Reaction Behavior of a Trace Element during the Pitch Pyrolysis Process

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ABSTRACT: The pyrolysis behavior of pitch determines the performance of pitch coke and directly affects the carbon anode air/CO₂ reactivity. The effects of pitch mass and pyrolysis rate on the pyrolysis process of pitch are studied using a self-made pyrolysis device. The effects of Na, Ca, and Mg on pyrolysis kinetics and carbon anode reactivity are also investigated. Results show that the pyrolysis of pitch on the surface and inside of the carbon anode can refer to the kinetic data of small mass asphalt (SMP) and large mass asphalt (LMP), respectively. The pyrolysis process of SMP and LMP conforms to the same dynamic model. The apparent activation energy of SMP is 48.62 kJ/mol and that of LMP is 128.46 kJ/mol. The mass and heating rate of pitch have obvious influences on the LMP pyrolysis process. The apparent activation energy of pyrolysis gradually increases with increasing contents of Na, Ca, and Mg. Moreover, the coke yield and the residual rate of the carbon anode in CO₂ or air increase first and then decrease.

1. INTRODUCTION

The prebaked anode is mainly used for the production of electrolytic aluminum by the Hall–Héroult process. Given the large-scale production of electrolytic cells, the aluminum electrolysis technology is developing in the direction of high efficiency, energy saving, and carbon reduction consumption, which results in high requirements for the quality of carbon anodes for aluminum electrolysis. The carbon anodes used in aluminum production are manufactured by carbonization of a blend of petroleum coke with a small proportion of coal tar binder pitch. Pitch coke is generated by pyrolysis of coal tar pitch, the pyrolysis behavior of pitch is a key factor, and the pitch coke reactivity directly determines the carbon anode performance. Scholars have investigated trace elements and additives for enhancing the pitch coke performance. The pyrolysis process of pitch can be analyzed by thermogravimetry, but the mass of the pitch is excessively small and its composition fluctuates greatly. The quality of pyrolysis samples must be increased to make the pyrolysis process meet the actual environment of carbon anodes and investigate the influences of trace elements. In this study, a self-made pyrolysis device is used to determine the effects of pitch mass and heating rate on large mass pitch (LMP) pyrolysis as well as the effects of Na, Ca, and Mg on pyrolysis kinetics. The results are close to the pyrolysis environment of pitch in the industrial production of carbon anodes. This work provides a scientific basis for trace element control in carbon anode production.

2. EXPERIMENTAL PROCEDURE

2.1. Materials. Table 1 shows the chemical composition of coal tar pitch obtained from the Carbon Factory of Chalco Guizhou Branch.

| Property               | Value  |
|-----------------------|--------|
| Softening point (°C)  | 112    |
| Quinoline insoluble (%) | 8.8    |
| Toluene insoluble (%) | 28.4   |
| β-resin insoluble (%) | 19.6   |
| Coking value (%)      | 57.8   |

Table 2 and 3 present the composition and size distribution of coke obtained from the same factory. The pitch/coke ratio was set as 15/100 wt % for preparing anode paste.

2.2. Experimental Procedure. 2.2.1. Designing of LMP Pyrolysis Device. The mass of test samples should be increased...
to study the pyrolysis process of pitch in the internal pitch of carbon anode and the influences of trace elements. A homemade pyrolysis device is used in this study (Figure 1).

The test sample is placed in a corundum crucible, which is then placed in a corundum device and suspended on the hook of the measurement mass at the bottom of an electronic balance. The mass data are transmitted to a computer in real time via an electronic balance with software. The temperature of the sample test is measured using a thermocouple. The temperature data are then transferred to a computer in real time via an electronic balance with software. The temperature and mass data is achieved by simultaneous collection of mass and temperature data.

Pitch pyrolysis evaporation is conducted under a certain pressure environment to simulate the roasting of the green anode. This study also uses a blower for negative pressure environment to simulate the roasting of the carbon anode and the influence of trace elements. A homemade pyrolysis device is used in this study (Figure 1).

Table 3. Size Distribution of Coke Particles Used for Carbon Anodes

| size range (mm) | wt % |
|----------------|------|
| <0.15          | 30   |
| 3–0.15         | 45   |
| 6–3            | 13   |
| 8–6            | 12   |

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3. RESULTS AND DISCUSSION

3.1. Volatiles Release Analysis of the Anode Baking Process. The schematic of volatiles release analysis in the anode baking process is shown in Figure 2. The green anode is filled with filler coke in the open ring roasting furnace box. Under the negative pressure of a certain fire flue, the pitch in the raw block is heated and decomposed from the volatiles parts, that is, from the vertical seam of the fire channel to the fire flue. The volatile parts are burned to generate heat. The

Figure 1. Schematic drawing of the LMP pyrolysis process.

Figure 2. Schematic drawing of volatiles release analysis in the anode baking process.
heat is transmitted from the fire flue to the material box, brick wall, filling coke, carbon anode surface, and carbon anode inside. This transmission causes the temperature of the carbon anode surface to be higher than that of inside the carbon anode.

During roasting, the pitch on the surface of the carbon anode evaporates first, and the pitch inside the carbon anode evaporates later. The closer the pitch is to the central part, the later it evaporates. The closer the central pitch escapes, the greater the resistance that needs to be overcome. This increased resistance is caused by the increasing thickness of the carbon anode product layer, as shown by the a–b–c–d baking process in Figure 2. The carbon anode size is large, that is, it can reach 1600 mm × 700 mm × 620 mm; consequently, the internal volatile escape resistance of the carbon anode is high.

The quality of conventional thermal weight analysis is considerably low, and the resistance is also low. In actual carbon anode production, the pyrolysis of the green anode surface pitch can be used as a reference for a conventional TG analysis law.

The pitch in the internal area of the green anode is affected by several factors, such as postcalcined coke granules, coke powder, sulfur content, and trace elements. Therefore, the mass of the pyrolysis samples must be increased to study the effects of these factors on the pyrolysis of pitch.

3.2. Effect of Mass and Heating Rate on the LMP Pyrolysis Process. The weight loss curves of different pitch masses (20, 30, and 50 g) are shown in Figure 3. With increasing pitch mass, the trend of weight loss in the pyrolysis process is similar, but the coking rate of pitch at 1050 °C is decreased from 61.14 to 57.94%. When the experimental mass of the pyrolysis samples must be increased to study the effects of these factors on the pyrolysis of pitch.

Figure 3. TG curves of different pitch masses at 5 °C/min.

3.3. Kinetic Analysis for SMP and LMP Pyrolysis. The pyrolysis reactions of pitch are very complex. The overall reaction is decomposed into volatiles and residual solid to simplify the modeling. The reaction rate can be represented as

\[
\frac{da}{dt} = K(1 - a)^n
\]

where \(a\) is the shape factor (for amorphous carbon, it is 0.90), \(\lambda\) is the X-ray wavelength, \(\theta\) is the Bragg angle, and \(B\) is the full width at half maximum of the peak in radians.

The distance between the aromatic layers (\(d_{002}\)) in pitch is estimated by Bragg’s law

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

As the heating rate increases, the average height (\(L_c\)) gradually decreases, whereas the distance among the aromatic layers (\(d_{002}\)) gradually increases. The heating rate has a great influence on the microstructure of pitch coke and should be selected carefully in accordance with the actual situation. To sum up, the heating rate of the pyrolysis process is selected as 5 °C/min.

Figure 4. (a) TG curves and (b) X-ray diffraction (XRD) curves of LMP pyrolysis at different heating rate.
where $\alpha$ is the rate of weight loss, $t$ is the reaction time, $n$ is the reaction order, and $K$ is the reaction rate constant. The rate constant can be expressed in the Arrhenius form

$$K = A \exp(-E/RT)$$

where $A$ is the pre-exponential factor, $E$ is the activation energy, $R$ is the universal gas constant, and $T$ is the absolute temperature of the sample.

At a constant heating rate ($\phi = \text{dT}/\text{dt}$), the substitution of eq 2 into eq 1 provides the following expression for the reaction rate

$$\frac{\text{d} \alpha}{\text{d} t} = A \exp(-E/RT)(1 - \alpha)^n / \phi$$

Equation 3 can be written as

$$\frac{\text{d} \alpha}{(1 - \alpha)^n} = A \exp(-E/RT) \frac{\text{d} t}{\phi}$$

Equation 4 points can be obtained as

$$\int_0^\alpha \frac{\text{d} \alpha}{(1 - \alpha)^n} = A / \phi \int_0^T \exp(-E/RT) \text{d} T$$

When the reaction order is not 1, eq 5 can be approximated as

$$[1 - (1 - \alpha)^{1-n}] / (1 - n) T^2 = A R (1 - 2RT/E) \exp(-E/RT) / (\phi E)$$

Logarithmic treatment can be obtained as

$$\ln[\{1 - (1 - \alpha)^{1-n}] / (1 - n) T^2\} = \ln[A R (1 - 2RT/E) / (\phi E)] - E / RT$$

Equation 7 can also be represented as

$$\ln[\{1 - (1 - \alpha)^{1-n}] / (1 - n) T^2\} = a + b / T$$

where $a = \ln[A R (1 - 2RT/E) / (\phi E)]$ and $b = -E/RT$.

The weight loss curves of SMP and LMP pyrolysis processes are shown in Figure 5. Compared to SMP, the pyrolysis kinetic model is consistent with the experimental data and the actual situation of the pyrolysis process of LMP. With the best linear pyrolysis data, the apparent activation energy can be calculated using the line slope of $b$ values (Table 4). In accordance with the actual preparation conditions for the carbon anode, the coke value (CV) at 1050 °C can be directly determined through the test results in Table 4.

The SMP pyrolysis results show that the apparent activation energy is 48.62 kJ/mol and the CV is 40.78% (Table 4). The LMP pyrolysis results show that the apparent activation energy is 128.46 kJ/mol and the CV is 59.87%.

In summary, the apparent activation energy, volatile escape resistance, and coke yield of LMP are higher than those of SMP. SMP is similar to the surface pitch pyrolysis environment of the carbon anode for the aluminum electrolysis industry, whereas LMP is similar to the internal pyrolysis environment.

### 3.4. Effect of Trace Element Content on the LMP Pyrolysis Process

A certain amount of trace elements is added to the pitch to investigate the effects of trace elements on pyrolysis kinetics. The experimental scheme is shown in Table 5. LMP pyrolysis equipment is used in the experiment for determination, and the experimental data are analyzed using the method for LMP pyrolysis. The LMP pyrolysis process from 400 to 600 °C is treated using eq 8. The test results obtained using the curve of $\ln[\{1 - (1 - \alpha)^{1-n}] / (1 - n) T^2\}$ versus $1/T$ are shown in Table 6. The linear fitting coefficient is greater than 0.99, which indicates that the pyrolysis kinetic model is consistent with the experimental data and the actual situation of the pyrolysis process of LMP. With the best linear pyrolysis data, the apparent activation energy can be calculated using the line slope of $b$-values (Table 6). The CV at 1050 °C can be directly read using the test results shown in Table 6.

### 3.5. Effect of Trace Element Content on the Carbon Anode Reactivity

The effect of sodium content on the carbon anode reactivity in CO$_2$ or air is shown in Figure 7a,b. As the Na element content increases, the carbon anode residue in CO$_2$ first increases and then decreases, reaching the maximum value of 58.92% at 500 mg/kg. Under this experimental condition, the content of Na is increased in moderation, and the reactivity of the carbon anode is improved.

The effect of the Na element content on the apparent activation energy of the pitch pyrolysis process is shown in Figure 7c. With increasing Na content, the apparent activation energy for LMP pyrolysis increases from 128.46 to 162.91 kJ/mol.
The effect of the Na content on the coking rate of LMP pyrolysis is shown in Figure 7d. As the Na element content increases, the LMP pyrolysis is the first increase and decreases; it is increased to 61.73% in 500 mg/kg, and the increase value is 1.86%.

The effect of the Ca content on the carbon anode reactivity in CO2 or air is shown in Figure 8a,b. As the Ca element content increases, the carbon anode residue in CO2 first increases and then decreases, that is, from 75.48 to 77.04% and then to 71.17%. This result is consistent with the trend in literature.18 The carbon anode residue in air also first increases and then decreases, reaching the maximum value of 59.9% at 500 mg/kg. This finding is also consistent with the trend in literature.18 Under this experimental condition, the content of Ca is increased in moderation, and the reactivity of the carbon anode is improved.

The effect of the Mg content on the carbon anode reactivity in CO2 or air is shown in Figure 9a,b. With increasing Mg content, the carbon anode residue in CO2 first increases and then decreases, that is, from 75.48 to 82.41% and then to 81.72%. The carbon anode residue in air also first increases and then decreases, reaching the maximum value of 61.82% at 500 mg/kg. Under this experimental condition, the content of Ca is increased in moderation, and the reactivity of the carbon anode is also improved.

The effect of the Mg content on the apparent activation energy of LMP pyrolysis is shown in Figure 9c. With increasing Mg content, the apparent activation energy also increases from 128.46 to 146.10 kJ/mol. The effect of the Mg content on the coking rate of the LMP pyrolysis process is shown in Figure 9d. As the Mg element content increases, the LMP pyrolysis is the first increase (to 61.07% in 300 mg/kg) and decrease.

To sum up, trace elements, namely, Na, Ca, and Mg, improve the apparent activation energy and coking rate of LMP pyrolysis.

Table 4. Linear Fit, Activation Energy, and Coke Value of SMP and LMP Pyrolysis Reactions

| sample     | a       | b       | R²     | n   | Eₐ (kJ/mol) | CV (%) |
|------------|---------|---------|--------|-----|-------------|--------|
| SMP/8 mg   | −4.501  | −847.910| 0.997  | 4.8 | 48.620      | 40.78  |
| LMP/30 g   | 3.353   | −15 450.58| 0.996  | 1.5 | 128.46      | 59.87  |

Table 5. Scheme of Adding Trace Elements to LMP

| sample     | pitch mass (g) | adding element | add mass (mg/kg) |
|------------|----------------|----------------|------------------|
| 0          | 30             | 0              | 0                |
| 1          | 30             | Na             | 300              |
| 2          | 30             | Na             | 500              |
| 3          | 30             | Na             | 1000             |
| 4          | 30             | Ca             | 300              |
| 5          | 30             | Ca             | 500              |
| 6          | 30             | Ca             | 1000             |
| 7          | 30             | Mg             | 300              |
| 8          | 30             | Mg             | 500              |
| 9          | 30             | Mg             | 1000             |

Table 6. Linear Fit, Activation Energy, and Coke Value of LMP pyrolysis reactions

| sample     | a       | b       | R²     | n   | Eₐ (kJ/mol) | CV (%) |
|------------|---------|---------|--------|-----|-------------|--------|
| 0          | 3.353   | −15 450.58| 0.996  | 1.5 | 128.46      | 59.87  |
| 1          | 7.599   | −18 672.35| 0.996  | 4.3 | 155.24      | 60.57  |
| 2          | 8.553   | −19 431.25| 0.996  | 5.7 | 161.55      | 61.73  |
| 3          | 7.224   | −18 392.57| 0.995  | 4.1 | 162.91      | 61.13  |
| 4          | 5.936   | −17 415.17| 0.995  | 5.0 | 144.79      | 61.57  |
| 5          | 7.297   | −18 410.90| 0.993  | 5.3 | 153.07      | 61.60  |
| 6          | 8.528   | −19 338.12| 0.998  | 5.2 | 160.78      | 61.37  |
| 7          | 4.724   | −16 554.75| 0.996  | 2.7 | 137.64      | 61.07  |
| 8          | 4.844   | −16 620.19| 0.995  | 2.1 | 138.18      | 61.00  |
| 9          | 7.280   | −18 830.08| 0.997  | 4.0 | 146.10      | 60.30  |

Figure 8. Effect of the Ca element content on the carbon anode reactivity and LMP pyrolysis process: (a) residual rate of the carbon anode in CO2, (b) residual rate of the carbon anode in air, (c) apparent activation energy of the LMP pyrolysis process, and (d) coke value of the LMP pyrolysis process.

Figure 7. Effect of the Na element content on the carbon anode reactivity and LMP pyrolysis process: (a) residual rate of the carbon anode in CO2, (b) residual rate of the carbon anode in air, (c) apparent activation energy of the LMP pyrolysis process, and (d) coke value of the LMP pyrolysis process.

Figure 9. Effect of the Mg element content on the carbon anode reactivity and LMP pyrolysis process: (a) residual rate of the carbon anode in CO2, (b) residual rate of the carbon anode in air, (c) apparent activation energy of the LMP pyrolysis process, and (d) coke value of the LMP pyrolysis process.
LMP coking. These elements ultimately affect the carbon anode reactivity in CO₂ or air, and the effect trend is consistent.

4. CONCLUSIONS

(1) The pyrolysis of carbon anode surface pitch can be used as a reference for the kinetic data of SMP. The pyrolysis of the pitch inside the carbon anode can draw on the kinetic data of LMP. The pyrolysis process of SMP and LMP conforms to the same dynamic model. The reaction series of the SMP specimen is 4.8 grade, the apparent activation energy is 48.62 kJ/mol, the reaction series of the LMP specimen is 1.5 grade, and the apparent activation energy is 128.46 kJ/mol. The mass and heating rate of LMP have obvious influences on the pyrolysis process of LMP and should be selected in accordance with the actual situation.

(2) With increasing trace element content, the apparent activation energy of LMP pyrolysis gradually increases, and the coke yield and the residual rate of the carbon anode in CO₂ or air first increase and then decrease. The reactivity of the carbon anode can be improved by adding a certain amount of Na, Ca, and Mg.

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Notes
The authors declare no competing financial interest.

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