Aluminum loss in KF-NaF-AlF$_3$ based electrolyte

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Abstract

Aluminum loss experiments in KF-NaF-AlF$_3$ based electrolyte were tested with graphite crucible, corundum crucible and carborundum crucible respectively. The results showed that aluminum loss was of 16 % or more in graphite crucible under static immersion conditions, much higher than that of in corundum crucible (< 0.3 %) and carborundum crucible (average value 1.53 %). The electrolyte crust of high alumina content and high molecular ratio on the surface of liquid aluminum was formed both in graphite crucible and in carborundum crucible because of the reaction of Al$_4$C$_3$ formation. The mechanism for higher aluminum loss in graphite crucible and in carborundum crucible under static immersion conditions was: Aluminum and carbon formed a Galvanic cell, that is, Aluminum reacted with oxygen ion in the electrolyte to form Al$_2$O$_3$; carbon contained in crucible reacted with aluminum ion to form Al$_4$C$_3$; and then the Al$_4$C$_3$ was dissolved in electrolyte or was decomposed by oxidation, which induced continuous loss of aluminum.

Keywords: Aluminum loss; KF-NaF-AlF$_3$ based electrolyte; low-temperature electrolyte; aluminum carbide (Al$_4$C$_3$).

1. Introduction

The NaF-AlF$_3$-Al$_2$O$_3$ based electrolyte is used in conventional aluminum reduction cells. The loss of aluminum dissolution in molten electrolyte is one of important factors which decreases current efficiency of electrolysis [1]. The solubility of aluminum in molten electrolyte (NaF-AlF$_3$-Al$_2$O$_3$) is not very high, only of 0.1 % - 0.2 % at 1000 °C [1, 2]. However, the dissolution loss of aluminum could be continuous in the actual electrolytic process.

In industrial aluminum reduction cell, the loss of aluminum is divided into four continuous steps:

(1) Aluminum is dissolved in the electrolyte of the interface;

(2) Dissolved aluminum diffuses outward from the interface;

(3) Dissolved aluminum goes into the molten bath and diffuses toward anodic gas layer;

(4) Dissolved aluminum is oxidized by the anodic gas.

In general, the most accepted point of view is that the mass transfer process of dissolved aluminum is control step in the static molten electrolyte without electrolysis, and the dissolution of aluminum is control step in the molten bath with strong mixing(such as in industrial cells), in which the diffusion is very intense[1, 4]. So the solubility of aluminum determines the loss rate of aluminum in industrial cells.

The solubility of aluminum is related to the factors of melt temperature, cryolite ratio, additives (CaF$_2$, MgF$_2$), alumina concentration, viscosity and surface tension and so on [1, 4, 5].Generally, the higher of reduction cell temperature the larger of aluminum solubility. The solubility of Al decreases with the decrease of cryolite ratio and alumina concentration, but the range of cryolite ratio should be between 2.2 and 2.8. After MgF$_2$ or CaF$_2$ is added or the viscosity of melt is increased, the solubility of Al would decrease as well.

Besides, crucible materials used in the tests have large effect on the aluminum dissolution loss. In 1997, Qiu Zhuxian et al used graphite crucible as containers, and determined the solubility of aluminum in low cryolite ratio bath by mass method [6]. The loss of aluminum was only

0.2 % in a graphite crucible in which the lining had been coated with boron nitride; while the loss was about 1.2 % without the boron nitride coated lining. The reason of the increased loss of aluminum could be that aluminum reacted with graphite sidewall to form Al_4C_3 since electrons flow passed through aluminum and graphite sidewall in the molten bath. In the industrial cell, however, the graphite sidewalls were covered with a layer of frozen bath, which helped reducing the Al_4C_3 formation.

Sterten et al [7] carried out system research, such as aluminum loss, cathodic current density, current efficiency in different composition of electrolytes, which contained potassium cryolite, sodium cryolite, lithium cryolite, aluminum fluoride, calcium fluoride and alumina. It was found that the loss of aluminum dissolution in graphite crucible was larger than that in quartz crucible, and the loss in low temperature electrolyte was much smaller than that in traditional electrolyte. But the current efficiency decreased with the addition of K_3AlF_6 , probably because a large amount of Al_4C_3 was generated.

Low temperature electrolysis (below 900 °C), which is considered as the most potential energy-saving technology and the main route to reduce inert anode corrosion, has become one of the most concerned and most active research topics in the international aluminum-smelting field [4, 8 - 10]. While the $NaF-KF-AlF_3$-based electrolyte with low cryolite ratio (1 < CR < 2) is considered as a promising electrolyte system for low temperature aluminum electrolysis [11 - 13].

The composition of $KF-NaF-AlF_3$ based electrolyte has more KF than that of the traditional $NaF-AlF_3-Al_2O_3$ electrolyte system, so the dissolved loss of Al in the electrolyte would be also different. According to references [7] and [14], the solubility of Al increased because of the presence of KF. But the dissolution loss of Al in the $KF-NaF-AlF_3$ based electrolyte (1 < CR < 2), and the effect of crucible materials on current efficiency and aluminum loss in the actual process of electrolysis is not yet very clear.

In the present work, the tests for dissolution loss of Al in $KF-NaF-AlF_3$ based electrolyte (1 < CR < 2) were carried out, and the effect of crucible materials on the current efficiency was explored with 20 A electrolysis.

2.   Experimental

The $KF-NaF-AlF_3$ based electrolyte was used, KF content was around 20 wt%, cryolite ratio was between 1.3 - 1.6 ([NaF]+[KF]) / [AlF$_3$]), alumina content was between 4.2 wt% and 5.2 wt%, temperature was about 820 °C. The electrolyte, consisted of industrial grade potassium fluoride, industrial grade sodium cryolite, industrial grade aluminum fluoride, was treated through pre-melting process. The ingredients of the materials are shown in Tables 1 – 3.

Table 1. Contents of industrial grade potassium fluoride.

Material name	Chemical Constituents, %				
Potassium fluoride（KF）	KF	KCl	H_2O	SO_4^{2-}	H_2SiF_6
	≥ 98.5	≤ 0.5	≤ 0.4	≤ 0.16	≤ 0.18

Table 2. Contents of industrial grade sodium cryolite.

Material name	Chemical Constituents, %						
Sodium cryolite（Na$_3$AlF$_6$）	F	Al	Na	SiO_2	Fe_2O_3	Mg^{2+}	Ca^{2+}
	51.76	15.11	30.43	0.21	0.05	0.003	0.03

Table 3. Contents of industrial aluminum fluoride.

Material name	Chemical Constituents, %						
Aluminum fluoride（AlF$_3$）	AlF_3	Al_2O_3	NaF	SiO_2	Fe_2O_3	SO_4^{2-}	others
	89.2	6.82	0.91	0.28	0.12	0.5	2.17

but the aluminum fog would be generated during aluminum melting.

(3) Under static immersion, the two main reasons causing high aluminum loss in graphite crucible and carborundum crucible were: aluminum reacted with oxygen carried by crucible to form Al_2O_3; Aluminum reacted with carbon contained in crucible to form Al_4C_3, and then the Al_4C_3 was dissolved or oxidized. However, the latter was the key factor to the continuous loss of aluminum, which could seriously affect the current efficiency.

(4) The crust on aluminum surface was composed of high cryolite ratio and high alumina concentration in graphite crucible and carborundum crucible due to the reaction of Al_4C_3 formation.

6.   References

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