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INVESTIGATION ON AIR REACTIVITY AND ELECTROLYSIS CONSUMPTION OF ANODE CARBONS WITH ANTHRACITE ADDITIONS

Jilai Xue, Meizhi Han, Jun Zhu, Luxing Feng, Huanhuan Ma
School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing
Xueyuan Road 30, Beijing 100083, China

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Abstract

The increasing price of coke raw materials and a shortage in local supply for anode manufacture has presented a long term challenge for aluminum smelters with added cost into the metal product. The aim of this work is to search alternative carbon raw materials to replace part of traditional coke raw materials or technology to reduce the material costs for the prebaked anodes. Some calcined anthracite was selected as a starting material chemically pretreated to remove its impurities. The pretreated anthracite was added to the carbon mixtures, formed, and baked into the anode samples using the process used in the existing industry. The air-reactivity and anode consumption were tested. The anode samples were also characterized using XRD and SEM to investigate microstructure and inner pores. The results show that the anodes with anthracite additions of 10 - 20 wt. % are promising for potential application. In addition, ultrasound is found to reduce the anode consumption due to its effect on removing the CO_2 gas bubbles.

Introduction

Modern aluminum smelters use pre-baked carbon anodes that are manufactured by baking a mixture of calcined petroleum coke and coal tar pitch [1-2]. It takes about 0.4 - 0.5 ton carbon to produce one ton aluminum, and the demand on the coke increases as the aluminum industry expands worldwide [3-5]. However, the oil reserves on earth are limited and China's reliance on oil imports reached more than 51.8% in 2008. The aluminum industry will likely face a shortage of petroleum coke for the anode manufacture in the future. Finding an alternative carbon material , like anthracite, to replace part of the anode coke may provide a long term solution to the shortage problem appeared from time to time in coke supply.

Carbon anodes are consumed during aluminum electrolysis due to reactions with CO_2 and air, as well as bubble brushing and materials defects. The anthracite aggregate in the anodes may bring in change in possible variation in these reactions and the anode consumption. Additional interesting related to the anode reactions and consumption is to look at any potential benefit from ultrasound-assisted aluminum electrolysis, which was reported to reduce cell voltage [6-8], but is still unclear that there is any effect on the anode consumption, especially in case of the anthracite addition.

In this work, calcined anthracite was selected as a starting material and chemically pretreated to reduce its content of impurities. The pretreated anthracite was added into the carbon mixtures in making the anodes. The anthracite containing anodes were characterized using XRD and SEM techniques. The air-reactivity of the anode samples was tested using ISO standard. The carbon anode consumption during the electrolysis and the influence of ultrasound was also investigated.

Experimental

Preparation of Carbon Anode Samples

The raw materials for the anode samples were made of calcined petroleum coke, coal tar pitch (ordinary industrial products) and the calcined anthracite which has been chemically pretreated to remove the impurities and reduce the ash content.

The petroleum coke and pretreated anthracite were mixed with 20 wt. % pitch binder at 150 ℃, and then the mixed powder was hot pressed into the mold by two-way pressing method. These green anodes were all baked at 1150 ℃ used for the air reactivity tests and aluminum electrolysis experiments.

Set-up for Air Reactivity Tests

Figure 1 shows the set-up for carbon anode air reactivity tests, which was built up according to ISO standard (ISO12989-2：2004E). The test specimen (Φ25×45 mm) was suspended by a metal wire inside a vertical corundum tube furnace controlled at a constant temperature and filled with air flow. The change of the specimen mass was recorded every minute and the data were stored in PC in connection with an electronic scale (range: 500 g, resolution: 0.0001 g).

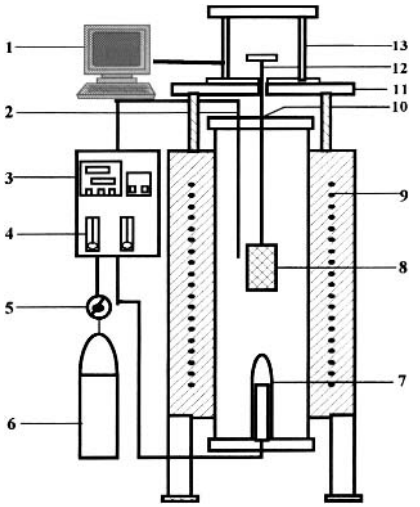


Figure 1. Set-up for carbon anode air reactivity tests.

1-PC; 2-Thermocouple; 3-Temperature controller; 4-Flowing meter; 5-Pressure-reducing valve; 6-Gas flask; 7-Preheat tube; 8-Sepcimen; 9-Heating element; 10-Gas outlet; 11-Supporting plate; 12-Connecting wire; 13-Electronic balance

Evaluation of Anode Consumption

In Figure 2, a laboratory electrolysis cell system is presented for the evaluation of the anode consumption. 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 sides. Both the anode and the cathode were connected to a DC power supply, and the anode rod was also used to introduce ultrasound. In the ultrasound system, a piezoelectric transducer and a frequency generator (20 kHz) were applied with a power capacity of ~900 W. The ultrasound was loaded 2 s and stopped 2 s, alternatively.

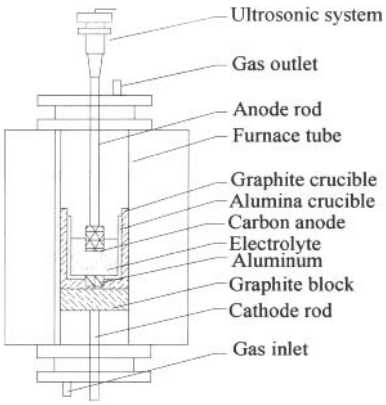


Figure 2. A laboratory set-up for anode consumption evaluation.

Table I lists the quantity and dimension of carbon anode samples used for evaluation of anode consumption during aluminum electrolysis. The electrolysis experiments were performed at 920 °C for 1.5 h under argon gas protection. For each run, the total mass of the cryolitic melt (industrial grade, cryolite ratio of 1.8) was 150 g containing 5 wt. % CaF_2 (analytical grade) and 4 wt. % Al_2O_3 (analytical grade).

Table I. Quantity and Dimension of Samples for Evaluating Carbon Anode Consumption in Aluminum Electrolysis

Anode material	high purity graphite		20 wt.% treated anthracite	
Sample No.	1	2	3	4
Mass(g)	3.3276	3.3903	43.6500	43.9600
Diameter(mm)	9.94	9.88	25	25.11
Height(mm)	29.79	30.18	58.6	57.68

XRD and SEM Inspection

The carbon aggregates of petroleum coke, pretreated and untreated anthracite were analyzed using X-ray diffraction (XRD) technique to identify the impurities. The anode samples made of the anthracite-coke mixtures were inspected by SEM to evaluate their pores and microstructure.

Results and Discussion

Variation in Impurities

Figure 3, 4, and 5 show the analysis results of the impurities in various carbon aggregates, where the petroleum coke demonstrates the highest purity among these carbon raw materials. The purity of the anthracite can be greatly increased after a chemical treatment that was performed in another laboratory for materials supply. This is because untreated anthracite contains many impurities, such as Fe, Al, Si, K, etc. which are harmful to the anode quality and thus must be removed before electrolysis.

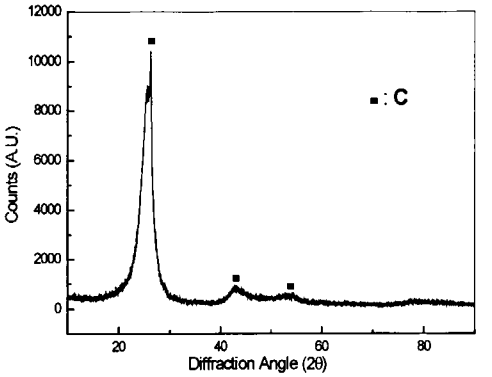


Figure 3. X-ray diffraction spectrum of petroleum coke.

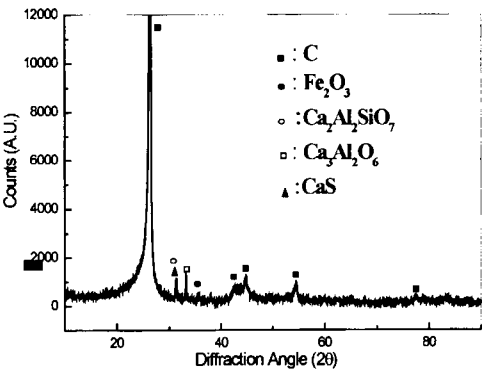


Figure 4. X-ray diffraction spectrum of untreated anthracite.

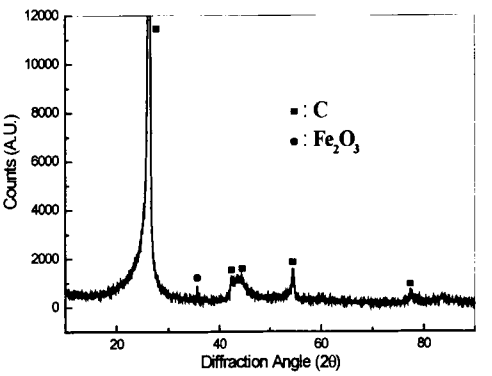


Figure 5. X-ray diffraction spectrum of anthracite after treatment.

Table II and Table III gives more details in ash level, volatiles and fixed carbons for the anode raw materials under investigation. These data demonstrate that the quality of the pretreated

anthracite is limited by the ash level, such as Fe content, Ca content, sulfide content, etc.

Table II. Analysis of Anode Carbon Raw Materials (wt. %)

Sample	Petroleum coke	Untreated anthracite	Pretreated anthracite
Ash	0.80	4.50	0.68
Moisture	0.07	0.02	0.37
Volatile	0.64	0.18	0.19
Fixed Carbon	98.49	95.3	98.76

Table III. Chemical Analysis of Ash Compositions in Various Carbon Aggregates (ppm)

Sample	Petroleum coke	Untreated anthracite	Treated anthracite
Na	100	319	68
Mg	109	2069	197
Al	461	5468	918
Si	695	4739	867
K	28	61	43
Ca	1067	4806	491
Fe	847	5846	410
Ti	56	183	59
P	12	77	11
S	79	1788	97

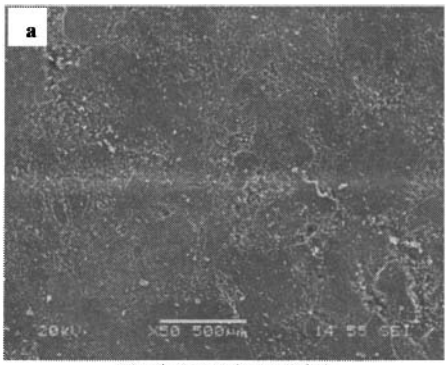
Effect on Porosity

Table IV shows the change of measured porosity in the carbon anode samples with varying amount of anthracite addition. In general, the density of the anode with anthracite addition was higher than that without it in the range of 10 - 40 wt. %. The porosity was found decreasing with the anthracite addition up to 20 wt. %, while it was increased again with further addition of anthracite to 40 wt. %. When the anthracite addition was 20%, the porosity was the lowest, which represented a 15% decrease in apparent porosity, compared to the anode with the pure coke aggregate.

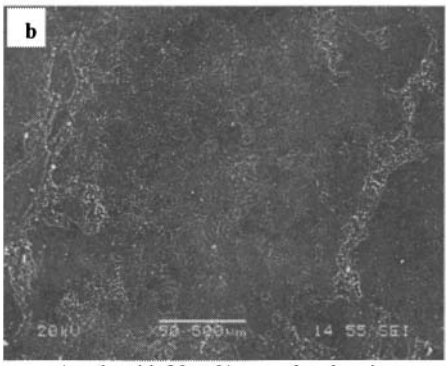
Table VI. Porosity and Density of Anode Samples with Varying Anthracite Additions

No.	Anthracite addition (wt. %)	Apparent porosity (%)	Apparent density (g/cm^3)
1	0	29.32	1.558
2	10	26.58	1.536
3	20	24.81	1.491
4	30	26.06	1.463
5	40	27.35	1.457

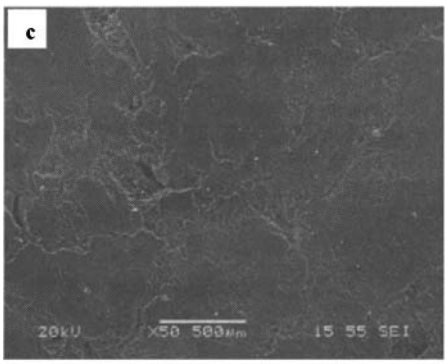
This phenomenon can be confirmed by SEM examination on the anode microstructure, as shown in Figure 6. The anode sample with 20 wt.% anthracite addition shows less porous than that with the pure coke addition, while the sample become more porous in the one with 40 wt.% anthracite addition. The porosity in the anode carbons are usually considered as one of important factors affecting the air reactivity.



Anode (Petroleum coke)



Anode with 20 wt% treated anthracite



Anode with 40 wt% anthracite

Figure 6 SEM photographs of the cross-section surface of carbon anode samples.

Effect on Air Reactivity

In aluminum electrolysis, the air oxidation of carbon anode is mainly occurred at the temperatures between 400 ℃ and 600 ℃

for its surface part exposed to air. The related reactions are described below:

$$C + O_2 - CO_2 \quad (1)$$

$$C + O_2 - CO \quad (2)$$

Total air reactivity, α_T, is the rate of mass loss of the carbon samples during the total testing time (3 hours) divided by the initial exposed surface area of the sample:

$$\alpha_T = 1000(m_i - m_f)/3A_E \quad (3)$$

Initial air reactivity, α_i, is the rate of mass loss of the carbon sample during the first 30 min of exposure to air in the reaction chamber divided by the initial exposed surface area of the sample:

$$\alpha_i = 2000(m_i - m_{30})/A_E \quad (4)$$

Final air reactivity, α_f, is the rate of mass loss of the carbon sample during the final 30 min of exposure to air in the reaction chamber divided by the initial exposed surface area of the sample:

where m_i is the initial sample mass, g; m_{30} is the sample mass, g, after 30 min of test exposure; m_{150} is the sample mass, g, after 150 min of test exposure; m_f is the final sample mass, g; A_E is the exposed surface area, cm^2.

$$\alpha_f = 2000(m_{150} - m_f)/A_E \quad (5)$$

Rate of mass loss, a, is the change of sample mass before and after the air reaction:

$$a = (W_0 - W_1)/W_0 * 100\% \quad (6)$$

where W_0 is the sample mass before the air reaction, g, and W_1 is the measured mass of the sample after the reaction, g.

Table V lists the reactivity data obtained with various carbon aggregate samples, where the anode sample with untreated anthracite addition has larger than the anode samples without the anthracite. The major reason is due to the high ash content associated with the untreated anthracite. After the chemical treatment for impurities removal, the anode with 10 wt. % addition of the treated anthracite can show a decrease in air reactivity, and the anode with 20 wt. % addition has the almost same level of air reactivity as the blank anode sample. The reductions in total amount of the ash after the treatment (from 4.5 wt. % down to 0.68 wt. %) can be the major contribution to such a decrease in air reactivity. The lowered individual impurity level of Fe, Si, as well as the lowered porosity, may also provide additional effect on the air activity decrease. However, the anode with more additions of anthracite up to 40 wt. % resulted in an increase in air reactivity, which is due to the increased amount of impurities with the increased amount of anthracite.

Figure 7 is the curves of the mass loss rate of various carbon aggregates against the testing time for the air reactivity. It is obvious that the slope of mass loss curve is the least for the anode with 10 wt. % addition of treated anthracite. Mass loss curves of the anodes with 10 and 20 wt. % pretreated anthracite show a trend of ending with a rate slow down to the value similar to the blank anode sample. The anode with 40 wt. % addition of the anthracite shows a sharp increase at the later stage of the air reaction test, which looks like a catalytic effect on the air reactivity due to its increased contents in impurities.

Table V. Air Reactivity Data of Carbon Anode Samples

No	Anthracite addition (wt. %)	α_T ($mg/cm^2 \cdot h$)	α_i ($mg/cm^2 \cdot h$)	α_f ($mg/cm^2 \cdot h$)	a (wt.%)
1	Blank sample	38.0	10.8	78.4	13.6
2	20 % untreated	83.7	17.9	153.1	31.0
3	10 % treated	25.9	15.7	54.9	13.1
4	20 % treated	38.3	13.4	56.9	13.8
5	30 % treated	62.5	10.9	150.0	22.7
6	40 % treated	80.6	22.6	209.6	30.2

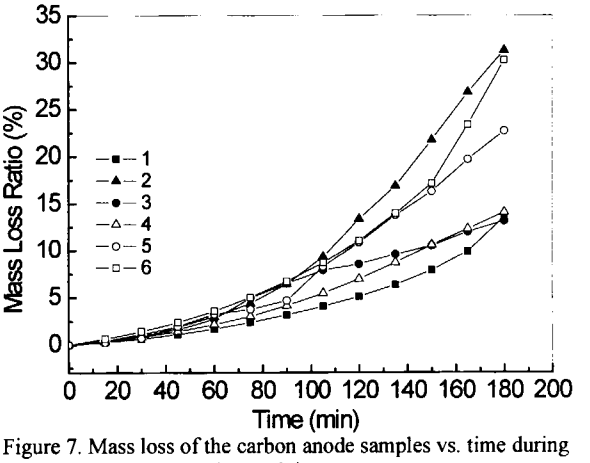


Figure 7. Mass loss of the carbon anode samples vs. time during air reactivity tests.

Effects on Electrolysis Consumption

During the aluminum electrolysis, the main reaction can be expressed as:

$$Al_2O_3 + C - Al + CO_2 \quad (7)$$

where the theoretical carbon anode consumption could be obtained, 333.3kg/t-Al.

Table IV shows the anode consumption data obtained after laboratory aluminum electrolysis. The total consumption of high purity graphite anode was 432.5 kg/t-Al, and the anode with 20 wt.% anthracite was 430.5 kg/t-Al. This amount of anthracite addition may have very small effect on the anode consumption. However, ultrasound can reduce the electrolysis consumption for both the pure graphite anode (down to 388.1 kg/t-Al), and the anode with 20 wt.% anthracite (down to 369.3 kg/t-Al).

Figure 8 is the photographs of carbon anodes after aluminum electrolysis. Change in mass and dimension of these anodes show

a similar trend that the ultrasound can reduce the anode consumption to some extend. It was thought that the anthracite powders may make a relative weak carbon structure that could increase the anode consumption with ultrasound. But the fact is the opposite. This may be because the ultrasound can remove the CO_2 gas bubbles quickly from the anode surface, thus reducing the contact time for the chemical reaction that results in the anode consumption. However, the mechanism behind such a phenomenon is still under investigation.

Table IV. Anode Consumption in Aluminum Electrolysis

Samples	Change in Height (mm)	Change in _Diameter (mm)	Change in Mass (g)	Anode consumption (Kg/t Al)
Pure graphite anode - I	0.44	1.13	0.2874	432.5
Pure graphite anode - II	0.24	1.04	0.2579	388.1
Anode (20% anthracite)-I	0.74	1.29	0.8942	430.5
Anode (20% anthracite)-II	0.56	0.98	0.8997	369.3

Anode-I has no ultrasound; anode-II has ultrasound.

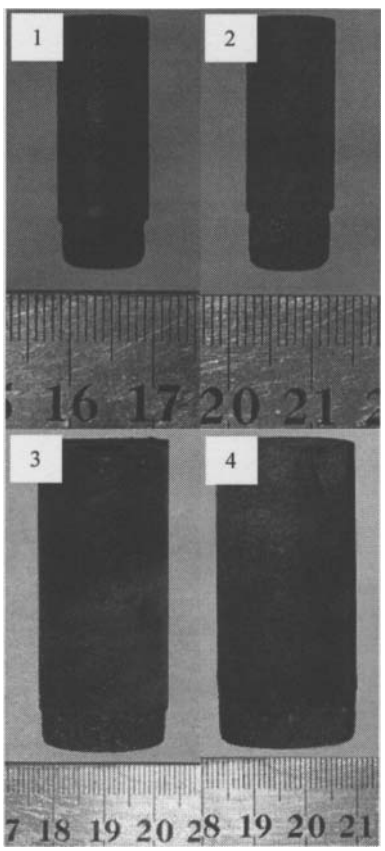


Figure 8. Photographs of carbon anodes after aluminum electrolysis (anode 2 and 4 with ultrasound).

Conclusions

1. Petroleum coke–anthracite mixture is used with pitch binder to make carbon anodes for use in aluminum electrolysis; the anthracite pretreated to remove impurities show no harmful effect on the anode air reactivity and anode consumption.

2. Porosity of the carbon anodes with 10 – 20 wt.% addition of pretreated anthracite decreases, while it increases with further addition of the anthracite up to 40 wt.%.

3. Air reactivity of the anode reduces with 10 – 20 wt.% anthracite addition, while it increases again with further addition up to 40 wt.%, and this may be due to reduced impurities and lowered total ash contents as well as decreased porosity.

4. Ultrasound can reduce the anode consumption in aluminum electrolysis that may be due to its effect on removing CO_2 gas bubbles.

Acknowledgement

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