Study on graphitization of anthracite and petroleum coke catalyzed by boric acid

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Abstract: Graphite carbon materials have excellent properties and are widely used. Traditional artificial graphite has high energy consumption and high cost, so reducing the energy consumption of artificial graphite has become a research hotspot in recent years. The effect of boric acid on the graphitization of anthracite and petroleum coke was studied, and the parameters such as boric acid content, roasting temperature and holding time were investigated in this paper. The results show that the optimum dosage of boric acid for graphitization of anthracite is 7.5%, and that of catalyst for graphitization of petroleum coke is 5%. The effect of roasting temperature on the graphitization of anthracite and petroleum coke catalyzed by boric acid is remarkable. The best temperature is 1400°C. Roasting holding time has positive effect on the graphitization of anthracite and petroleum coke catalyzed by boric acid. The best roasting holding time is 120min. Under the optimal experimental conditions, the highest graphitization degree of anthracite and petroleum coke catalyzed by boric acid are 23.58% and 23.56%, respectively. The effect of boric acid on anthracite is better than that of petroleum coke.

1. Introduction
Graphite is widely used in chemical, mechanical, construction, metallurgy, emerging energy, biomedicine, nuclear power, aerospace and other industrial fields [1, 2]. The natural graphite is a non-renewable resource. In order to meet the increasing demand of graphite market, the application of graphitizable carbon materials to produce artificial graphite has been paid more and more attention [3-7]. According to a lot of researches, it is found that adding some substances into the artificial graphite can reduce energy consumption and production costs, for remarkably reducing the temperature required for the graphitization of carbon materials, and improve its microstructure and the performance of carbon materials in the process of artificial graphite. In order to achieve the purpose of conversion of ordinary carbon to carbon graphitization, the catalyst was used in the process. There are many kinds of catalysts which can be used in the process of graphitization of carbon materials, such as metals, metal compounds and boride [8, 9]. Among them, boron and boride are widely used. In the process of industrial aluminum electrolysis, the common cathode carbon block can be converted into the carbon block with higher graphitization degree at the temperature of 850°C–1000°C. In this paper,
the raw materials of cathode carbon block such as anthracite and petroleum coke, were used as experimental carbon materials and boric acid was used as catalyst. The effect of two kinds of carbon materials on the graphitization catalyzed by boric acid was studied, which provided the basic data for the later research of low temperature graphitization of cathode carbon block.

2. Experimental

2.1 Experimental materials and equipments
The materials needed for the experiment are anthracite, petroleum coke, boric acid, hydrochloric acid, hydrofluoric acid, silver nitrate, anhydrous alcohol and so on. The experimental equipment mainly includes high-speed universal grinder, high-temperature box furnace, electronic balance, standard screen, oven, magnetic constant temperature agitator, circulating water multi-purpose vacuum pump and X-ray diffractometer.

2.2 Preparation of experimental sample
Anthracite and petroleum coke were crushed by high-speed universal pulverizer in turn, and then sieved to obtain anthracite and petroleum coke powder with uniform particle size less than 0.075mm.

(1) Anthracite coal is deashed. The acid solution was made from 37% hydrochloric acid, 50% hydrofluoric acid and deionized water in the proportion of 3:2:5. At the ratio of solid to liquid 1:10, taking 10g anthracite powder and adding some acid solution to mix it evenly, then stirring it at 80°C for 120min, and vacuum filtering it and washing it thoroughly with deionized water until there is no chloride ion residue in the sample (testing for chloride ion residue by adding silver nitrate). The samples were dried in an oven at 50°C for 24 hours, and then the dried samples were put into a sealing bag.

(2) At room temperature, boric acid with different quality was dissolved into 100ml ethanol solution in the fume hood, and heated for 120min to make it dissolve completely. Then, the uniformly dispersed boric acid-ethanol sol was obtained.

(3) The demineralized anthracite or petroleum coke samples prepared at 10g were added to boric acid-ethanol sol. The anthracite or petroleum coke samples were uniformly dispersed in the sol by stirring at high speed for 120min with a magnetic mixer. The samples containing 0, 2.5%, 5%, 7.5%, 10% and 12.5% boric acid were prepared.

2.3 Experimental method
The samples were put into a corundum crucible for 10g, then placed in a high temperature box furnace and treated with high temperature at a certain temperature. The heating rate was 10°C/min, and the temperature was kept for a certain time. The samples were taken out for analysis at room temperature with a cooling rate of 3°C/min to 1000°C, followed by a cooling rate of 5°C/min after 1000°C to room temperature.

2.4 Sample testing and characterization
The analysis equipment is Rigaku D/MAX 2500V X-ray diffractometer. The light source is copper target of X-ray tube (CuKα), λ is 0.15416nm, tube pressure is 40KV, tube current is 150mA, step width is 0.012θ, scanning step length is 0.02°, scanning speed is 2°/min and the scanning range is 20°~35°. High purity silicon powder (Si) is used as the standard sample to calibrate the measurement error of diffraction peak 2θ of the measured sample [10].

The interlayer spacing of ideal graphitized crystals is 0.3354nm, and that of incomplete graphitized crystals is 0.3440nm. The (002) diffraction peaks of anthracite and petroleum coke are determined by X-ray diffraction method. \( d_{002} \) is obtained according to Bragg Formula (1) [11].

\[
d_{002} = \frac{\lambda}{2 \sin \theta}
\]

(1)

The degree of graphitization (g) can be obtained from Formula (1) [12].
where $\lambda$ is the wavelength of X-ray, $\lambda = 0.15416\text{nm}$; $\theta$ is the diffraction angle corresponding to the (002) peak, the unit is degree.

### 3 Experimental results and discussion

#### 3.1 Effect of boric acid content

The samples were graphitized and analyzed by XRD. The content of boric acid is 0, 2.5%, 5%, 7.5%, 10% and 12.5%, respectively. The XRD patterns of graphitization of anthracite and petroleum coke catalyzed by boric acid are shown in Fig. 1. Based on XRD pattern analysis and Bragg Formula, the calculated results of the interlayer spacing ($d_{002}$) and graphitization degree of anthracite and petroleum coke are shown in Table 1.

As can be seen from Fig. 1, with the increase of boric acid content, the diffraction angle of (002) diffraction peak of anthracite and petroleum coke changed obviously. The diffraction angle shifted first to the right and then to the left, the closer the (002) peak to the right, the more sharply symmetrical it is. With the increase of boric acid content, the graphitization degree of anthracite and petroleum coke increased firstly and then decreased. From Table 1, when the content of boric acid increased to 7.5%, the graphitization degree of anthracite reached the highest, and the graphitization degree was 23.58%. When the content of boric acid was 5%, the graphitization degree of petroleum coke reached the highest, the graphitization degree was 23.56%. Therefore, it intimates that the catalytic effect of boric acid on anthracite is better than that on petroleum coke.

![Fig. 1 XRD patterns of anthracite and petroleum coke graphitization catalyzed by boric acid with different contents](image)

![Table 1 The results of anthracite and petroleum coke graphitization catalyzed by boric acid with different contents](table)

| Boric acid/\(^{\circ}\) | Interlayer spacing/\(\text{nm}\) | Degree of graphitization/\(^{\circ}\) | Interlayer spacing/\(\text{nm}\) | Degree of graphitization/\(^{\circ}\) |
|----------------------|-----------------|----------------|-----------------|----------------|
| 0\(^{\circ}\)       | 0.3626\(^{\circ}\) | 0\(^{\circ}\) | 0.3643\(^{\circ}\) | 0\(^{\circ}\) |
| 2.5\(^{\circ}\)      | 0.3433\(^{\circ}\) | 8.25\(^{\circ}\) | 0.3431\(^{\circ}\) | 10.12\(^{\circ}\) |
| 5\(^{\circ}\)        | 0.3423\(^{\circ}\) | 19.35\(^{\circ}\) | 0.3419\(^{\circ}\) | 23.56\(^{\circ}\) |
| 7.5\(^{\circ}\)      | 0.3419\(^{\circ}\) | 23.58\(^{\circ}\) | 0.3426\(^{\circ}\) | 15.46\(^{\circ}\) |
| 10\(^{\circ}\)       | 0.3422\(^{\circ}\) | 20.36\(^{\circ}\) | 0.3429\(^{\circ}\) | 12.46\(^{\circ}\) |
| 12.5\(^{\circ}\)     | 0.3427\(^{\circ}\) | 15.42\(^{\circ}\) | 0.3431\(^{\circ}\) | 9.85\(^{\circ}\) |
3.2 Effect of roasting temperature
The XRD patterns of graphitization of anthracite and petroleum coke catalyzed by boric acid at different temperatures are shown in Fig.2. The results of graphitization of anthracite and petroleum coke catalyzed by boric acid at different temperatures are shown in Table 2.

![Fig.2 XRD patterns of anthracite and petroleum coke graphitization catalyzed by boric acid with different temperatures](image)

Table 2 The results of anthracite and petroleum coke graphitization catalyzed by boric acid with different temperatures

| Roasting temperature°C | Anthracite | Interlayer spacing/μm | Degree of graphitization/% | Petroleum coke | Interlayer spacing/μm | Degree of graphitization/% |
|------------------------|-----------|-----------------------|---------------------------|----------------|-----------------------|---------------------------|
| 1000                   | 0.3457    | 0                     | 0.3456                    | 0              | 0                     | 0.3442                    |
| 1100                   | 0.3451    | 0                     | 0.3435                    | 0              | 0                     | 0.3442                    |
| 1200                   | 0.3436    | 4.65                  | 0.3435                    | 5.81           |                       |                           |
| 1300                   | 0.3423    | 19.77                 | 0.3428                    | 13.95          |                       |                           |
| 1400                   | 0.3419    | 23.58                 | 0.3419                    | 23.56          |                       |                           |

As can be seen from Fig.2 that the peak of anthracite and petroleum coke (002) gradually protrudes with the increase of roasting temperature. The diffraction angle shifts to the right, and the peak of anthracite and petroleum coke (002) has the most prominent symmetry and the largest diffraction angle when the temperature reaches 1400°C. Table 2 shows that the graphitization degree of anthracite catalysed by boric acid is 23.58% and that of petroleum coke catalyzed by boric acid is 23.56% at the temperature 1400°C. At the same time, it can be predicted that the graphitization effect of anthracite and petroleum coke will increase with the increase of roasting temperature.

3.3 Effect of roasting holding time
The XRD patterns of graphitization of anthracite and petroleum coke catalyzed by boric acid at different roasting holding times are shown in Fig.3. The results of graphitization of anthracite and petroleum coke catalyzed by boric acid at different roasting holding times are shown in Table 3.
Fig. 3 XRD patterns of anthracite and petroleum coke graphitization catalyzed by boric acid with different time.

Table 3 The results of anthracite and petroleum coke graphitization catalyzed by boric acid with different time.

| Roasting holding time/min | Anthracite | Petroleum coke |
|--------------------------|------------|----------------|
|                          | Intercalation spacing/nm | Degree of graphitization/% | Intercalation spacing/nm | Degree of graphitization/% |
| 60           | 0.3436   | 4.65          | 0.3438   | 2.33          |
| 90           | 0.3433   | 8.14          | 0.3426   | 16.28         |
| 120          | 0.3419   | 23.58         | 0.3419   | 23.56         |
| 150          | 0.3419   | 24.42         | 0.3418   | 25.58         |
| 180          | 0.3419   | 24.48         | 0.3418   | 25.58         |

It can be seen from Fig. 3 that the peak of anthracite and petroleum coke (002) is gradually prominent and the diffraction angle shifts to the right with the increase of roasting holding time. The peak shape changes little from 120min to 180min, the diffraction angle shifts slightly to the right. According to Table 3, it can be seen that the effect of boric acid on the catalysis of anthracite and petroleum coke has little change from 120min to 180min. The effect of boric acid on the catalysis of anthracite and petroleum coke can be ensured at 120min.

4 Conclusions

(1) The optimum dosage of boric acid for graphitization of anthracite is 7.5%, and that of catalyst for graphitization of petroleum coke is 5%. The catalytic effect of boric acid on anthracite is better than that of petroleum coke.

(2) The effect of roasting temperature on the graphitization of anthracite and petroleum coke catalyzed by boric acid is remarkable. The best temperature is 1400°C.

(3) Roasting holding time has positive effect on the graphitization of anthracite and petroleum coke catalyzed by boric acid. The best roasting holding time is 120min.

(4) Under the optimal experimental conditions, the highest graphitization degree of anthracite and petroleum coke catalyzed by boric acid are 23.58% and 23.56%, respectively.

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