Phase Composition and Its Impacts on Bath Ratio Determination of Aluminum Electrolyte with Additives of KF and NaCl

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Abstract — **Phases of aluminum electrolytes with additives of NaCl and KF were investigated. The definition and determination of the cryolite ratio of bath were discussed based on the results of phase composition. The deduced cryolite ratio equation was justified by fluoride-ion selective electrode analysis (FISEA). Experimental results show that FISEA has good performance with high accuracy and reproducibility for an aluminum bath containing NaCl and KF.**

*Keywords—**aluminum electrolyte; phase; bath ratio***

I. Introduction

The electrolyte used in industrial aluminum reduction cells is composed primarily of molten cryolite, Na_3AlF_6, which has higher solubility of alumina than any other fluoride compounds. In the progress of bath chemistry, other compounds, including AlF_3, CaF_2, MgF_2, and LiF were added to molten cryolite to modify the physico-chemical properties in order to improve the cell performance [1-2].

It is well known that the cryolite ratio (CR), defined as the ratio of the number of moles of NaF to the number of moles of AlF_3 in aluminum electrolyte, is one of the key parameters in aluminum electrolysis. The ratio of the wt. % NaF to wt. % AlF_3, termed bath ratio (BR), is also used in some Chinese primary aluminum smelters. The compound cryolite containing 3 moles of NaF and 1 moles of AlF_3 is considered as neutral. An electrolyte containing excess AlF_3 has a cryolite ratio lower than 3 and is referred to as an acid bath; conversely, an electrolyte containing excess NaF has a cryolite ratio higher than 3 is referred to as basic bath.

In China, some reduction plants have tried to lower energy consumption by lowering the electrolysis temperature. Some materials, such as MgF_2, NaCl, KF and LiF, were added to the cryolite bath to achieve low temperature operations [3]. As a consequence, the bath composition has become more complex, and the method for determining the cryolite ratio needs to be improved. There are several methods for determining the cryolite ratio, such as pyrotitration method, thorium nitrate titration, optical method, electrical conductivity method, fluoride-ion selective electrode analysis (FISEA), X-ray diffraction method (XRD), and so on [4-5]. Currently, the X-ray diffraction method, the most popular method, is only used to determine the cryolite ratio of Na_3AlF_6-AlF_3-Al_2O_3-CaF_2 melts. In the presence of MgF_2, NaCl, KF and LiF, accurate determination of the bath ratio becomes difficult for XRD.

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In principle, all methods are based on the phases of electrolyte. We have previously reported the phase investigation of aluminum bath [6]. In that paper, the study mainly focused on the LiF and MgF_2 in strong acidic and basic electrolytes.

In this paper, the phases of electrolytes with additives, NaCl and KF, were determined by X-ray diffraction (XRD). Impacts of additives on cryolite ratio analysis are discussed based on the new results of the phases. The deduced cryolite ratio equation is justified by FISEA. .

II. Experimental

Reagent chemicals, CaF_2 (99%), NaCl (99%), NaF (99%), Al_2O_3 (99%), Na_3AlF_6 (99%) are commercially available and used after appropriate drying treatments. KF was dried under vacuum at 400°C for 6hr. In view of the relatively large quantity of melt required and the number of samples, it is not practical to use vacuum-sublimed AlF_3. $AlF_3 \cdot 3H_2O$ mixed with NH_4F (70:30, wt %) was dried at 200℃ for 3hr and 500℃ for 3hr. All chemicals after dry treatment were kept in a dry box.

In all cases, bath samples were prepared under nitrogen gas atmosphere. A furnace was preheated to about 50 degrees above the melting point of the composition under investigation. The melt constituents were mixed in the dry state and placed in a graphite crucible, which was then placed inside the hot surface. As soon as melting occurred, the crucible contents were stirred with a graphite rod to insure homogeneity and then chilled. This procedure was designed to cut down the time that the melts were at high temperature; consequently composition changes due to volatilization or hydrolysis were kept to a minimum.

The chilled melt was pulverized and sampled.

The samples were characterized with X-ray diffraction (XRD, Rigaku Industrial Co., Ltd., Multi Flex) with CuKα radiation. The NaF: AlF_3 molar ratio was determined by FISEA. Forty-two (42) samples were prepared for XRD characterization.

III. Results and Discussion

A. *Phase Characterization*

The XRD results for additives in the melt of NaF-AlF_3-Al_2O_3 are listed in Table 1. Phases of NaCl and KF are not affected by the acidity change of the bath. No new form was found for NaCl. Seen in Fig. 1, K_2NaAlF_6 was observed in the phase composition of electrolytes with different acidities. KF reacts with chiolite (Na5Al3F14) to form K_2NaAlF_6, as shown by Equation (1). In a neutral and a basic bath, KF reacts with cryolite to form K_2NaAlF_6 and NaF, as shown by Equation (2).

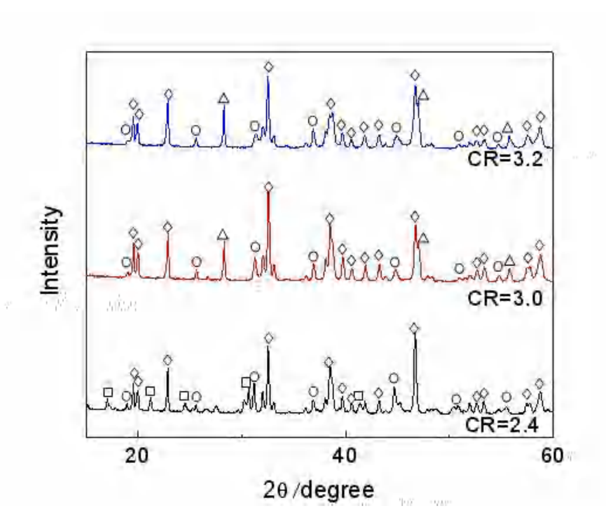
$$2KF+Na_5Al_3F_{14}\rightarrow Na_3AlF_6+2KF\cdot NaF\cdot AlF_3 \quad (1)$$

$$2KF+Na_3AlF_6\rightarrow 2NaF+2KF\cdot NaF\cdot AlF_3 \quad (2)$$

Unfortunately, forms of Al_2O_3 in melts were not found in our XRD investigation. In some cases, a very weak Al_2O_3 peak is visible in highly acidic electrolytes or electrolytes containing high content of additives.

TABLE 1. PHASE OF ADDITIVES IN THE MELT OF NAF-ALF_3-AL_2O_3

Additives	**Phase composition**		
	CR<3.0	**CR=3.0**	**CR=3.2**
NaCl	NaCl	NaCl	NaCl
KF	K_2NaAlF_6	K_2NaAlF_6	K_2NaAlF_6



◇Na3AlF6; □$Na_2Ca_3Al_2F_{14}$; ○K_2NaAlF_6; △CaF_2

Fig.1. XRD patterns of KF in the system of NaF-AlF_3-CaF_2-Al_2O_3. The samples contain 5wt.% KF. CR is termed as molar ratio of NaF to AlF_3.

B. *Influences of Additives on the Cryolite Ratio*

The above experimental results constitute the theoretical basis of pyrotitration, electrical conductivity method, and fluoride-ion selective electrode analysis (FISEA) for determining the cryolite ratio.

A general equation for calculating cryolite ratio is [5]

$$K=\frac{3W\beta_1-2N}{W\beta_2+N} \quad (3)$$

where K is the NaF/AlF_3 molar ratio, W is the weight of electrolyte sample (g), N is the weight of NaF added, *and* β_1, β_2 are correction factors due to the presence of additives.

Influences of additives on the cryolite ratio can be corrected by adjusting correction factors.

For NaCl + CaF_2: NaCl is still as such in the neutral and the basic electrolytes.

$$\beta_1=\beta_2=1-Al_2O_3\%-CaF_2\%-NaCl\%$$

For KF + CaF_2: KF forms K_2NaAlF_6 in the neutral and the basic electrolytes.

$$\beta_1=1-Al_2O_3\%-CaF_2\%-0.759KF\%$$

$$\beta_2=1-Al_2O_3\%-CaF_2\%-1.362KF\%$$

The validity of the above analyses was testified by FISEA. Fifty (50) weighed-in samples were analyzed by FISEA following the procedure described in literature [5]. The samples were also measured by an industrial electrolyte analyzer, which is based on the principle of XRD. Due to space limitations, only selected results are listed in Table 2. The average deviation of the FISEA was about 0.04 units. The accuracy of the industrial electrolyte analyzer is good when CRs are less than 2.6. However, the accuracy becomes poorer and poorer with the decreasing in the acidity.

TABLE 2. RESULTS OF CR OF ELECTROLYTES WITH FISEA

Samples	**wt. %**				$K_{Weighed\text{-}in}$	K_{FISEA}	K_{XRD}
	CaF_2	**Al_2O_3**	**KF**	**NaCl**			
1	5	5	3		2.0	1.96	1.99
2	5	5	5		2.2	2.25	2.23
3	5	5	7		2.4	2.50	2.35
4	5	5	3		2.6	2.65	2.83
5	5	5	5		2.8	2.86	2.69
6	5	5		3	2.0	1.99	2.00
7	5	5		5	2.2	2.19	2.19
8	5	5		7	2.4	2.34	2.47
9	5	5		3	2.6	2.61	2.47
10	5	5		5	2.8	2.81	2.68

IV. Conclusion

Experimental results confirm that FISEA can be used for determining the cryolite ratio of aluminum electrolyte containing NaCl and KF. The accuracy and reproducibility of FISEA are acceptable, which may act as a better calibrating method for cryolite ratio measuring in industrial smelters.

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