EFFECTS OF CURRENT DENSITY AND TEMPERATURE ON ANODE CARBON CONSUMPTION IN ALUMINUM ELECTROLYSIS

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Abstract

The effects of anode current density, electrolysis temperature and KF addition in electrolyte on the consumption of prebaked anode during aluminum electrolysis was investigated in a closed laboratory cell. The current density varied from 0.75 to 1.1 A/cm^2, the electrolysis temperature varied from 930 to 960 °C with modified electrolyte composition. KF content varied from 0 to 4 wt% in the electrolyte of the industrial composition. Electrolysis durations was 2 h, the distance between the electrodes was 35 mm. The total consumption of anode, the amount of carbon dust and the amount of carbon gasification were determined under the operating conditions similar to the industrial application. It is established that the increased current density and the KF addition reduces the anode consumption, but the consumption increases again when the current density is more than 0.9 A/cm^2. The anode consumption increases with increasing electrolysis temperature.

Introduction

The net consumption of prebaked anodes in aluminum reduction cells is usually from 420 to 450 kg/t-Al in China [1]. The data of the world advanced aluminum smelter is ~ 410 kg/t-Al, such as Dubai smelter DX+ cells, the average net carbon anode consumption is 404 - 408 kg/t-Al with the current efficiency of 95.5% [2]. The theoretical consumption is 350 kg/t-Al corresponding a current efficiency of 95.5%, and thus the excess consumption is more than 60/t-Al. During aluminum electrolysis, carbon was mainly consumed by electrochemical reaction (1) as follows:

$$2Al_2O_3 + 3C - 4Al + 3CO_2 \qquad (1)$$
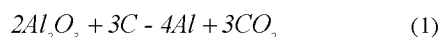
Respect to Faraday's law, the excess consumption is mainly composed of excess carbon gasification (caused by Boudoir reaction (2)) and carbon dusting (detached carbon particles) [3], while the reaction (3) could be neglected as the electrolysis was performed in an inert atmosphere of argon.

$$C + CO_2 - 2CO \qquad (2)$$

$$C + O_2 - CO_2 \qquad (3)$$

The consumption of the anode under the conditions of industrial electrolysis is determined mainly by its own properties and the electrolysis parameters [4].

Cutshall [5], Hume *et al.* [6], and Kuang *et al.* [3] studied the influence of the anode current density on carbon consumption using different anode materials. Generally, the carbon consumption increases with decreasing current density, while it can reach a minimum at 0.8 - 0.9 A/cm^2 for industrial cells, as reported by Smorodinov [7] or at 0.94 - 1.03 A/cm^2.as by Revazyan [8]. This diversity has to be rechecked under identical electrolysis condition.

An increase of about 2 wt% in anode carbon consumption was found in correspond with each 10 °C increase of temperature in the range of 970 to 1030 °C during aluminum electrolysis. While, the CO_2 reactivity showed an increase by nearly 50 % in laboratory tests with increasing temperature from 950 to 1000 °C [7, 9]. It was established [10] that, at a constant temperature, the anode consumption decreased upon the addition of KF, NaF, LiF, NaCl, LiCl, and KCl into the melt with a cryolite ratio of 2.8. It is also noticed that KF content in cryolitic electrolyte, originally being brought from alumina addition, usually increases with prolonged time in cell operation and results in an unwanted superheating state in the cell. A number of research data on the anode consumption were based on the operating temperatures of about 960 °C [3-9], but the industrial practice for today has a tendency of operating the cells at a relative lower temperatures about 940 °C or even 930 °C. It needs additional evaluation on the anode consumption at lower operating temperatures.

The present work is to investigate the electrolysis consumption of the carbon anodes as functions of the current density, electrolysis temperature and KF addition in aluminum electrolyte. The purpose is to obtain the information on the anode consumption for improving cell energy efficiency through an operation strategy with relative lower temperature and higher current density.

Experimental

Materials and Analysis

The electrolyte composition was similar to that used in industrial cells and prepared by mixing cryolite with AlF_3, CaF_2 and Al_2O_3. Cryolite (industrial grade) and Al_2O_3 (industrial grade) were obtained from an aluminum smelter; AlF_3 (analytically grade) and CaF_2 (analytically grade) were obtained from Aladdin Industrial Corporation. The powdered electrolyte mixture was dried at 150 °C for 12 h prior to use to remove the moisture absorbed.

Anode samples were 20 mm each in diameter and 30 mm in length, which were taken from the same prebaked anode supplied by Sunstone Development Co., Ltd. The properties of the anode samples were tested according to relevant international standards (ISO), and the porosity of the anodes was measured through quantitative image analysis [13]. The resulting data have been averaged, as given in Table I.

Table I. Selected Properties of Anode Samples Tested

Property		Fresh prebaked anode	With 20% anode butts
Apparent Density /gcm^{-3}		1.59±0. 01	1.60±0. 01
Flexural Strength /MPa		9.91±0. 01	10.77±0. 02
Compressive Strength /MPa		41.25±0. 02	39.56±0. 01
Air Permeability /nPm		1.06±0. 01	1.04±0. 01
Density in Water /gcm^{-3}		2.087±0. 001	2.090±0. 001
Porosity /%		26.9±0. 2	25.6±0. 2
Thermal Expansivity /K^{-1}		10^{-6}±10^{-7}	10^{-6}±10^{-7}
Resistance /μΩ·m		56.50±0. 04	53.67±0. 03
CO$_2$ Reactivity /%	Residue	95.4±0. 2	91.45±0. 1
	Dust	0.1±0. 05	2.44±0. 03
	Loss	4.50±0. 04	6.11±0. 02
Air Reactivity /%	Residue	92.60±0. 06	82.06±0. 05
	Dust	0.1±0. 03	3.57±0. 05
	Loss	7.30±0. 04	14.37±0. 06
S /%		1.82±0. 03	2.18±0. 07
Elements /ppm	V	178±5	237±4
	Ni	206±3	170±4
	Si	315±5	155±3
	Fe	315±4	524±4
	Al	248±2	506±4
	Na	51±1	386±3
	Ca	130±2	245±2
	Zn	27±1	22±1
	Pb	17±1	17±1

Electrolysis Consumption Tests

Figure 1 shows the laboratory electrolysis consumption test system. All tests were performed under argon atmosphere, and DC current was controlled by a Multichannel Potentiostat/Galvanostat instrument. A high purity carbon crucible was placed in a vertical tube furnace and used as the cathode. The crucible was fitted with a bottom open alumina lining to prevent the current flowing through the cell side.
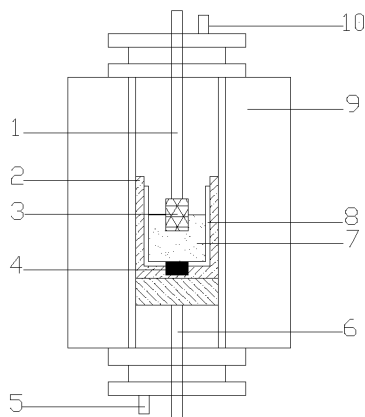

Figure 1. A schematic diagram of experimental cell used for electrolysis consumption tests: 1- Anode rod; 2- Graphite crucible; 3- Anode sample; 4- Aluminum metal; 5- Gas inlet; 6- Graphite cathode rod; 7- Electrolyte; 8- Alumina crucible; 9- Furnace tube; 10- Gas outlet

During the tests to investigate the effects of anode current density, only the electrolysis current was changed. The electrolysis temperature was 950 °C and the electrolyte consisted of industrial cryolite with additions of 5 wt% CaF$_2$, and 6 wt% Al$_2$O$_3$ with cryolite ratio in mole =2.34.

Another set of electrolysis tests were performed at the anode current density of 0.8 A/cm^2, and the temperature varied from 930 to 960 °C. The electrolyte consisted of industrial cryolite with additions of 5 wt% CaF$_2$, and 6 wt% Al$_2$O$_3$. The CR varied from 2.25 to 2.4 to get stable electrolysis process.

Before starting a test, the anode was maintained above the electrolyte for 30 min, and then it was down into the electrolyte melt at open circuit conditions. The electrolysis tests were performed at anode current density of 0.75 - 1.1 A/cm^2 for 2 h, in which the anode - cathode distance was kept about 35 mm.

The anode was taken out from electrolyte after 2h of electrolysis, and then turn off Multichannel Potentiostat/ Galvanostat instrument, which could reduce residual electrolyte of the anode surface to get exact consumption results. During electrolysis, industrial argon was supplied to furnace tube at a rate of 30 mL/min. The exit gas from the furnace was introduced to the gas absorption line, as shown in Figure 1.

The total carbon consumption was determined by weighing the anode before and after electrolysis [12]. By the known amount of passed electricity, the theoretical aluminum produced was determined, and the total carbon consumption in term of kg/t-Al was calculated using the following formulae:

$$M_{CC} = \frac{m_0 - m_1}{m} * 10^6 \qquad (4)$$

Where m_0 is the initial mass of the test specimen, expressed in grams; m_1 is the mass of the residual test specimen, expressed in grams; m is the mass of the theoretical aluminum produced, expressed in grams.

The carbon dust was collected from the upper part of electrolyte after the experiment, and additionally fired in air at 650 °C. After the combustion of the carbon dust, the weight of residue was determined and the weight of consumed carbon was calculated out, which was the amount of anode transferred into the dust.

The amount of gasified carbon was calculated by the difference between the total carbon consumption and carbon dust. This procedure determinates the specific consumption of the anode and the amount of carbon dust with a relative error of ±5 and ±10%, respectively.

Results and Discussion

Effect of Anode Current Density

In Table II, the measured data show that the total carbon consumption decreases with increasing the current density from 0.75 to 0.9 A/cm^2, while it increases with further increasing the current density from 0.9 up to 1.1 A/ cm^2. It is noticed that the value of total carbon consumption is the lowest one at the current density around 0.9 A/cm^2, which is agreed with the data obtained by Smodrodinov [6].

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Both gasified carbon and carbon dust show the same trend with the total carbon consumption. For a normal current density of 0.8 A/cm^2, the dusting was about 28 kg/t-Al for the fresh prebaked anode, and 36 kg/t-Al for the anode with 20 wt% addition of anode butts, which are similar to the results from Zhuang et al. [3].

It is found that the anode carbon consumption with 20 wt% anode butts is higher than that with the fresh prebaked anode. A possible explanation for this behavior is that the anode with 20 wt% anode butts has higher impurity contents than that for fresh anode. These impurities (such as V, Fe, and especially Na) increase anode reactivity which make the CO_2 reactivity of the anode with 20 wt% anode butts stronger than fresh anode (91.45 and 95.4 wt%, residue), and produce more dust (2.44 and 0.1 wt%). It may indicate that most of the dust formed is consumed by Boudouard reaction (Eq. (2)) which is mainly affected by CO_2 reactivity. Stronger CO_2 reactivity makes more carbon dusts during electrolysis process.

Table II. Anode Consumptions with Various Anode Current Densities

Experiment No.	Anode butts addition (%)	Current density (A/cm^2)	Total carbon consumption (kg/t-Al)	Gasified carbon (kg/t-Al)	Carbon dust (kg/t-Al)
1		0.75	411±20.6	369±18.5	42±4.2
2		0.80	396±19.8	368±18.4	28±2.8
3	0	0.85	389±19.5	364±18.2	25±2.5
4		0.90	373±18.7	355±17.8	18±1.8
5		1.0	415±20.8	358±17.9	57±5.7
6		1.1	420±21.0	372±18.6	48±4.8
7	20	0.75	426±21.3	371±18.6	50±5.0
8		0.8	400±20.0	364±18.2	36±3.6

Figure 2 to Figure 4 demonstrate the relationships between anode carbon consumption and anode current density. It can be seen that the anode carbon consumption, the carbon dust and the gasfication decrease in general when anode current density increase from 0.75 to 0.9 A/cm^2. It is noteworthy that the M_{CD} curves drop (134 kg/(t-Al A/cm^2)i) more sharply than for the M_{CG} (93 kg/(t-Al A/cm^2)i). This means that the degree of anode current density affecting the carbon dust is bigger than that of the gasification.

Effect of Electrolysis Temperature

Table III presents the detailed results of the anode consumption vs. electrolysis temperature. As it can be seen, the anode consumption reduces by 15 kg/t-Al when the electrolysis temperature reduces from 960 to 940 °C. This means the anode carbon consumption decreases by about 1 wt% per 5 °C decrease of electrolysis temperature.
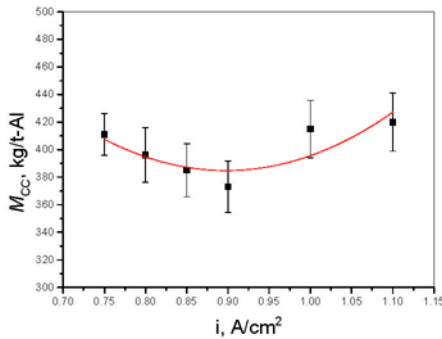

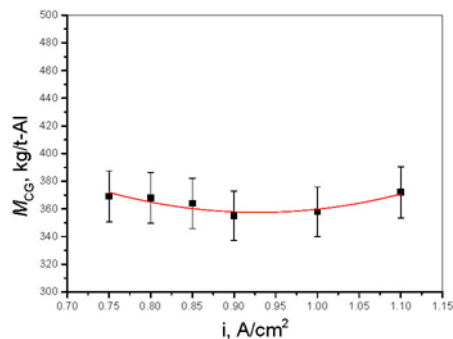Figure 2. Relationship between total carbon consumption and anode current density

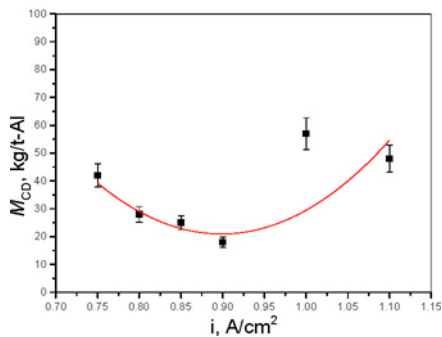Figure 4. Relationship between gasified carbon (M_{CG}) and anode current density

Figure 3. Relationship between carbon dust (M_{CD}) and anode current density
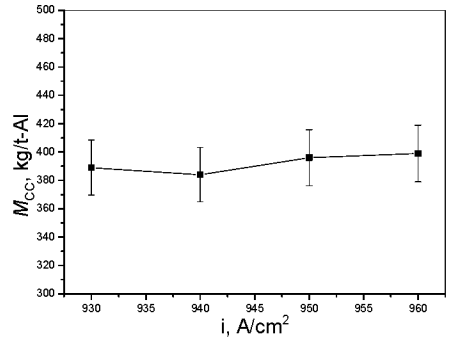

Figure 5. Relationship between total carbon consumption and electrolysis temperature
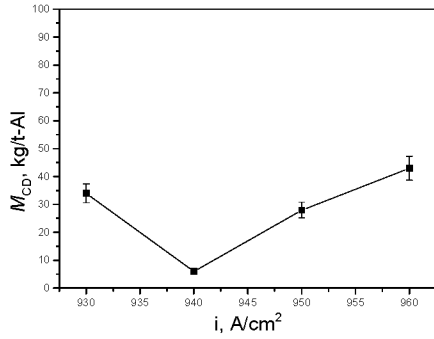
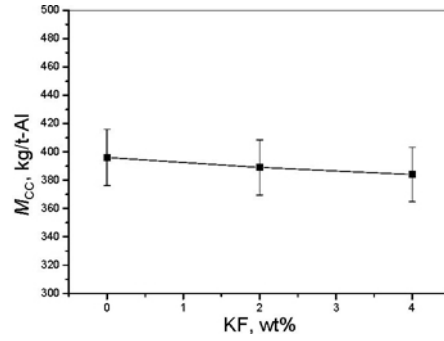Figure 6. Relationship between carbon dust and electrolysis temperature

Figure 8. Relationship between total carbon consumption and KF addition in cryolitic melts at 950 ºC
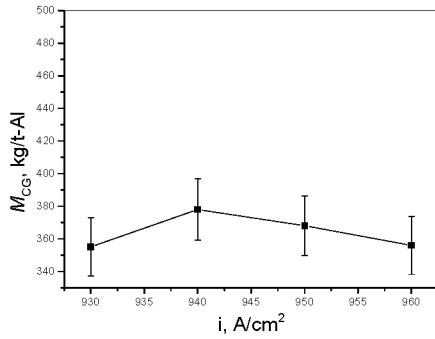

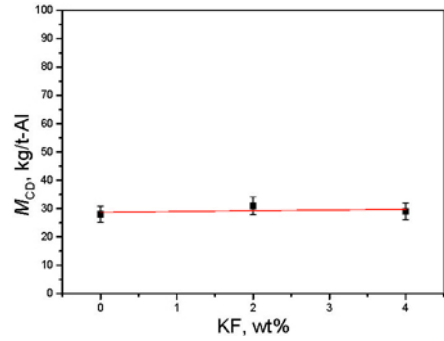Figure 7. Relationship between gasified carbon and electrolysis temperature

Figure 9. Relationship between carbon dust and KF addition in cryolitic melts at 950 ºC

Figure 5 to Figure 7 show that the electrolysis temperature is an important factor influencing the anode consumption, carbon dust, and gasification. The consumption decreased with decreasing electrolysis temperature, and the carbon dust follows the same trend at the temperature between 940 and 960 ºC, while the gasified carbon is adverse. The gasified carbon decreased with increasing electrolysis temperature. The results indicate that the rate of CO formation decreases with increasing electrolysis temperature, although the Boudoir relative rate increases [7, 9], which should be of interest with respect to the mechanism of the reactions occurring at the anodes.

Effect of KF Addition

The dependence of the anode carbon consumption on KF content was investigated for the modified electrolytes in laboratory aluminum electrolysis. The anode current was 0.8 A/cm^2, and the electrolysis temperature was at 950 ºC. The results for fresh prebaked anodes with varying KF content are listed in Table IV, and the dependences of carbon consumption on KF content in cryolitic melts are presented in Figure 8 to Figure 10.

Table III. Anode Consumption with Various Electrolysis Temperatures

Experiment No.	Temperature (ºC)	Electrolyte composition	Total carbon consumption (kg/t-Al)	Gasified carbon (kg/t-Al)	Carbon dust (kg/t-Al)
9	960	Na$_3$AlF$_6$-5%CaF$_2$-6%Al$_2$O$_3$ CR=2.4	399±20.0	356±17.8	43±4.3
10	950	CR=2.34	396±19.8	368±18.4	28±2.8
11	940	CR=2.30	384±19.2	378±18.9	6±0.6
12	930	CR=2.25	389±19.5	355±17.8	34±3.4

Table IV. Anode Consumption with Various KF Additions in Electrolyte at 950 ºC

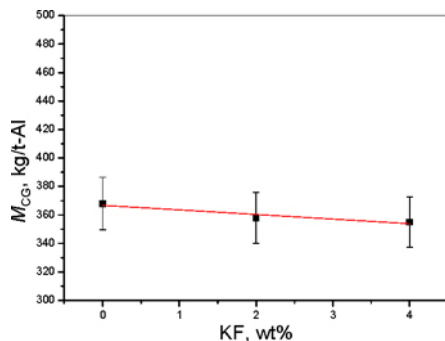| Experiment No.	Electrolyte composition				Total carbon consumption (kg/t-Al)	Gasified carbon (kg/t-Al)	Carbon dust (kg/t-Al)
	CR	CaF$_2$	Al$_2$O$_3$	KF			
13				0	396±19.8	368±18.4	28±2.8
14	2.34	5	6	2	389±19.5	358±17.9	31±3.1
15				4	384±19.2	355±17.8	29±2.9

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Figure 10. Relationship between gasified carbon and KF addition in cryolitic melts at 950 °C

An increase in the amount of KF from 0 to 4 wt% in electrolyte resulted in the decrease in carbon consumption by 12 kg/t-Al (see Figure 8) which due to the decrease in the rate of reactions (2) with the formation of CO (see Figure 10). On the contrary, as KF content in the electrolyte increases, a small increase in the amount of carbon dust by 1 kg/t-Al is observed (see Figure 9). In this case, $\left| \partial M_{CD} / \partial[KF] \right|$ (slope of the M_{CD} curve) is smaller than $\left| \partial M_{CG} / \partial[KF] \right|$ (slope of the M_{CG} curve), 0.2 and 3.2 kg/(t-Al wt%) KF, respectively.

Conclusion

1. The carbon consumptions of fresh prebaked anode and of the anode with 20 wt% butts decrease with increasing anode current density up to 0.9 A/cm^2, while increase again when the current density becomes higher; at low current density, the M_{CD} curves drop more sharply than for the M_{CG}, respectively.

2. The anode carbon consumption decreases by about 1 wt% per 5 °C with decreasing electrolysis temperature from 960 to 940 °C.

3. KF Addition in the cryolitic melt can reduce the anode carbon consumption, in which the $\left| \partial M_{CD} / \partial[KF] \right|$ of carbon dust is smaller than the $\left| \partial M_{CG} / \partial[KF] \right|$ of gasification.

4. The decreases in anode carbon consumptions with modifying anode current density and KF additions are mainly contributed from the reduced gasification, which may be related to possible inhibition of Boudoir reaction.

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