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STUDY ON GRAPHITIZATION OF CATHODE CARBON BLOCKS FOR ALUMINUM ELECTROLYSIS

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Abstract

High quality graphite cathode carbon blocks require low resistivity, strong resistant erosion to molten salts and liquid aluminum in the aluminum electrolytic cells. High quality cathode materials can decrease cathode voltage and then reduce the power consumption, and improve service life of the cell. Applying hot mould technology under 40 MPa pressure, different amounts of petroleum coke in anthracite mixtures is graphitized in graphitizing furnace. By the X-ray diffraction parameters, density, compressive strength and resistivity drop are measured. The experimental results show that compressive strength and volume density of graphite blocks containing 30% of petroleum coke are 1.366 g/cm3 and 4.8 MPa, respectively, resistivity drop from 114μΩm to 13μΩm, mostly in accordance with block production requirements.

Introduction

Graphitized cathode blocks are now widely used, especially in modern high-amperage aluminum electrolysis cells. Compared to semi-graphitic or graphitic materials, fully graphitized cathode blocks have desired properties such as low sodium expansion, low electrical resistivity and high thermal conductivity [1,2]. In recent years, more and more aluminum producers have decreased cathode voltage drop, reduced energy consumption and optimized the operation of large-scale aluminum reduction cells to make production costs lower. For example, the graphitized cathode block of Zhengzhou aluminum institute and carbon factory association made two years industrial test in three 350 kA aluminum reduction cells. The result showed that the cathode voltage drop of the test cell reduced 80～100 mV compared to an ordinary cell, current efficiency increased about 1% and per ton of aluminum, resulting in energy savings of 300 kWh.

In the work described in this paper, we selected Ningxia anthracite as the main material, adding 20% pitch with 0%, 30%, 40%, 45% of the petroleum coke powder, respectively. After the materials were mixed, formed and graphitized, the block properties such as density, resistivity and compressive strength, etc., were tested. Cathode block properties with different additions of petroleum coke and graphitizing temperatures were analyzed.

Experimental

Anthracites selection and characterization

Anthracites denoted Qingtongxia Aluminum Limited Corporation, from Ningxia in northwest China were selected for this study. Its proximate and elemental analysis is shown in Table I.

Table I. Proximate and elemental analysis of anthracite.

Proximate analyses (wt %)		Elemental analyses (wt %)			
water	0.19	SiO_2	37.03	Fe_2O_3	15.90
ash	6.44	CaO	11.26	K_2O	0.96
volatile matter	9.31	MgO	3.05	Na_2O	1.97
fixed carbon	84.06	Al_2O_3	19.41	SO_2	8.06
sulfur	0.22	TiO_2	0.90	P_2O_5	0.42

Graphitized cathode blocks production process

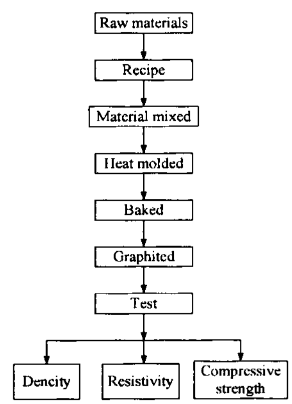

Figure 1. Graphitized cathode blocks produced process.

This experiment selected anthracite as the main material, mixed with 20% pitch with 0%, 20%, 40%, 45% of the petroleum coke powder, respectively. Matched materials were premixed at room temperature. The sample, Ø(64±1)mm×(45 ~ 50)mm, formed under 40MPa pressure in hot mold. Baking took place in a resistance furnace for 14h. Graphitization was performed a graphitization furnace for 3.5h. The graphitized cathode block production process is shown in Figure 1.

Recipe

The raw materials and particle size distribution of the cathode blocks are shown in Table II.

Hot forming

Forming of the blocks is briefly described as follows. The sample was placed in a mold that was placed in a vertical hydraulic press. And 15 MPa pressure was applied. An electrical current was then applied for 15 min to increase the temperature. When the conditions were steady, the pressure was increased to 35 MPa and maintained for 5 min. After the temperature of sample dropped to 70～80 °C, it was removed from the mold. Following baking the sample was ready for the graphitization furnace.

Table II. Cathode blocks raw materials particle size ratio.

Sample	Cathode blocks		Anthracite(mm)			Petroleum coke(mm)
	Anthracite (%)	Petroleum coke (%)	2～0.5 (%)	0.5～0.2 (%)	<0.2 (%)	<0.2 (%)
A	100	0	45	10	45	0
B	70	30	45	10	15	30
C	60	40	45	10	5	40
D	55	45	45	10	0	45

Graphitization process

The baked cathode block was placed in a graphitization furnace surrounded by petroleum coke powder and heat preservation material in order to displace the air and decreased the heat loss. The graphitization furnace and the power regime of the graphitization process are shown in Figure 2.

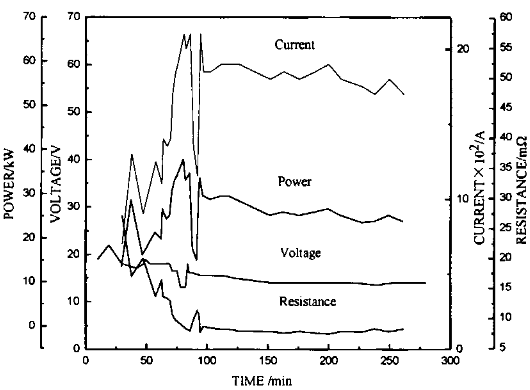

Figure 2. The power regime of graphitization process.

Results and Discussion

Cathode blocks quantity effect of heat molding technological conditions

(1) The effect of mixing on cathode block quality

During the cathode blocks hot forming process, we found that block II (Figure3) was poorer bonded than block I during de-molding. The forming conditions were similar, 140 °C of forming temperature and 35MPa of molding pressure. However, analyses indicated that the samples may have been non-uniformly mixed.

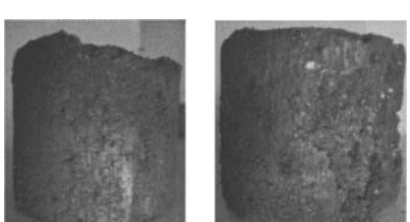
I II

Figure 3. Blocks of different mixing conditions.

(2) The effect of de-mold temperature on cathode block quality

The appearance of the de-mold temperature on cathode blocks are shown in Figure 4. The blocks had large cracks when the de-mold temperature was higher than 120 °C or at room temperature. The block appearance was smooth and large cracks did not appear at de-mold temperatures in the 70-80 °C range.

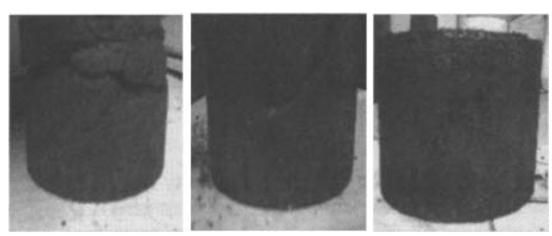
III IV V

Figure 4. The cathode blocks of different de-mold temperatures.

III. Block of de-mold temperature above 120 °C

IV. Block of de-mold temperature at room temperature

V. Block of de-mold temperature at 70 °C～80 °C

The effect of forming conditions on block properties

(1) Block apparent density

Cathode blocks with high bulk density might have better resistance to erosion of bath and molten metal, lower gas permeability and reduced reaction with CO_2 and air. The effect of petroleum coke additions (Table II) on apparent density of the blocks are shown in Figure 5. Apparent densities in the range of 1.043 g/cm^3 to 1.449 g/ cm^3 were measured.

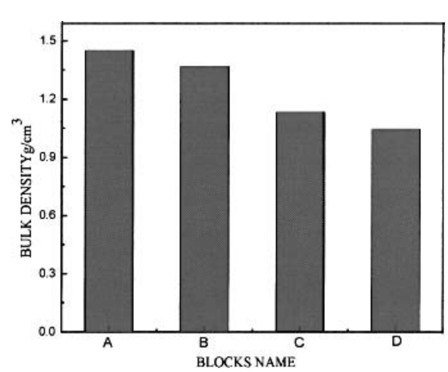

Figure 5. Apparent density of cathode blocks.

Lower resistivity of cathode blocks may reduce power consumption. The electrical resistivity of cathode blocks is normally below 60μΩm. The blocks with 30% and 45% petroleum coke added to the anthracite obtained electrical resistivity of 13μΩm and 21μΩm, respectively. Blocks with 40% petroleum coke and no petroleum coke (100% anthracite) had higher resistivity, 26μΩm and 32μΩm, respectively.

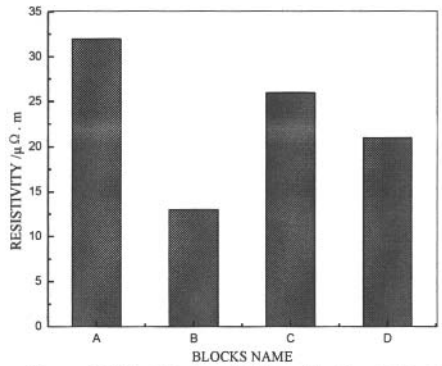

Figure 6. Electrical resistivity of cathode blocks.

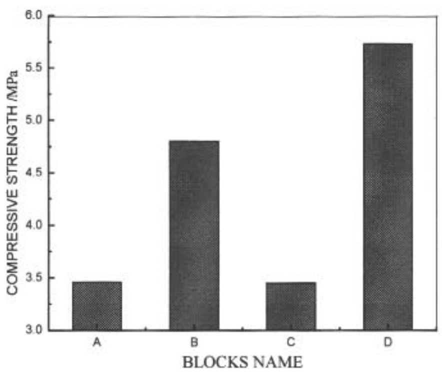

Figure 7. Compressive strength of cathode blocks.

(2) Electrical resistivity

(3) Compressive strength

Cathode carbon block should have a certain compressive strength to prevent thermal shock. A compressive strength comparative analysis of four raw materials is shown in Figure 7. The experimental results showed that, compressive strength of 45% and 30% petroleum coke blocks were larger, respectively 5.73MPa and 4.80MPa. Blocks with 40% petroleum coke resistivity and without petroleum coke had lower strength, respectively for 3.456 MPa and 3.46 MPa.

Conclusions

The influence of petroleum coke powder added on graphite cathode block bulk density, resistivity and compressive strength were investigated. The hot forming technology conditions that affect the cathode block quality were analyzed. The main conclusion could be summarized as follows: (1) Mixing in homogeneity has a serious impact on the quality of cathode block. (2) Large cracks appeared in blocks de-molded at temperatures above 120 °C. De-molding temperatures in the range 70-80 °C had good quality. (3) Among the petroleum coke-added blocks, the one containing 30% petroleum coke had the highest apparent density, the lowest electrical resistivity and the highest impressive strength.

References

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