation of low-temperature, potassium cryolite-based aluminium electrolysis in 20 and 100 ampere cells fitted with vertical metal anodes and wetted cathodes was performed by Tkacheva et al. [11].

Sodium is always present as an undesired impurity in aluminium produced by the Hall-Héroult process, but in molten cryolite based electrolytes, dissolved Na must be considered in addition to dissolved Al [12]. Tabereaux [13] found that a high sodium content in aluminium in industrial reduction cells correlates with a high current efficiency during electrolysis. So involving KF as a major component in the KF-AlF₃-NaF system, the metal will also contain potassium and sodium as impurities due to exchange equilibria. The following equilibria are established at the aluminium-electrolyte interface:



Most of the previous work was focused on studying the physicochemical properties and testing the behaviour of inert anodes in the NaF-KF-AlF₃-Al₂O₃ system. The aim of this work is to investigate the NaF-KF-AlF₃-Al₂O₃ system in order to get a quantitative understanding of the potential as a low temperature electrolyte for aluminium electrolysis. The current efficiency was studied in a laboratory cell. The effect on the content of NaF in

the NaF-KF-AlF₃-Al₂O₃ system was studied, involving KF as a major component. The data on the content of potassium and sodium in the KF-AlF₃-NaF based melts are presented.

Experimental

The laboratory cell, which was similar to the cell developed by Solli et al. [14-16], was designed specifically with the aim of obtaining good and reproducible convective conditions, and to give an almost flat metal surface (cathode) during electrolysis. The anode, the cathode, and the electrolyte were contained in a graphite crucible with a cylindrical sintercorundum side lining. The cell was placed in a vertical tube furnace with argon atmosphere and positioned to avoid temperature gradients in the electrolyte. The cathode was aluminium wetted on a stainless steel plate. This ensured a close to flat aluminium surface, and consequently an even current distribution on the cathode surface. The steel plate rested on a layer of alumina on top of a lining made of high purity cast alumina cement. This arrangement ensured negligible transport of aluminium and electrolyte down to the graphite crucible, and a minimum of metal loss due to formation of aluminium carbide. A graphite anode was placed about 1 cm above the steel cathode.

The electrolysis time was 4 hours for each experiment at a cathodic current density of 0.85 A·cm⁻². The maximum cell voltage was 10 V. The steel plate was weighed before the experiment. After the experiment, the steel plate and aluminium were removed from the cell and the current efficiency was determined from the weight gain. The electrolyte was saturated in alumina at the start of the experiment. The ratio between molar concentrations of the alkali fluorides and the aluminium fluoride, $KR = (N_{KF} + N_{NaF}) / N_{AlF_3}$, was always kept constant equal to 1.3 or 1.5. The cryolite-based melts contained 0, 5 or 10 wt% NaF, meaning that NaF was replacing KF to keep KR constant. The temperature was 750 °C for KR=1.3 and 800 °C for KR=1.5.

The contents of sodium, potassium in the aluminium pad at different current densities with additive of NaF were determined. Sampling of metal was performed every 1 hour at different current densities during electrolysis. Metal samples were dissolved and analysed by ICP-MS.

Results and Discussion

Current Efficiency

Current efficiencies were obtained at the different contents of NaF at 750 °C for KR=1.3 as shown in Figure 1. The current efficiency decreased with increasing content of NaF. The relationship between cell voltage and time during electrolysis is shown in Figure 2.

The expected benefit of using NaF-KF-AlF₃ mixtures is the combination of the high electrical conductivity of Na-cryolite with the enhanced alumina solubility in K-cryolite melts. However, NaF increases the liquidus temperature in the potassium cryolite system. This fact is especially important when selecting electrolyte composition for aluminium electrolysis. When the cryolite-based melts contained 10 mass% NaF, the liquidus temperature of KF-AlF₃-NaF system at cryolite ratio 1.3 is higher than 750 °C according to Apisarov [7]. Although the electrolysis can still be operated below this calculated liquidus temperature,

the process caused high cell voltage fluctuations and changed current distribution, which also interfered with the formation and coalescence of aluminium metal product on the wetted cathode. Some undissolved alumina was found at the anode after the experiment. High unstable voltage fluctuations were observed during electrolysis. When the cryolite-based melts contained 5 wt% NaF, the cell voltage raised during the second half of the process. Since the transport processes at the cathode leads to enrichment of NaF and KF at the cathode (increased KR), it is probable that solid cryolite was formed at the cathode; particularly, in melts rich in NaF, which have higher liquidus temperature. Besides the increased cell voltage, this could also explain that the current efficiency decreased with increasing NaF content, because the metal forms small spheres with larger surface area.

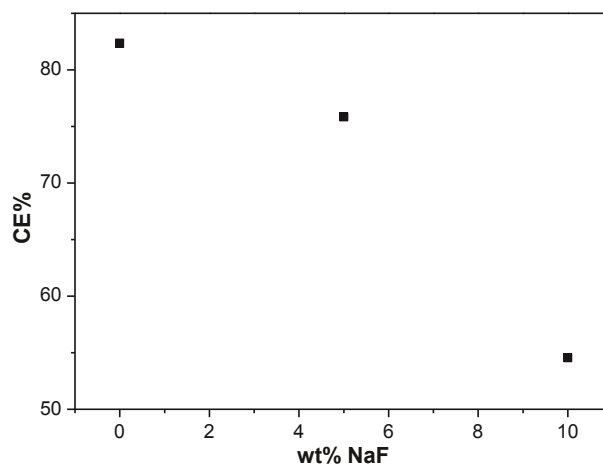


Figure 1. Current efficiency for aluminium deposition as a function of the content of NaF in molten KF-AlF₃-NaF (KR=1.3) - Al₂O₃ (sat) system at 750 °C.

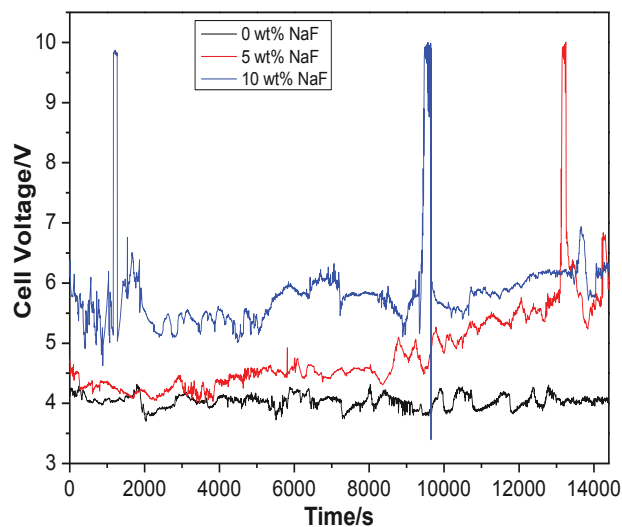


Figure 2. The cell voltages for aluminium deposition as a function of time in molten KF-AlF₃-NaF (KR=1.3) - Al₂O₃ (sat) system at 750 °C as a function the content of NaF during electrolysis.

Current efficiencies were obtained at different contents of NaF at 800 °C for KR=1.5 as shown in Figure 3. The current efficiencies decreased with increasing content of NaF. The relationship

between time and cell voltage during electrolysis is shown in Figure 4.

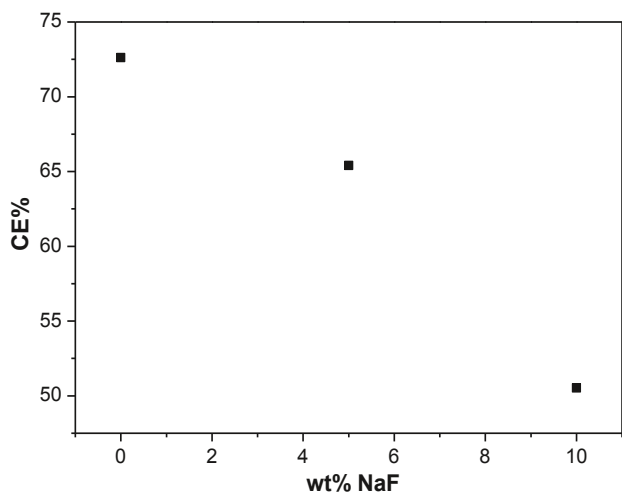


Figure 3. Current efficiency for aluminium deposition as a function of the content of NaF in molten $\text{KF-AlF}_3\text{-NaF}$ ($\text{KR}=1.5$) - Al_2O_3 (sat) system at 800°C .

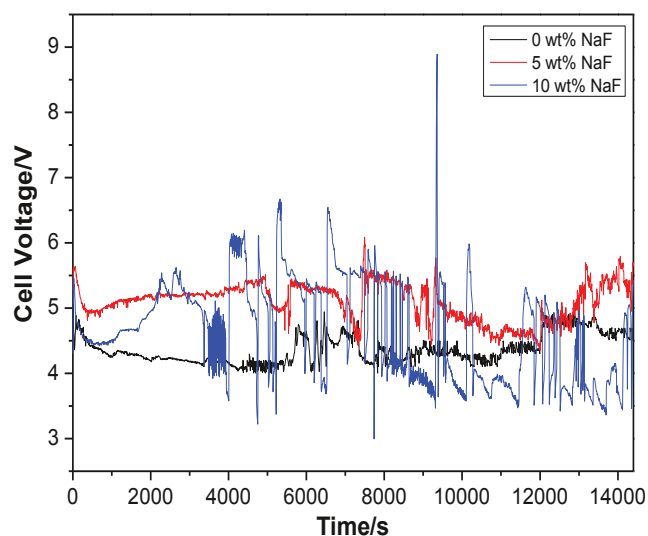


Figure 4. The cell voltages for aluminium deposition as a function of time in molten $\text{KF-AlF}_3\text{-NaF}$ ($\text{KR}=1.5$) - Al_2O_3 (sat) system at 800°C for different contents of NaF during electrolysis.

According to Apisarov [7], the liquidus temperature is around 780 and 790°C respectively when the cryolite-based melts contained 5 mass% and 10 mass% NaF. Large voltage oscillations were observed at 5 and 10 mass% NaF in the melts. This might be because the operation temperature is very close to the liquidus temperature that results in formation of a layer of solid cryolite at the cathode. High cell voltage fluctuations and deterioration of current distribution would inhibit the formation of an adequate coalesced aluminium metal product so that the current efficiency decreased.

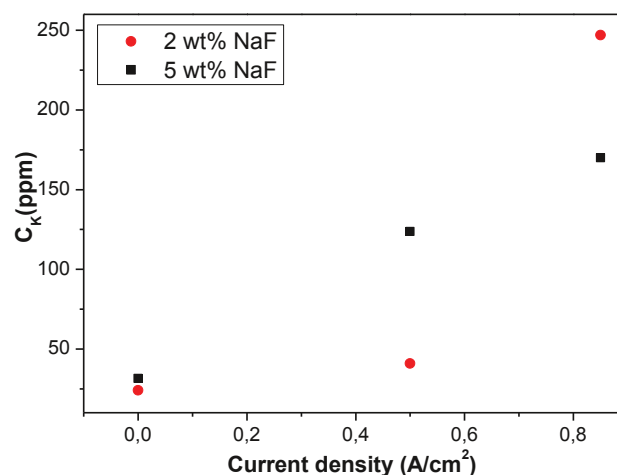
It was found that the NaF presence in the potassium cryolite has a negative impact on cell operation, as it caused cell voltage anomalies when experiments were performed. Tkacheva et

al. [11] found that an increase in temperature can minimize the amplitude of voltage oscillation. The operating temperature needs to be adjusted to take the NaF content in the electrolyte into account, so the cell voltage anomalies caused by the NaF presence in the potassium cryolite can be avoided by careful control of operating parameters. More experiments are needed to determine the effect of NaF on cell operation in laboratory cells because they will be beneficial for increasing our understanding of processes that cause loss in current efficiency.

The Cathode Process

Sampling of metal was performed every 1 hour at different current densities. After the electrolysis for every current density, a waiting time of 15 min to establish equilibrium before the sampling. The contents of sodium and potassium in polarized aluminium were obtained at different current densities and two different KR with additions of NaF, in shown Figures 5 and 6.

(a) K



(b) Na

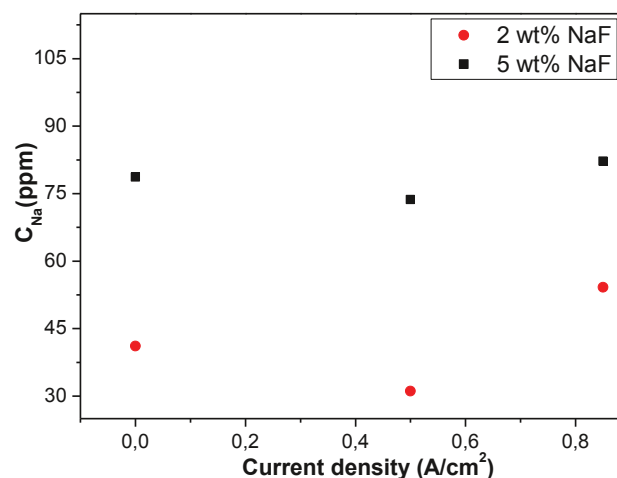
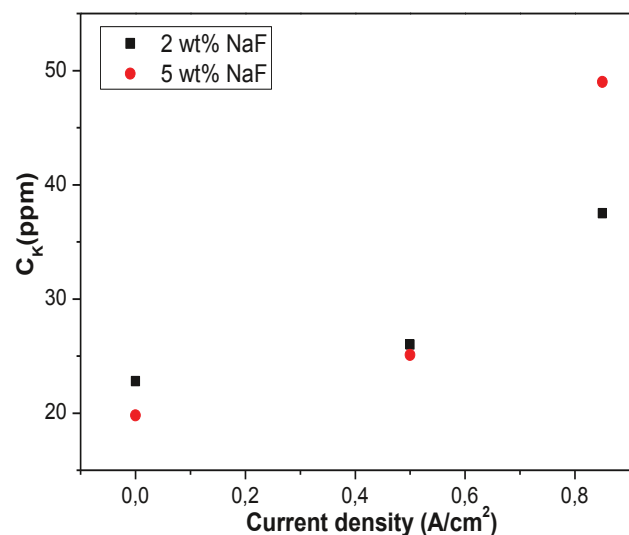


Figure 5. The contents of K and Na in aluminium at different current densities with additions of NaF in molten KF-AlF_3 ($\text{KR}=1.5$) - Al_2O_3 (sat) system at 800°C .

The rate of chemical and electrochemical reactions taking place at the aluminium/melt interface at the temperatures of electrolysis is high because of the very high exchange current densities [17]. Thus, there is equilibrium between the melt adjacent to the cathode and the metal. The equilibrium content of sodium and potassium in aluminium can be described by the Reactions 1 and 2 in the Introduction.

(a) K



(b) Na

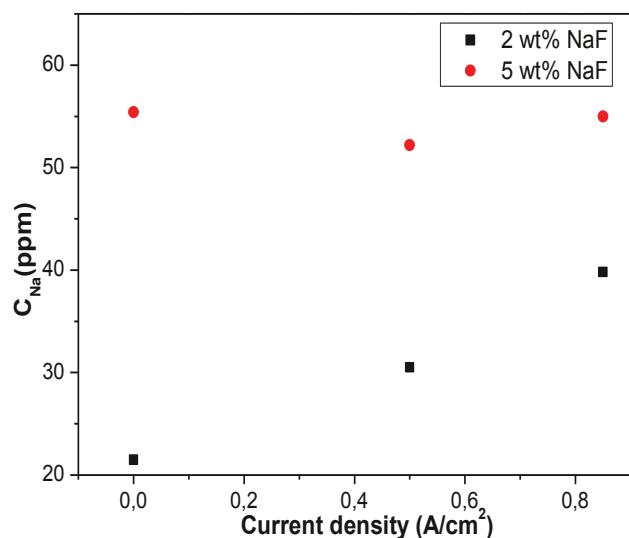


Figure 6. The contents of K and Na in aluminium at different current densities with additions of NaF in molten KF-AlF₃ (KR=1.3) - Al₂O₃ (sat) system at 750 °C.

From Figures 5 and 6, it was found that the concentration of potassium in aluminium increases with increasing current density. As aluminium metal is being produced at the cathode, the local concentration of KF in the near-cathode region can be higher than that in the bulk during electrolysis. Increasing current density leads to the molar ratio KR increases at the metal/melt interface. This change in composition between the bulk of the electrolyte

and the layer adjacent to the cathode causes the cathodic concentration overvoltage. With increasing KR the potassium activity increases, and so does the potassium content in the aluminium.

The concentration of sodium in aluminium increases slightly with increasing current density. Although the addition of NaF was rather small, the content of sodium in aluminium is high compared to potassium. This might be explained by the contribution of sodium cations to the transport of electrical charge in the cell because the ionic radius of the latter is indeed slightly bigger, and since K⁺ ions are less mobile, the enrichment of NaF at the aluminium/melt interface is more likely.

Concluding Remarks

The current efficiencies achieved in the present work were rather disappointing, considering that the melts used were very acidic and at low temperature. Current efficiencies of about 94 percent are obtained in the same apparatus when using today's standard bath compositions. The reason is probably formation of solid cryolite at the cathode, which may be a serious problem also in an industrial process, at least when using a process where inert anodes are combined with wettable cathodes. The only way to get around this problem seems to be the use of high superheat, which would partly counteract the advantages of using a very acidic bath.

The contents of sodium and potassium in polarized aluminium were obtained at different current densities and at cryolite ratio 1.3 and 1.5 with additions of NaF. The concentration of potassium in aluminium increased with increasing cathodic current density. The concentration of sodium in aluminium increased slightly with increasing cathodic current density.

Acknowledgment

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