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INFLUENCE OF ULTRAFINE POWDER ON THE PROPERTIES OF CARBON ANODE USED IN ALUMINUM ELECTROLYSIS

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Abstract

The ultrafine powder (<400 mesh) content of ball mill product has a great influence on the carbon anode quality. Experiments based on the aggregate recipe and raw material of an aluminum carbon anode plant in China have been conducted. The ultrafine powder was separated from the ball mill product by screening. On the premise of unchanged powder purity and content, anode samples with different ultrafine powder content were prepared and the properties were analyzed. Ultrafine powder materials were characterized by Blaine Number and BET specific area. Results showed that good electrical conductivity, thermal conductivity and air/CO_2 reactivity behavior could be obtained with low ultrafine powder content (3100~4000 Blaine, 2.510-3.734 m^2/g specific area). Anode properties such as baked density and air permeability were closely related with the ultrafine powder content and the Blaine value of powder material. The results can be used to optimize the properties of carbon anode.

Introduction

Carbon anodes used in aluminum electrolysis are a mixture of a various grain sizes of calcined coke, recycled spent anode butts and coal tar pitch, which are kneaded together, formed to the desired shape and then baked. The mixture is a distributed structure system. In this system, carbon particles and powder are bonded by intermolecular forces and mechanical adhesion. Coke powder, especially the ultrafine powder (<400 mesh; 37 μm) of anode formulation has a large influence on anode performance. It can fill the open porosity in the distributed system structure, which increases density. It also has a high specific surface area which directly influences the pitch content of the anode. Thus, ultrafine powder control is very important to the stability of anode quality.

In this paper, the formulation of a carbon anode plant in China was used as the basis for the study. Based on fixed ball mill product content and powder purity, combined with the analysis of Blaine Number and BET specific surface area, the effect of ultrafine powder content of ball mill product on the properties of carbon anode was studied.

Experimental

Method to measure coke powder

The BET specific surface area and Blaine Number were used to characterize the properties of the powder materials with different ultrafine content. Powder purity and ultrafine powder content of ball mill product were controlled by screening.

The Blaine Number used in the anode carbon industry is based on a testing method for specific surface-Blaine which is widely used in cement industry. Fischer [1] outlines how the Blaine air permeability apparatus can be adapted to measure and compare coke dust granulometries. The calculated value of the specific surface is referred to as the Blaine Number, a dimension index. It is designed for comparison of similar materials and is not intended to be an absolute measure of specific surface area [2].

The Blaine number and specific surface area of graphite, anthracite coal and calcined coke powder of different particle size were measured, with the RDC 155 Dust Fineness by Blaine, and BET specific surface instruments. Results are shown in Figure 1.

The Blaine Number of non-porous and ball-like graphite and anthracite coal powder has a linear relation with the BET specific surface area. The calcined coke powder does not have a linear relation because of its porous and irregularly-shaped structure. When the specific surface area is more than $5.5m^2/g$, the Blaine Number increases rapidly.

So, while the BET specific surface area has some referential value, it can not be used alone to characterize the granulometries of ultrafine coke powder. A combination with analysis of the Blaine Number is required to characterize the granulometries of the powder more in detail.

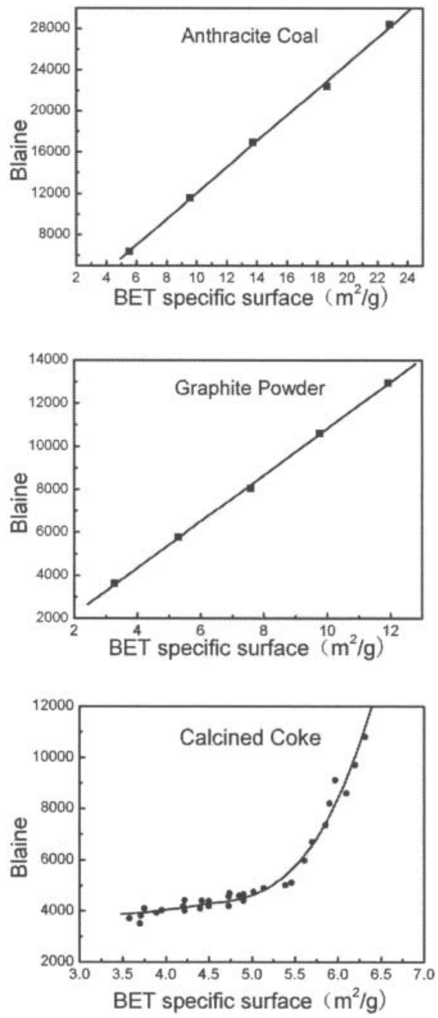

Figure1 Blaine number vs. BET specific surface area

Design of Experiment

The dry aggregate formulation of the carbon anode is shown in Table 1. The sizing of the coke powder was controlled to 70% passing 74μm by screening. Anode samples were prepared with the size of Φ50×100mm. Kneading, paste cooling, forming and the highest baking temperature were set as 180°C, 160°C, 155°C and 1200°C respectively.

A detailed plan was developed to increase the ultrafine powder content of the ball mill product material in increments of 7 wt%, from 0 wt% to 70 wt%. The anode properties of the samples produced were then investigated. An assessment of the pitch content to be applied to all recipes was initially determined. It was then fixed to decrease the effect of pitch content on the results. An increase in ultrafine powder content will cause the optimum pitch content to increase, because of the increase in the specific surface area. Accordingly, the recipe with an ultrafine powder content of 70 wt% was chosen to evaluate the pitch content to be used for all experiments. The pitch content was increased in 0.5 wt% steps from 16 wt% to 19 wt%. Ten anode samples prepared from each recipe.

Table 1 Dry formulation of carbon anodes

	Particle Size(mm)	Proportion (wt%)
Coarse particle	3-6	25
Particle	1-3	24
Small particle	1-0.3	21
Coke Powder	<0.15	30

Results and Discussion

Determination of Pitch Content

The properties of the baked anodes with 70 wt% ultrafine powder content and the different pitch contents are shown in Figure 2. The shadow graph shows the distribution of the properties of all anode samples tested.

Baked density, electrical resistivity, compressive strength and air permeability deteriorated with increasing pitch content. According to R&D Carbon work on optimum pitch content [3], the pitch content of 17 wt% can be considered as excess. A pitch content of 17 wt% was therefore used as the fixed pitch content in all later experiments.

Variation trend of baked anode properties with different ultrafine powder contents

The Blaine Number and BET specific surface area of the calcined coke powder material with different ultrafine contents are shown in Table II. The trend of the Blaine value with specific surface area is similar to Figure 1. There was no linear relationship between these two parameters.

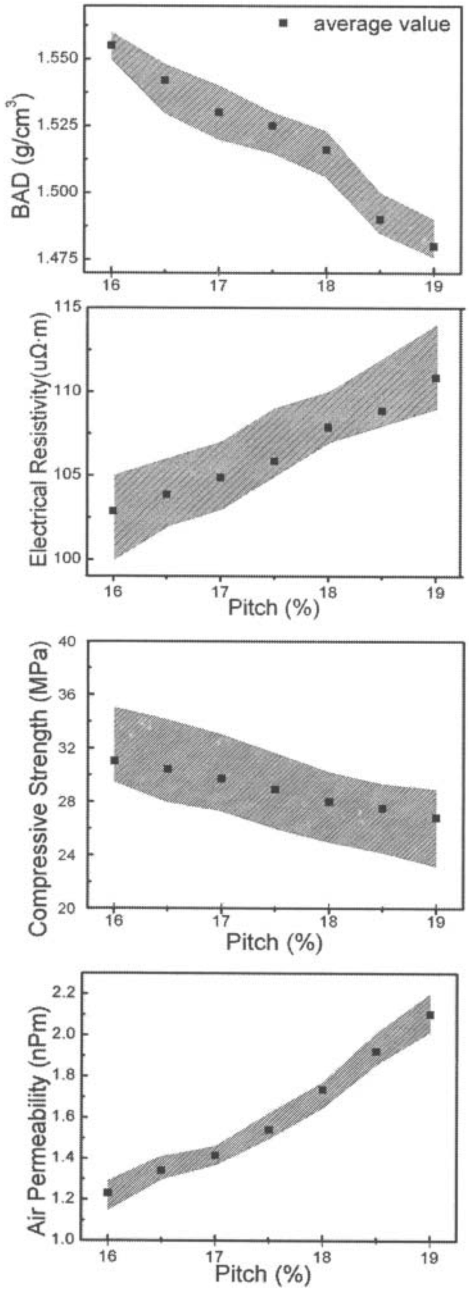

Figure 2 Baked anode properties vs. Pitch content

The test results of anode properties are shown in Figure 3. The red points represent the properties of anodes adopted for the original recipe of the plant. Comparison of baked anode properties with different ultrafine powder content yields the following observations:

- Baked Apparent Density (BAD) showed a peak when the ultrafine powder content was about 35 wt% (4300 Blaine, 4.17 m^2/g specific surface area) because of the improved particle packing. But as shown above, BAD was also influenced by the pitch content.

Table II Blaine and BET Specific Surface Area Test Results of Powder Materials

Powder sample	Ultrafine powder (%)	Blaine Number	BET specific surface(m^2/g)
1	0	2427	2.127
2	7	3151	2.51
3	14	3523	2.904
4	21	3860	3.321
5	28	4011	3.734
6	35	4321	4.174
7	42	4720	4.548
8	49	5120	4.945
9	56	5886	5.393
10	63	7508	5.750
11	70	10484	6.113

- The baked anodes with Blaine values of 3100-4000 showed good electrical resistivity. At higher Blaine Numbers, electrical resistivity increased rapidly. Theoretically, with ultrafine powder content increasing, anode electrical resistivity should improve, since the optimum pitch content of the recipe would have increased, approaching to the actual value of 17 wt%. The deterioration of electrical resistivity could not be due to the lack of pitch. It is suggested that large numbers of boundary layers were produced by ultrafine powder and pitch within the anode and caused the increase in electrical resistivity.

- Air permeability decreased with the increase of ultrafine powder content with a linear relationship. It indicated that ultrafine powder can efficiently fill the pores in carbon anode and improve the anode structure.

- When the ultrafine powder content was more than 28 wt% (Blaine 4000), thermal conductivity decreased shapely with the rise of ultrafine powder content.

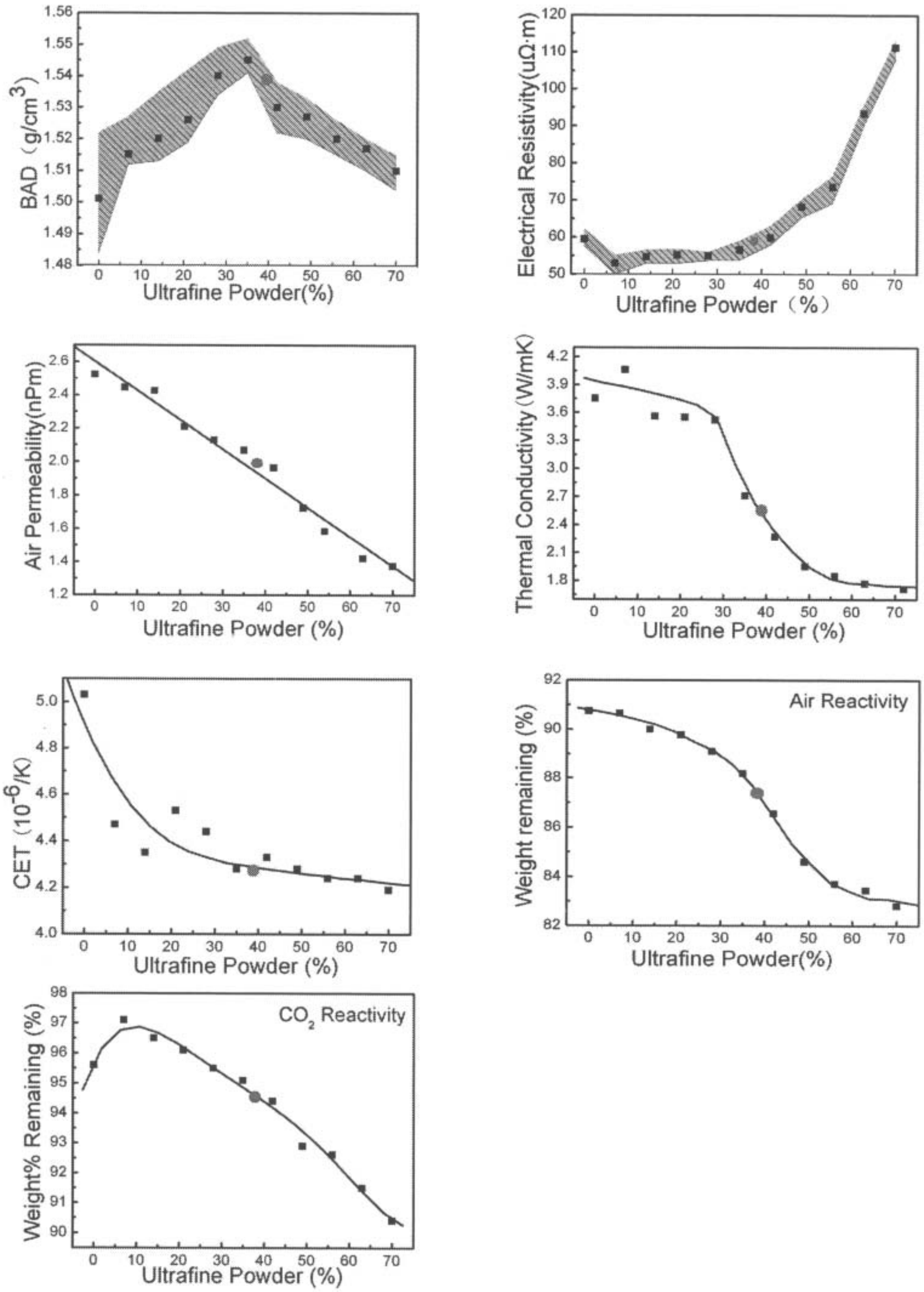

Figure 3 Properties of Baked Anode with Different Ultrafine Powder Content

- The baked anode without ultrafine powder had a high coefficient of thermal expansion (CTE) - 5.03×10^{-6}/K. As ultrafine powder was added to the recipe, the CTE decreased significantly.

- The baked anodes with a lower ultrafine powder content had the lowest reactivity. However, different from its reactivity to air, a recipe with no ultrafine powder had a negative impact on the anode CO_2 reactivity. The baked anode with 7% ultrafine powder content (Blaine 3100) had the lowest reactivity to CO_2. Vichtus and Cannova [4] indicated that anode air and CO_2 reactivity should decrease with the decrease of air permeability. However, in this work, the trend is different because ultrafine powder has two effects on anode reactivity. On the one hand, ultrafine powder can fill the porosity in anode to prevent O_2 and CO_2 infiltration . On the other hand, powder, especially ultrafine powder, is easier to react with O_2 and CO_2, which can generate additional porosity when the anode is in use in the cell.

- Through optimising the ultrafine powder content of ball mill product, there is still large scope for the carbon anode plant to improve its anode performance.

Conclusion

On the basis of unchanged powder purity and content, the ultrafine powder content of the ball mill product has a significant impact on carbon anode properties. During anode production, the stability of anode properties can be improved if the concept of Blaine Number is used for the powder purity control.

In this paper, the main results were obtained as follow:

1. The Blaine value of non-porous graphite and anthracite coal powder had a linear relation with their BET specific surface area, while the calcined coke powder showed different behaviour because of its porosity and irregularly-shape structure. Blaine Number is recommended to be combined with specific surface area to characterize the granulometries of coke fines more precisely.

2. With the same aggregate formulation, powder purity and pitch content, optimizing the ultrafine powder content had a positive impact on the anode baked density, electrical resistivity, air permeability, thermal conductivity, CTE, and air/CO_2 reactivity. Based on an overall consideration of various factors, it is suggested that the Blaine Number of powder material be controlled between 3100 and 4000.

3. Increasing the ultrafine powder content of the ball mill product will decrease air permeability. However, it will increase the reactivity of the baked anode to O_2 and CO_2.

4. The influence of ultrafine powder on carbon anode properties is complex and multiband is influenced by many factors. Ultrafine powder content should be controlled according to the requirements of the plant. Increasing or decreasing the ultrafine powder content without careful experimentation would probably result in deterioration in the properties of carbon anode.

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