EFFECT OF LiAlO$_2$ AND KF ON PHYSICOCHEMICAL PROPERTIES FOR INDUSTRIAL ALUMINUM ELECTROLYTE

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Abstract

The aluminum electrolytes of 300 kA series cell in a Chinese aluminum plant were investigated. Compositions and physicochemical properties of these electrolyte samples were analyzed, and the effects of contents of additive LiAlO$_2$ and KF on physicochemical properties were studied. The results show that with the increasing content of the LiAlO$_2$ from 0 to 8.52 wt%, the liquidus temperature decreases gradually from 940.7 °C to 917.0 °C, whereas the alumina solubility obtained by oxygen content increases in the initial stage and then reduces. When increasing the content of LiAlO$_2$ up to 3 wt%, the alumina solubility reaches the highest value of 6.44 wt%. The liquidus temperature decreases by 2.3-2.5 °C with per 1 wt% addition of KF, and meanwhile, the alumina solubility increases by 0.05-0.13 wt% correspondingly.

Introduction

At present day and age, commercial primary aluminum was mainly produced by Hall-Héroult process under approximate 960 °C, although much progress have been made using this conventional bath, there were still numerous shortcomings such as great energy consumption, high carbon expenditure, serious environmental pollution, unstable production and high electrolysis temperature as well [1]. The technique with low temperature and low voltage has been the main development as an energy-saving technology in the aluminum electrolysis. Low temperature can inhibit the second interaction, and reduce aluminum dissolved loss. Therefore, it increases current efficiency in the case of low voltage (low ACD). Meanwhile, low-temperature electrolysis could reduce volatilization of electrolytes and decrease the consumption of material [2] as well as reduce the cell heat loss. So it is favorable to establish energy balance of the electrolysis cell in the case of low voltage. But the key to realize low temperature and low voltage technique is to make sure that the dissolving capacity of alumina, the conductivity of the electrolytes, or any other property is not decreased in the new conditions.

It can make up for the degradation of the electrolysis performance at low temperature by using lithium salt and potassium salt as additives of the electrolytes. Lithium salt observably decreases the liquidus temperature and increases the conductivity [3] of electrolytes, while potassium salt can enhance the dissolving capacity of alumina in electrolytes [4]. Haibo [5] has studied several electrolytes of the NaF-KF-LiF-AlF$_3$ system, of which the liquidus temperatures are between 890-920 °C, and compared the results to the current industrial electrolytes. The dissolving capacity of alumina was not decreased while the conductivity was increased by 5-10 %. Based on the Na$_3$AlF$_6$-K$_3$AlF$_6$-AlF$_3$-LiF system, Youguo [6] designed several electrolytes of "low temperature, high dissolving capacity of alumina, and high

conductivity", in which the ratio of K$_3$AlF$_6$ to K$_3$AlF$_6$+Na$_3$AlF$_6$ content was 10-30 %, the LiF content was 2-4 wt%, and the overheat was 20 °C. The current electrolyte was added LiF and KAlF$_4$ by Frolov [7].Its liquidus temperature decreased by 18 °C, while the dissolving rate increased slightly and the conductivity increased by 15-20 %, and, finally, the cell voltage decreased by 200 mV at the same ACD. However, the LiAlO$_2$ as a new lithium salt additive to aluminum electrolyte has attained little attention according to published literature.

Therefore, based on the representative industrial electrolytes in Chinese plants and the addition of LiAlO$_2$ and KF, the compositions and physicochemical properties of these electrolyte samples were analyzed. Further, the effects of LiAlO$_2$ and KF contents on physicochemical properties were studied in this work.

Experimental

Experimental Materials

The electrolyte samples were from 10 adjacent cells of the same 300 kA potline of Chinese aluminum plant. LiAlO$_2$, γ-LiAlO$_2$, was of reagent grade. The purity of corundum disks were above 99 %. KF had been under strict dehydration treatment before being used. All the raw materials were preprocessed for 48 hours at 120 °C.

Method

Cryolite ratio and CaF$_2$ content were determined by diffractometer and the content of LiF, KF and MgF$_2$ were determined by ICP.

Liquidus temperature determined by thermal analysis (TA) is based on recording the temperature during cooling. When the first solid precipitates, there will be a more or less distinct break in the temperature curve ("thermal arrest") because the system gives off heat during solidification [8]. The experimental device is described in reference [9]. The cooling rate was controlled at 0.5-0.8 °C /min to minimize the error.

The alumina solubility was determined by rotating a high-purity corundum disk in the electrolyte melt, is the disk being fixed to a stainless steel rod. The experimental setup and procedure were similar to that in reference [10]. The rotating speed was about 250 rpm. A sample was taken every 30 minutes, and the alumina content was determined by a LECO RO500 oxygen analyzer.

Results and discussion

Compositions and Physicochemical Properties of Industrial Electrolytes

Compositions, liquidus temperatures, and alumina saturation solubility of the samples from Cell No.3078-3087 have been measured, and results are shown in Table I and II, respectively.

Table I. Compositions of several industrial electrolytes

Cell No.	CR	Electrolytes composition/ wt%					
		Na_3AlF_6	CaF_2	Al_2O_3	LiF	MgF_2	KF
3078	2.51	81.38	5.27	1.71	1.01	0.78	1.01
3079	2.33	77.74	5.35	2.72	0.98	0.41	1.09
3080	2.36	78.48	5.13	2.95	0.97	0.36	0.98
3081	2.41	80.32	5.53	1.62	1.03	0.38	1.10
3082	2.37	78.22	5.61	1.68	1.02	0.39	0.90
3083	2.38	79.31	5.28	3.17	0.94	0.34	0.92
3084	2.33	79.40	5.17	2.42	0.94	0.33	1.21
3085	2.36	79.80	5.35	1.59	0.96	0.38	0.91
3086	2.34	78.61	5.05	3.44	0.88	0.33	0.93
3087	2.30	78.62	5.07	2.93	0.88	0.35	1.03
Mean value	2.37	79.19	5.28	2.42	0.96	0.41	1.01

According to Table I, the cryolite ratio of samples are about 2.37, the maximum is up to 2.51 whilst the minimum is 2.30. Besides, the content of CaF_2 is approximately 5.28 wt%, which is a typical level in aluminum electrolytes in China. In terms of Al_2O_3, the mean content is 2.42 wt%, while the average contents of LiF and KF are all about 1 wt%, MgF_2 0.41 wt%. In general, the compositions of samples in these 10 cells maintain stable. The electrolyte is a representative of industrial electrolyte system with low cryolite ratio and low content of additions. Table II demonstrates liquidus temperatures of these samples and their alumina saturation solubility with superheat 12 °C.

Table II. Liquidus temperatures and alumina saturation solubility of industrial electrolytes

Sample No.	Liquidus temperature / °C	Alumina saturation solubility / wt%
3078	944.1	5.38
3079	944.1	5.27
3080	942.6	5.60
3081	951.2	5.45
3082	947.4	5.35
3083	944.1	5.29
3084	941.3	5.68
3085	946.5	5.39
3086	940.3	5.44
3087	945.6	5.71

To be specific, liquidus temperatures of the samples lay between 940.3 °C and 951.2 °C, the mean value is 946.0 °C. Therefore, the electrolysis temperature is around 950-960 °C. Meanwhile, the alumina saturation solubility is about 5.46 wt%, and the maximum is only 5.71 wt%.

Effect of $LiAlO_2$ on the Liquidus Temperature of Electrolytes
From the analysis results above, the disadvantages of the electrolytes are high liquidus temperature and low alumina saturation solubility. However, the electrolytic process at low temperature is beneficial for saving energy and reducing consumption of aluminum electrolysis. Therefore, it is beneficial to decrease the liquidus temperature, but not to weaken other physicochemical properties. As a new kind of lithium salt, $LiAlO_2$ was considered as a potential to improve performance of the electrolytes. As experimental electrolyte, a representative composition based on the samples analyzed in Table I were used. The composition is shown in Table III. Considering that excessive lithium may lead to degradation of alumina solubility and reduction of the product purity, the LiF content calculated from lithium in electrolytes is less than 5 wt%. Furthermore, the total content of additions should not be too high. Therefore, the $LiAlO_2$ content was kept at less than 8.52 wt%. Results of liquidus temperatures of the experimental electrolyte with adding $LiAlO_2$ are illustrated in Table IV.

Table III. Composition of experimental electrolyte

Composition	Value
Cryolite Ratio	2.33
CaF_2	5.20 wt%
Al_2O_3	1.61 wt%
LiF	0.96 wt%
MgF_2	0.41 wt%
KF	0.98 wt%

Table IV. Liquidus temperatures of electrolytes with adding $LiAlO_2$

No.	Initial electrolyte content/ wt%	$LiAlO_2$ content / wt%	LiF total content / wt%	Liquidus temperature / °C
0#	100.00	0.00	0.96	940.7
1#	98.38	1.62	1.50	930.4
2#	97.00	3.00	2.04	924.3
3#	95.62	4.38	2.58	919.5
4#	94.24	5.76	3.12	921.3
5#	92.86	7.14	3.66	920.0
6#	91.48	8.52	4.20	917.0

*LiF total content includes the initial content and the equivalent translated from $LiAlO_2$.

From Table IV, it can be seen that with the additive of $LiAlO_2$, liquidus temperatures decrease gradually. Liquidus temperature is an expression of interactive forces among different ions in the melt. When a compound is introduced to the electrolyte, the acting force between atoms or molecules is weakened so that the liquidus temperature declines [11]. Specifically, the liquidus temperature decreases by approximate 10 °C when 1.62 wt% $LiAlO_2$ is added to the initial electrolytes. After that, every 1 wt% addition of $LiAlO_2$, the decline of the liquidus temperature is between 3.6 °C and 4.3 °C. Furthermore, as the content of $LiAlO_2$ reaches 4.38-7.14 wt%, the effect of adding $LiAlO_2$ on decreasing liquidus temperatures is ignorable, and the liquidus temperatures remain around 920 °C. The liquidus temperatures decrease by 2.2 °C with 1 wt% $LiAlO_2$ addition when the content of $LiAlO_2$ is more than 7.14 wt%, and the decreasing rate is half of that with low content of lithium salt.

<u>Effect of LiAlO₂ on the Alumina Saturation Solubility</u>
As can be seen from Table II, the alumina saturation solubility of the industrial electrolytes is approximately 5.46 wt%. It has been reported that lithium fluoride weakens the solubility of alumina in aluminum electrolytes by Yang [10] and Youguo [12]. The influence of $LiAlO_2$ on the alumina saturation solubility in industrial electrolytes has been investigated in this work. The alumina saturation solubility of 1#, 2#, and 3# samples were measured with superheat 12 °C, and the results of oxygen concentration (Table V) were analyzed by LECO analyzer.

Table V. Oxygen concentration and alumina
saturation solubility of 7#, 8#, and 9#

S.T./ h	7# 1.61 wt% $LiAlO_2$		8# 3.00 wt% $LiAlO_2$		9# 4.38 wt% $LiAlO_2$	
	O.C. / wt%	A.S.S. / wt%	O.C. / wt%	A.S.S. / wt%	O.C. / wt%	A.S.S. / wt%
4.0	2.71	5.76	2.78	5.91	2.88	6.12
4.5	2.83	6.01	2.88	6.12	2.91	6.18
5.0	2.91	6.18	2.96	6.29	2.93	6.23
5.5	2.96	6.29	3.02	6.42	2.95	6.27
6.0	2.97	6.31	3.04	6.46	2.96	6.29
6.5	2.97	6.31	3.04	6.46	2.96	6.29
7.0	2.97	6.31	3.03	6.44	2.96	6.29
M.	2.97	6.31	3.03	6.44	2.96	6.29

*S.T. = Sampling time after the corundum disk rotating.
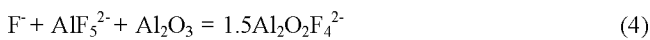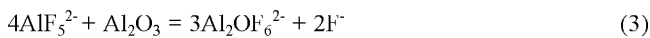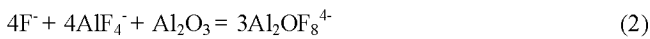*O.C. = Oxygen concentration.
*A.S.S. = Alumina saturation solubility.
*M. = Mean of last 4 values.

The concentration of oxygen is derived from $LiAlO_2$, the corundum disk and initial electrolyte. Consequently, the alumina concentration in the system could be calculated by the following equation:

$$C_{Al_2O_3} = \left[C_{oxygen} - C_{LiAlO_2} \times \frac{32}{66} \right] \times \frac{102}{48} \tag{1}$$

The results calculated from Equation 1 are showed in Figure 1. As a whole, the alumina concentration tends to decrease as the $LiAlO_2$ content increases, and only 1.5 wt% alumina dissolves in the melt with 4.38 wt% $LiAlO_2$. This could be explained as follows. According to the report by Robert et al. [13] and Gilbert et al. [14], AlF_4^- and AlF_5^{2-} are the dominant anions in MF-AlF₃ (M=Li, Na, K) melt with 1 < CR < 3, and the formation of oxide complex in MF-AlF₃ (M=Li, Na, K) melts mainly comply to reactions (2) through (4):

$$4F^- + 4AlF_4^- + Al_2O_3 = 3Al_2OF_8^{4-} \tag{2}$$

$$4AlF_5^{2-} + Al_2O_3 = 3Al_2OF_6^{2-} + 2F^- \tag{3}$$

$$F^- + AlF_5^{2-} + Al_2O_3 = 1.5Al_2O_2F_4^{2-} \tag{4}$$

Because the radius of sodium cation is larger than that of the lithium cation, which results in an increase on the electric potential of the M^+-A^- interactions in the sequence $Na^+ < Li^+$, the

interactions between Na^+ and the A^- (including AlF_6^{3-}, AlF_5^{2-}, and AlF_4^-) are weaker than the interactions between Li^+ and those anions. Therefore, when Li^+ is added to the melt, the equilibriums in reactions (2) through (4) will shift to the left and lead to the reduction in alumina solubility. [15]
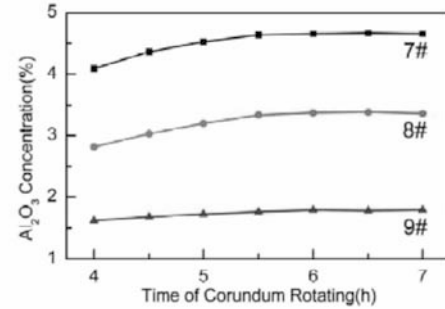

Figure 1. Al_2O_3 Concentration Calculated from Equation 1

Furthermore, Reaction (5) may be valid in the melts with $LiAlO_2$. With increase of the $LiAlO_2$ concentration the equilibrium shifts to the right. The number of Al-O-F anions increases and the equilibrium in Reaction (4) shifts to the left and the alumina solubility decreases.

$$AlO_2^- + AlF_4^- = Al_2O_2F_4^{2-} \tag{5}$$

However, as for the electrolytes containing $LiAlO_2$, alumina concentration obtained by Equation 1 is not a valid representation of the content of aluminum and oxygen. The one calculated by the total oxygen content is more appropriate to show solubility of Al-O anions in the electrolytes. Consequently, alumina saturation solubility is still determined by measuring the total content of oxygen in the melt. The results are shown in Table V, and the alumina saturation solubility in 7#, 8# and 9# are 6.31 wt%, 6.44 wt% and 6.29 wt%, respectively. When adding $LiAlO_2$ in the range of 0 wt% to 4.38 wt%, the alumina solubility decreases gradually because of the increase of Li^+; in other words, the calculated alumina concentration increases as a result of the increase of AlO_2^-. From Table V and Figure 1, as for 7#, oxygen is mainly from Al_2O_3, while it is mainly from AlO_2^- for 9#. Therefore, referring to alumina solubility, the figure first ascends and then descends when adding $LiAlO_2$ in the range of 0 wt% to 4.38 wt%, the maximum value at 3 wt% $LiAlO_2$.

<u>Effects of the Combined Addition of LiAlO₂ and KF on the Physicochemical Properties of Electrolytes</u>
According to Figure 1, it can be seen that in the 3 electrolytes, the ability to dissolve Al_2O_3 is the largest in 7#, while the ability to dissolve Al-O cations (AlO_2^- and Al_2O_3) is the largest in 8#. But as a whole, these two are still not high. It is reported that potassium salt is able to improve alumina solubility in aluminum electrolytes. Also it is expected to decrease the liquidus temperature without decreasing the alumina solubility or any other property by using the combined addition of $LiAlO_2$ and KF. Table VI shows the liquidus temperatures of 1#, 2# electrolytes with 1-3 wt% content of KF, respectively.

Table VI. Liquidus temperatures of electrolytes
with the combined addition

No.	LiAlO$_2$ content/ wt%	Added KF content/ wt%	Liquidus temperature/ °C
1#	1.61	0	930.4
10#	1.61	1	927.6
11#	1.61	2	925.1
12#	1.61	3	922.8
2#	3.00	0	924.3
13#	3.00	1	921.7
14#	3.00	2	919.3
15#	3.00	3	916.9

As shown in Table VI, the liquidus temperatures decrease by 2.3-2.8 °C for every 1 wt% addition of KF to the electrolytes with LiAlO$_2$, while to pure cryolite, the depression is 4.4 °C [8].

Table VII. Alumina solubility of electrolytes
with the combined addition

No.	LiAlO$_2$ content / wt%	Added KF content / wt%	Oxygen content / wt%	Alumina saturation solubility/ wt%
1#	1.61	0	2.97	6.31
16#	1.61	1	3.03	6.44
17#	1.61	2	3.07	6.52
18#	1.61	3	3.10	6.58
2#	3.00	0	3.03	6.44
19#	3.00	1	3.08	6.55
20#	3.00	2	3.12	6.62
21#	3.00	3	3.14	6.67

*The superheat is 12 °C.

As can be seen from Table VII, to some extent, alumina solubility has been improved after adding KF, and it increases by about 0.05-0.13 wt% with every 1 wt% KF in the melts. This fact can be explained by a difference in ionic potentials of alkali cations. The potassium cation that has the lowest ionic potential creates a weaker bond with fluorine in the aluminum-fluoride complexes. With additions of K$^+$, the equilibriums in reactions (2) through (4) will shift to the right and result in increased alumina solubility. In terms of the melts with 1.62 wt% LiAlO$_2$, the freezing point deceases to 922.8 °C by adding 3 wt% KF, and the alumina saturation solubility is up to 6.58 wt%. When the content of LiAlO$_2$ is 3 wt%, the influence of KF on the alumina solubility gradually becomes smaller in the range of 0.11 wt% to 0.05 wt% as the KF content increases by 1 wt%. Adding 3 wt% KF, the alumina saturation solubility is up to 6.67 wt%.

Conclusion

The aluminum electrolytes of 300 kA potline cell in a Chinese aluminum plant were investigated. Compositions and physicochemical properties of these electrolyte samples were analyzed, and the effects of LiAlO$_2$ and KF on liquidus temperature and alumina saturation solubility were studied. The conclusions are as follows:

(1) The mean composition of industrial electrolytes is CR 2.37,

CaF$_2$ 5.28 wt%, Al$_2$O$_3$ 2.42 wt%, LiF about 1 wt%, MgF$_2$ 0.41 wt%, KF about 1 wt%. The mean liquidus temperature is 946.0 °C, and the average alumina saturation solubility is 5.46 wt% when the superheat is 12 °C.

(2) When LiAlO$_2$ content is below 4.38 wt%, increasing the LiAlO$_2$ content decreases the liquidus temperature. Adding 1.61 wt% LiAlO$_2$ can effectively decrease the liquidus temperature of industrial electrolytes by approximate 10 °C. But the influence is ignorable when LiAlO$_2$ content is above 4.38 wt%. The alumina solubility reaches the highest value of 6.44 wt% in the melt with 3 wt% LiAlO$_2$.

(3) With the liquidus temperature decreasing, the alumina saturation solubility could be improved to some extent by using the combined addition of LiAlO$_2$ and KF. The liquidus temperature decreases by approximate 2.5 °C and the alumina saturation solubility increases by about 0.05-0.13 wt% with each 1 wt% addition of KF. The liquidus temperature of the electrolytes with 3 wt% LiAlO$_2$ and 3 wt% KF is decreasing to 916.9 °C, while the alumina saturation solubility is increasing to 6.67 wt%.

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