Effect of Composition and Temperature on Current Efficiency for Aluminium Electrolysis from Cryolite-Based Molten Alumina Electrolytes

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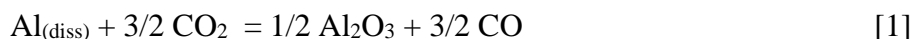[b] SINTEF Materials and Chemistry, Trondheim 7465, NORWAY
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The current efficiency (CE) for aluminium electrolysis in modern cells can be as high as 96 %. The main reason for loss in current efficiency is the so-called back reaction between dissolved metal and the anode product of CO_2. Decreasing temperature of the cell may give higher current efficiency. However, low superheat may cause solidification of melt. A laboratory cell to determine the current efficiency was recently modified to obtain more reliable results. Electrolysis was performed at constant current density and the current efficiency was determined from the weight of deposited aluminium. Effects of electrolyte composition by addition of LiF and temperature were studied. The loss in current efficiency is strongly related to the content of dissolved metal in the electrolyte. The effect of LiF addition on the current efficiency was discussed in this study.

Introduction

Industrial aluminium production is carried out by the Hall-Héroult process[1]. The electrolyte composition is normally based on the system Na_3AlF_6-AlF_3-CaF_2-Al_2O_3. The current efficiency of industrial cell can be as high as 96 %. The main reason for loss of current efficiency is the back reaction between dissolved metal in the electrolyte (counted as aluminium) and the anode product as shown in the following reaction:

$$Al_{(diss)} + 3/2\ CO_2 = 1/2\ Al_2O_3 + 3/2\ CO \qquad [1]$$

The current efficiency can be improved by suppression of metal dissolution from deposited metal. Metal dissolution into the electrolyte can be suppressed by controlling the electrolysis conditions. The NaF/AlF_3 molar ratio (so-called cryolite ratio, CR) changes the metal solubility, in such a way that AlF_3 content is beneficial in reducing the metal solubility in cryolitic melts. As the result, the AlF_3 content in the electrolyte strongly affects the current efficiency[2], and low cryolite ratio could give high current efficiency in the laboratory cell[3-6]. Also, the electrolyte temperature contributes to change the current efficiency. It has been reported that lowering the superheat by 1 ºC improved the current

efficiency by 0.2 % in the industrial cell[7]. From these results, it is important to control the temperature and composition of the electrolyte for improvement of the current efficiency. The liquidus temperature of the cryolite based melt has been reported by Solheim *et al.*[8]. The calculated liquidus temperature is expressed by the following equation;

$$
\begin{aligned}
T_{\text{liq}}/{}^{\circ}\text{C} \quad = \quad & 1011 + 0.50C_{\text{AlF}_3} - 0.13C_{\text{AlF}_3}^{2.2} - \frac{3.45C_{\text{CaF}_2}}{1 + 0.0173C_{\text{CaF}_2}} + 0.124C_{\text{CaF}_2} \cdot C_{\text{AlF}_3} \\
& - \; 0.00542(C_{\text{CaF}_2} \cdot C_{\text{AlF}_3})^{1.5} - \frac{7.93C_{\text{Al}_2\text{O}_3}}{1 + 0.0936C_{\text{Al}_2\text{O}_3} - 0.0017C_{\text{Al}_2\text{O}_3}^2 - 0.0023C_{\text{AlF}_3} \cdot C_{\text{Al}_2\text{O}_3}} \\
& - \; \frac{8.90C_{\text{LiF}}}{1 + 0.0047C_{\text{LiF}} + 0.0010C_{\text{AlF}_3}^2} - 3.95C_{\text{MgF}_2} - 3.95C_{\text{KF}} \qquad\qquad [2]
\end{aligned}
$$

where *C* is the concentration of each compound in weight percent. From this equation, it is observed that not only the main components AlF_3, CaF_2 and Al_2O_3, but also LiF and others reduce the liquidus temperature. Especially, LiF addition in cryolite melts has desirable effects on some properties such as electrical conductivity and metal solubility. There are some reports that indicate improved current efficiency by addition of LiF[9-19]. However, it is not fully clarified whether this beneficial effect is due to the LiF addition itself, or caused by other electrolyte changes or reduced temperature. Therefore, the effect of temperature and LiF content on current efficiency with various conditions was investigated in this study.

Experimental Procedures

The cell for the laboratory electrolysis experiment is shown in Figure 1. This cell was designed for the measurement of current efficiency with various electrolytic conditions by Solli *et al.*[3-6]. The major melt composition is Na_3AlF_6-AlF_3 with CaF_2 and saturated Al_2O_3 and the cryolite ratio of the bath was 2.2. The electrolysis condition for this study was based on the recent industrial cell condition. The detailed electrolysis conditions are listed in Table 1. The electrolysis temperature in this study was 965℃, however, previous our electrolysis experiments were conducted at 980℃ with 2.5 of cryolite ratio. The electrolysis was performed for 4 hours with constant current. Al_2O_3 powder was added every 15 minutes to the melt to avoid depletion of alumina during electrolysis. After the electrolysis, the cathode plate with deposited Al was cleaned by $AlCl_3$ aqueous solution for 30 minutes to remove remaining electrolyte on the surface of Al. The current efficiency was calculated from the weight of the actual deposited Al and theoretical deposited weight by Faraday's law.

Table 1   Experimental conditions for electrolysis cell

Melt Compositions (wt.%)					Liquidus Temp.,	Electrolysis Temp.,	Current Density,
Excess AlF_3	CaF_2	Al_2O_3	LiF	Na_3AlF_6	T_{liq} /℃*	T_{cell} /℃	*i* /A cm^{-2}
11.55	5.00	4.00	0-5.00	Bal.	909	965	0.90

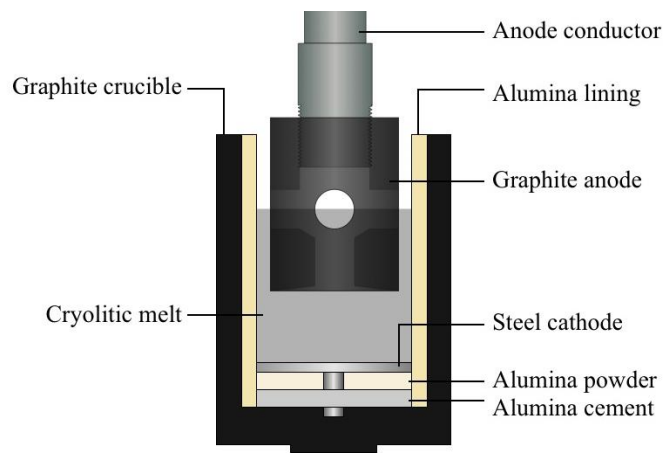*Liquidus temperature was calculated by eq. [2].

Figure 1.   The cell design for CE measurement.

Results and Discussion

The current efficiencies for experiments for the bath without LiF, with 2.5 wt.% and 5.0 wt.% LiF were 95.3, 96.3 and 94.1 %, respectively. The current efficiency with the new base composition was higher than that with old bath with 2.5 of cryolite ratio in any LiF concentration. The highest CE was achieved at the bath composition with 2.5 wt.% LiF. However, there was >1 % decrease of current efficiency by 5 wt.% LiF addition in comparison with the bath including 2.5 wt.% LiF. CE was decreased in the condition with 5 wt.% of LiF bath. There was no advantage in the current efficiency by too much high LiF addition, but it must be expected that the current efficiency would have increased if the superheat were kept constant, i.e., by lowering the temperature. On the other hand, Cui *et al.* previously reported that 5 wt.% LiF addition to the bath with 2.5 of CR produced about
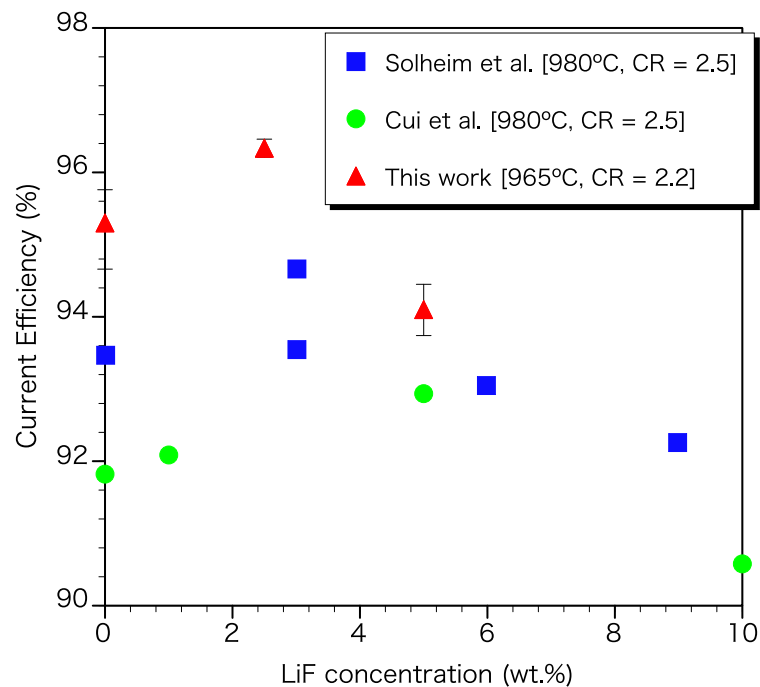

Figure 2.   The CE changes with LiF concentration.

1 % increase of the current efficiency[18]. The optimum LiF concentration for the cryolitic bath may be different with the major bath composition such as CR value.

There has been some discussion concerning the effect of superheat on the current efficiency. Figure 3 shows the relationship between superheat of the cell and the current efficiency. There is no noticeable linear relationship in the results by different authors, but it seems that the current efficiency decreases with increasing the superheat. It also indicates there are large variations in the current efficiency at the same superheat. Therefore, it is not completely described the trend for the current efficiency on the bath composition using the superheat.
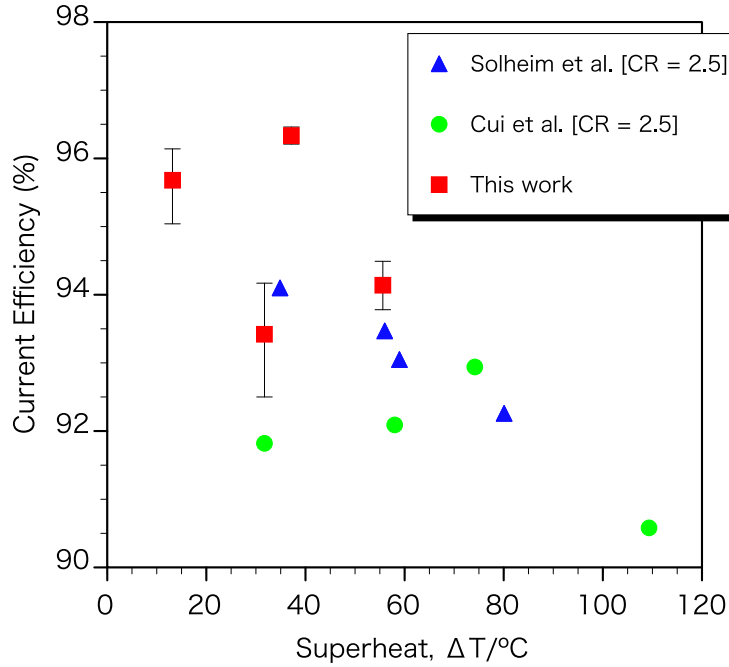

Figure 3. The relationship between the current efficiency and the superheat.

It was also reported by Dewing that the current efficiency varies as a function of superheat, AlF$_3$ and LiF contents of the electrolyte[20]. The relationship between the CE loss value and cell conditions was expressed by the following equation;

$$\log[CE\ loss(\%)] = 0.0095[superheat\,(\text{in}\,^{\text{o}}\text{C})] - 0.019C_{\text{AlF}_3} - 0.060C_{\text{LiF}} + 0.65 \qquad [3]$$

Figure 4 shows the relationship between the calculated CE loss and the actual CE values. The superheat was calculated by eq. [2] and the value of the constant term in eq. [3] was determined to be 0.65 for the good agreement between calculated and actual values. From this relationship, the current efficiency could be estimated by the composition and the temperature of the electrolysis cell. The relationship also indicates that the contents of AlF$_3$ and LiF directly affect the loss of the current efficiency by decreasing the solubility of the deposited metal[19].

Although eq. [3] appears to describe the experimental results very well, it is possible that the fit is partly incidental. The effect of superheat is probably indirect:

1) Low superheat gives lower temperature (at constant electrolyte composition), which is beneficial due to reduced metal solubility.
2) Low superheat indicates that the sideledge of the industrial cell is thick, and consequently, that the metal area is relatively small, which is beneficial for the current efficiency in the industrial cell (this effect cannot be reproduced in a laboratory cell without changing the dimensions of the crucible or anode).
3) Low superheat may lead to crystallization of solid cryolite at the cathode due to the nature of the cathode reaction. The effect may be positive (if the precipitate forms "islands" leading to reduced area for metal dissolution), but it may also be strongly negative (if the metal starts forming small spheres on top of a solid layer).
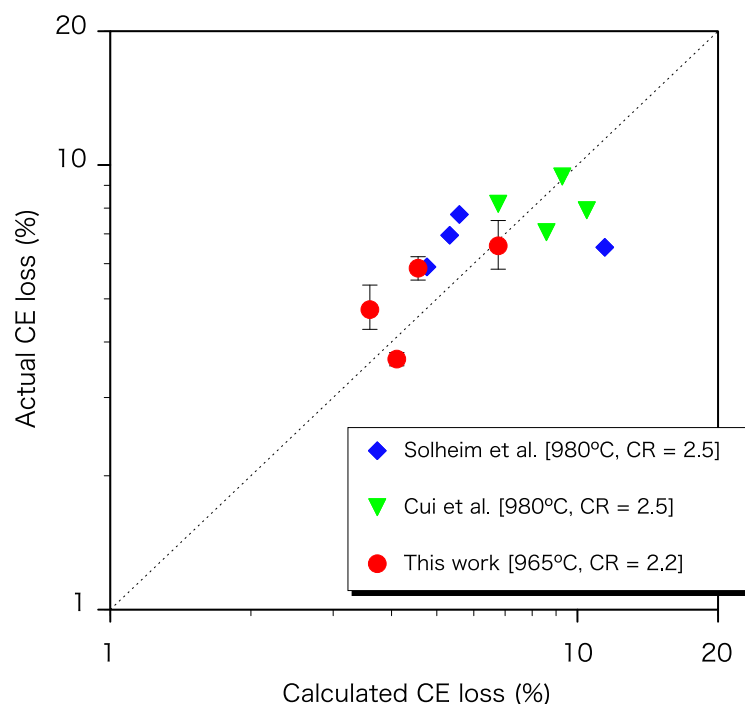

Figure 4.   The relationship between actual and calculate CE losses.

Conclusions

The effect of LiF addition in cryolitic melt on the current efficiency was investigated. The highest CE value of 96.3% were obtained at the 2.5 wt.% of LiF added bath. And too much LiF addition lowers the CE because LiF significantly lowered the liquidus temperature. The current efficiency depends not only on the superheat but also AlF_3 and LiF contents of the melt since the solubility of the dissolved metal changes the cell temperature and composition. The calculated CE has a good agreement with the actual results. The contents of AlF_3 and LiF in the electrolyte directly affected the current efficiency. The low superheat may obtain high current efficiency however it has possibility of the solidification of cryolite.

References

1. J. Thonstad, P. Fellner, G.M. Haarberg, J. Híveš, H. Kvande and Å. Sterten. *Aluminium electrolysis: Fundamentals of the Hall-Héroult process 3rd edition*, Aluminium-Verlag, Düsseldorf (2001).
2. Å. Sterten. J. Appl. Electrochem., 18 (1988) 473-483.
3. P.A. Solli, T. Haarberg, T. Eggen, E. Skybakmoen and Å. Solheim. Light Metals 1994, 195-203.
4. P.A. Solli, T. Eggen, S. Rolseth, E. Skybakmoen and Å. Solheim. J. Appl. Electrochem., 26 (1996) 1019-1025.
5. P.A. Solli, T. Eggen, E. Skybakmoen and Å. Solheim. J. Appl. Electrochem., 27 (1997) 939-946.
6. Å. Sterten, P.A. Solli and E. Skybakmoen. J. Appl. Electrochem., 28 (1998) 781-789.
7. H. Kvande. Light Metals 1989, 261-268.
8. Å. Solheim, S. Rolseth, E. Skybakmoen, L. Støen, Å. Sterten and T. Støre. Metall. Mater. Trans. B., 27B (1996) 739-744.
9. R.D. Peterson and X. Wang. Light Metals 1991, 331-337.
10. X. Wang, R.D. Peterson and N.E. Richards. Light Metals 1991, 323-330.
11. N.V. Vasyunina, I.P. Vasyunina, Y.G. Mikhalev and P.V. Polyakov. Russian J. Non-Ferrous Metals, 52 (2011) 360-363.
12. H. Kvande. JOM, 46 (1994) 22-28.
13. B. Langon and P. Varin. Light Metals 1986, 343-347.
14. A.T. Tabereaux, T.A. Alcorn and L. Trembley. Light Metals 1993, 221-226.
15. R.G. Cheney. Light Metals 1983, 519-536.
16. D.R. Shirley. Light Metals 1985, 471-484.
17. L. Vujasinovic and S. Gulin. Light Metals 1990, 341-345.
18. P. Cui, Å. Solheim and G.M. Haarberg. ECS Trans., 64 (2014) 351-355.
19. Å. Solheim, H. Gudbrandsen, K.S. Osen, and J. Kvello. Proceedings of 33rd International ICSOBA Conference, Dubai, United Arab Emirates, 29 November-1 December 2015, Travaux No. 44, pp. 625-634.
20. E.W. Dewing. Metall. Mater. Trans. B., 22B (1991) 177-182.