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## Effect of Nickel Content on Carbon Anode Reactivity

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In order to ascertain the impact of nickel content on carbon anode reactivity, different nickel content of carbon anodes were prepared with the single factor experimental method and test its reactivity in CO<sub>2</sub> and air atmosphere respectively. The microstructure of carbon anodes and pitch cokes were tested by XRD. The pitch pyrolysis process was tested with TG-DTG method. The results show that the bulk density of carbon anode can be improved, the rate of residual and chalking of carbon anode can also be significantly improved, even a small increase in Ni content. Nickel can refine the crystallite size of carbon anode and pitch coke, promote the asphalt carbonization. Nickel can increase the apparent activation energy of asphalt pyrolysis process to 52.964 KJ/mol, increase the rate of pitch coke yield and reaction order is 4.7.

**Keywords:** Carbon anode, Pitch coke, Nickel, CO<sub>2</sub> reactivity, Air reactivity.

### INTRODUCTION

Hall-Hérault process is the only method currently used to produce aluminum in the primary aluminum industry [1]. Carbon anodes are used in alumina electrolysis to produce aluminum. The baked anodes are placed in an electrolysis cell and their quality directly influences the operation conditions and tech-economic data of the aluminum electrolysis cells [2]. The anodes are used as sacrificial electrodes in the aluminum smelting process. Carbon anodes should be oxidation-resistant in gaseous environments in order to minimize losses due to air oxidation on the surface of the exposed piece and carbon oxidation caused by the carbon dioxide generated during the aluminum production. The theoretical consumption of the anode is 334 kg of C/ton of aluminum. Because of the high operating temperature in the reduction cell, excess anode consumption from gasification with carbon dioxide generated by the electrolysis reaction and gasification with oxygen are significant contributors to additional carbon consumption above the theoretical value.

Carbon anodes are made from a mixture of petroleum coke, coal tar pitch and recycled anode butts. The pitch coke will be generated with the pyrolysis processing of coal tar pitch, the pitch pyrolysis process is a key factor [3-6], the pitch coke reactivity will directly determine the carbon anode performance.

In the existing literature, there are a several studies on asphalt modified [7-14], trace elements [15-18] and additives [19] for the pitch coke performance.

The quality of the petroleum coke is dependent upon the quality of the crude oil feed stocks used during petroleum refining and upon coke-processing parameters. The current trend in petroleum refining indicates a continued increase in sulfur content and trace elements as refiners increase their use of sour crude feed stocks. Because of declining petroleum coke quality, the quality of carbon anodes has been seriously influenced by increased the trace elements content and the impact of nickel element content remains poorly understood.

This paper aims at assessing the influence of nickel content on carbon anode reactivity. In this works, the different Ni content of carbon anodes were prepared with the single factor experimental method and test its reactivity in CO<sub>2</sub> and air atmosphere respectively. The microstructure of carbon anodes and pitch cokes were tested by XRD. The pitch pyrolysis process was tested with the TG-DTG method.

### EXPERIMENTAL

The raw materials were obtained from the Carbon Factory of Chalco Guizhou Branch. Chemical compositions of the coke and pitch properties are given in Tables 1 and 2, respectively.

TABLE-1  
CHEMICAL COMPOSITION OF COKE  
USED FOR ANODE FABRICATION

| S (%) | Na (ppm) | Ni (ppm) | Ca (ppm) | Si (ppm) | V (ppm) | Mg (ppm) |
|-------|----------|----------|----------|----------|---------|----------|
| 2.98  | 370      | 210      | 570      | 500      | 480     | 100      |

TABLE-2  
PROPERTIES OF COAL TAR PITCH USED  
AS BINDER IN ANODE SAMPLES

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

The coke was classified into desired size fractions and a fine fraction was made using a ball mill. Table-3 shows the size distribution of coke particles used for making the anode paste. The pitch/coke ratio was 15/100 for all samples.

TABLE-3  
SIZE DISTRIBUTION OF COKE  
PARTICLES IN PASTE SAMPLES

| Size range (mm) | 8~6 | 6~3 | 3~0.15 | <0.15 |
|-----------------|-----|-----|--------|-------|
| Wt. %           | 12  | 13  | 45     | 30    |

**Sample preparation:** In order to ascertain the impact of nickel on carbon anode, different Ni content of carbon anodes were prepared with the single factor experimental method by adding the amount of Ni in the form of nickel oxide 100, 200, 350, 500 and 1000 ppm. Pitch, nickel and different size fractions of coke were individually weighed and added into the mixer to avoid variation in the composition of samples. The mixer was used to mix for 10 min at 165 °C, the paste was pressed in mold press at 50 MPa to obtain cylinders of 50 mm diameter and 100 mm height. All the samples were baked under the condition of heating rate 15 °C/h, final baking temperature 1050 °C, holding time 8 h. All samples were cooled down to room temperature and stored for further testing.

**Anode characterization tests:** The bulk density can be easily obtained by comparing the volume and quality. The CO<sub>2</sub> reactivity and air reactivity of baked anodes were measured using standards ISO 12988-1 and 12988-2, respectively. Cylindrical anode samples with a diameter of 0.05 m and a height of 0.06 m were measured using the RDC-146 apparatus. The CO<sub>2</sub> reactivity involves exposing anode samples to CO<sub>2</sub> gas flow (200 L/h) for 9.5 h at 960 °C. This temperature represents the temperature of the anode bottom in an electrolysis cell. Similarly, for air reactivity measured, the same size anode samples were exposed to air (200 L/h) for 11.5 h at 550 °C which is an approximate temperature of the top of the anode in the cell during electrolysis and then cooling from 550 to 400 °C at 15 °C/h. The RDC-151 apparatus was used for air reactivity measurements.

After cooling and weighing, the samples are mechanically tumbled with steel balls in a separate piece of equipment (RDC-181, tumbling apparatus) to remove any loosely-bound particles. The total weight loss (the difference between the original sample weight and that of the residue after tumbling) can then be divided into two components: the loss due to burning and

the loss due to dusting. The remaining part is the residue rate, the weight loss expect burning loss part is the chalking rate. The higher the residue is, the lower the reactivity of anode is.

**X-ray diffraction analysis:** For X-ray diffraction analysis, pitch is grinding through the 200 mesh sieve. Pitch and different nickel contents of pitch are mixing in V-type three-dimensional mixer for 5 h, speed is 12 rpm. The pitch coke was prepared with the methods of GB/T 8727-2008, the conditions were isolated from the air, final temperature is 550 °C and holding time is 2 h. The pitch coke and carbon anode XRD analysis were conducted with a diffractometer (Philips X'Pert MPD Pro) using a CuK<sub>α</sub> target ( $\lambda = 0.15406$  nm, 40 kv and 30 mA). Measurements were made in the 2 $\theta$  range of 10-90° at a speed of 8 °/min. Samples were prepared to achieve a particle size less than 10  $\mu$ m.

**Thermal analysis:** For simultaneous thermogravimetric (TG) and derivative thermogravimetry (DTG) analyses, Pitch and different Ni contents of pitch were prepared with the same method as XRD analysis. The TG-DTG analyses were conducted with thermal analyzer equipment NETZSCH STA 449F3 using an atmospheric N<sub>2</sub> stream of 60 mL/min, while heating from room temperature to 1100 °C involved a linear temperature increase of 10 °C/min.

## CALCULATION METHODS

Pyrolysis reactions of pitch are very complex. To simplify modeling, the overall reaction decomposes into volatiles and residual solid. The reaction rate can be represented as:

$$d\alpha / dt = K(1 - \alpha)^n \quad (1)$$

where  $\alpha$ -the rate of weight loss, t-reaction time, n-reaction order, K-reaction rate constant. The rate constant can be expressed in the Arrhenius form,

$$K = A \exp(-E / RT) \quad (2)$$

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

Under a constant heating rate ( $\phi = dT/dt$ ), substitution of eqn. 2 into 1 gives the following expression for the rate of reaction:

$$d\alpha / dt = A \exp(-E / RT)(1 - \alpha)^n / \phi \quad (3)$$

Eqn. 3 can be written as:

$$d\alpha / (1 - \alpha)^n = A \exp(-E / RT) dT / \phi \quad (4)$$

Eqn. 4 points can be obtained:

$$\int_0^\alpha d\alpha / (1 - \alpha)^n = A / \phi \int_0^T \exp(-E / RT) dT \quad (5)$$

When the reaction order is 1, eqn. 5 is approximated available:

$$-\ln(1 - \alpha) = (ART^2 / \phi E)(1 - 2RT / E) \exp(-E / RT) \quad (6)$$

Logarithmic treatment can be obtained:

$$\ln[-\ln(1 - \alpha) / T^2] = \ln\{(AR / \phi E)[1 - (2RT / E)]\} - E / RT \quad (7)$$

Eqn. 7 can also be represented as:

$$\ln[-\ln(1 - \alpha) / T^2] = a + b / T \quad (8)$$

where  $a = \ln\{(AR / \phi E)[1 - (2RT / E)]\}$ ,  $b = -E/R$ .

When the reaction order is not 1, eqn. 5 can be approximated available:

$$\left[1 - (1 - \alpha)^{1-n} / (1 - n)T^2\right] = AR(1 - 2RT/E) \exp(-E/RT) / (\phi E) \quad (9)$$

Logarithmic treatment can be obtained:

$$\ln\left\{\left[1 - (1 - \alpha)^{1-n} / (1 - n)T^2\right]\right\} = \ln[AR(1 - 2RT/E) / \phi E] - E/RT \quad (10)$$

Eqn. 10 can also be represented as:

$$\ln\left\{\left[1 - (1 - \alpha)^{1-n} / (1 - n)T^2\right]\right\} = a + b/T \quad (11)$$

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

## RESULTS AND DISCUSSION

### Effect of nickel content on bulk density of carbon anode:

Fig. 1 shows the effect of nickel on bulk density of carbon anode. Fig. 1 shows that the nickel content in raw materials is 210 ppm, bulk density is  $1.461 \text{ g/cm}^3$ . With increasing content of nickel elements, bulk density increased dramatically to  $1.488 \text{ g/cm}^3$  contained 410 ppm. Then, Ni content continues to grow, increasing trend of slowing down.

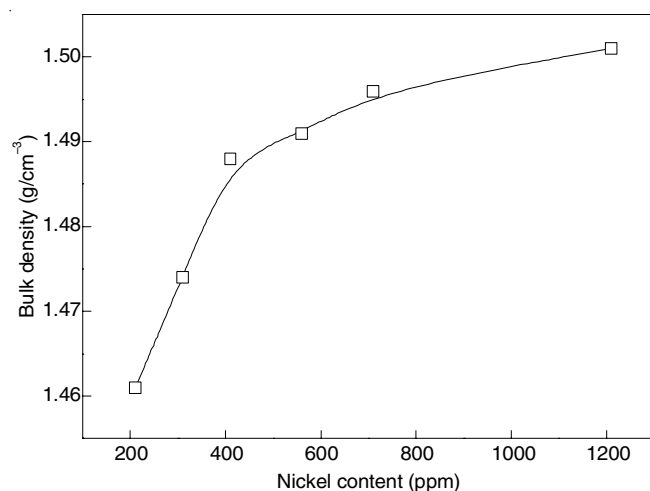


Fig. 1. Effect of nickel content on bulk density

### Effect of nickel content on residue rate and chalking rate of carbon anode:

Fig. 2 shows the changes in the residue rate in  $\text{CO}_2$  atmosphere with the increase in nickel content in the anodes. In the range of 210 to 710 ppm, with the increase of the nickel element concentration, the results shown in Fig. 1 demonstrate that the residue rate in  $\text{CO}_2$  significantly increased from 76.48 to 87.82 %. In other words, there are slow down the reaction  $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$  with the increase nickel concentration in the samples. Then, Ni content continues increasing to 1210 ppm, the residue rate in  $\text{CO}_2$  was slowly decreased to 83.07 %.

Fig. 2 also shows the changes of the residue rate in air. With the increase of the nickel concentration, the results shown in Fig. 2 demonstrate that the residue in air significantly increased from 51.87 to 66.73 %. This means that it has weakened the reaction  $\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$  with the increase nickel concentration in the carbon anodes. And, the residual in air has more rapidly increasing trend from 210 to 410 ppm.

Fig. 3 shows the changes of the chalking rate in  $\text{CO}_2$  atmosphere with the increase in nickel content in the anodes.

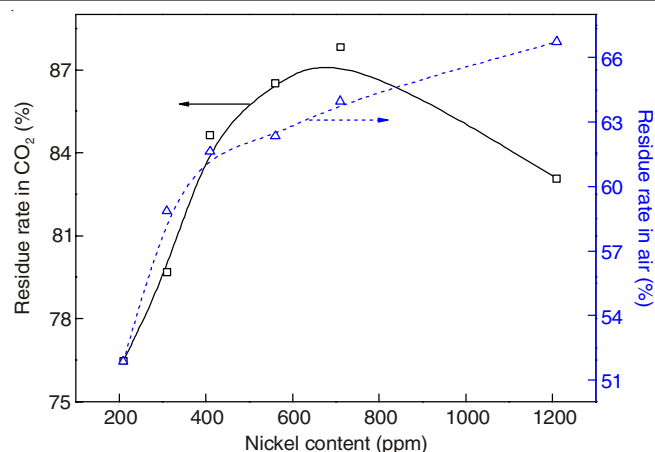


Fig. 2. Effect of nickel on residual rate in  $\text{CO}_2$  or air

The chalking rate in  $\text{CO}_2$  has rapidly declined from 210 to 710 ppm and then the chalking rate has slowly risen more than 710 ppm. Meanwhile, the chalking rate in air has existed similar trends, there is a minimum value at 410 ppm.

In summary, it can significantly improve the residual rate of carbon anode in  $\text{CO}_2$  and air atmosphere, rapidly decline the chalking rate in  $\text{CO}_2$  and air. In other words, it can significantly improve the  $\text{CO}_2$  reactivity and air reactivity of baked anodes, especially when the increase of Ni element content is less.

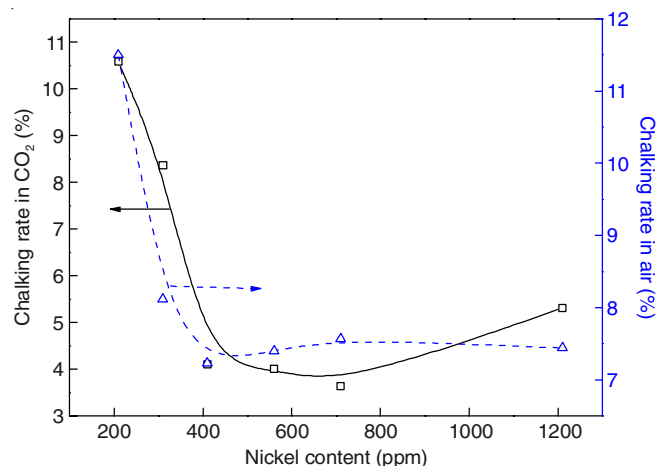


Fig. 3. Effect of nickel content on chalking rate in  $\text{CO}_2$  or air

**Crystalline structure of anodes and cokes:** XRD patterns for the anodes and cokes have previously been published [6,14]. The patterns in these studies are similar to those that have been reported in the literature for carbon electrode. All XRD patterns showed four peaks: (002), (100), (004) and (110). X-ray diffractograms of the prepared carbons and pitch cokes with and without nickel element are shown in Fig. 4.

The presence of a sharp (002) peak indicated that the composite samples have a highly ordered structure. The crystallite height  $L_c$  was estimated using the Scherrer equation  $L_c = A\lambda / (B \cos \theta)$ , where  $A$  is the shape factor (for amorphous carbon 0.90);  $\lambda$  the X-ray wavelength;  $\theta$  the Bragg angle; and  $B$  is the full width at half maximum of the peak in radians. From Fig. 4, the (002) peak becomes slightly wider and the

TABLE-4  
LINEAR FIT OF PITCH WITH OR WITHOUT ADDITION OF NICKEL

| Sample | 222-560 °C  |           |                |     | 560-1100 °C |          |                |
|--------|-------------|-----------|----------------|-----|-------------|----------|----------------|
|        | Y = a + b*x |           | R <sup>2</sup> | n   | Y = a + b*x |          | R <sup>2</sup> |
|        | a           | b         |                |     | a           | b        |                |
| P      | -4.501      | -5847.910 | 0.997          | 4.8 | -13.389     | 1408.877 | 0.997          |
| P + Ni | -4.723      | -5891.841 | 0.987          | 4.7 | -14.183     | 1601.360 | 0.994          |

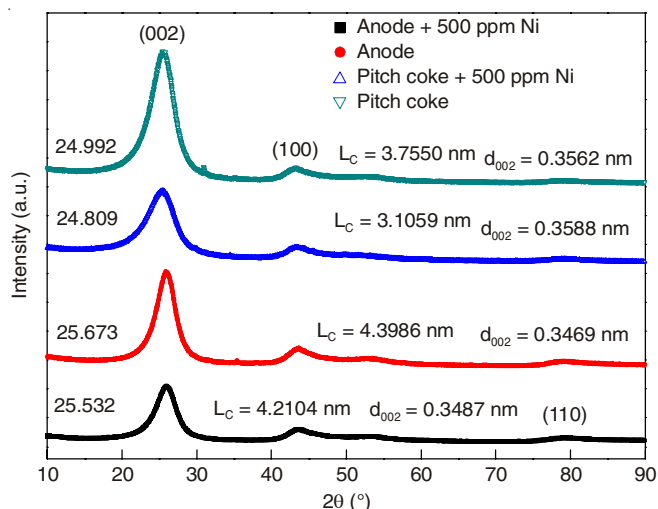


Fig. 4. XRD curves of carbon anode and pitch coke with or without addition of nickel

crystallite height  $L_c$  of anodes shows a decreasing trend with the addition of Ni from 4.3986 to 4.2104 nm and the interlayer distance  $d_{002}$  shows an increasing trend from 0.3469 to 0.3487 nm. Similarly, with the addition of Ni elements the (002) peak also becomes slightly wider, the  $L_c$  of the pitch cokes also shows a decreasing trend from 3.755 nm to 3.1059 nm and the  $d_{002}$  also shows an increasing trend from 0.3562 to 0.3588 nm.

As discussed above, with the addition of nickel, the XRD diffraction of carbon anodes and pitch cokes show that the crystallite height were refined, the carbonization degree were promoted. Maybe the hetero atoms, such as nickel element, that remain stable after the heat-treatment process act as cross-linking agents and made the microstructure more disorder [20].

**Pitch pyrolysis kinetic analysis:** Fig. 5 shows the weight loss curves of the pitch (with a “P” mark) samples with or without addition of nickel (500 ppm, with “P + Ni” mark).

When the order of reaction is 1, the correlation coefficient ( $R^2$ ) of pitch pyrolysis process from 222 to 560 °C is low using eqn. 8. In other words, the 1 of reaction order is not appropriate for the pitch pyrolysis process.

When the order of reaction is not 1, the pitch pyrolysis process from 222 to 560 °C was treated using eqn. 11. Using  $\ln\{[1-(1-\alpha)^{1-n}]/(1-n)T^2\}$  vs.  $1/T$  curve for treatment of test results, there were two linear regions in  $1/T$  for 0.002-0.0012 (222-560 °C) and 0.0012-0.00073 (560-1100 °C) (Fig. 6, Table-4). Assume the values of different reaction order, there was the best linear relationship when reaction order is 4.8. By the line slope of b-value can be calculated apparent activation energy is 48.619 KJ/mol (Table-5). Fitting a linear correlation coefficient is 0.997, indicating that the pyrolysis model in good agreement with the actual. And, intersection of the two curves is termination temperature ( $T_f$ ) 543.45 °C.

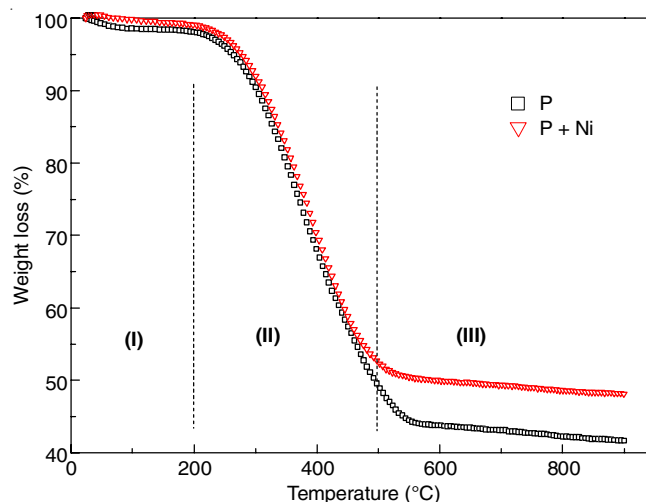


Fig. 5. Weight loss vs. temperature data of the pitch with or without addition of nickel

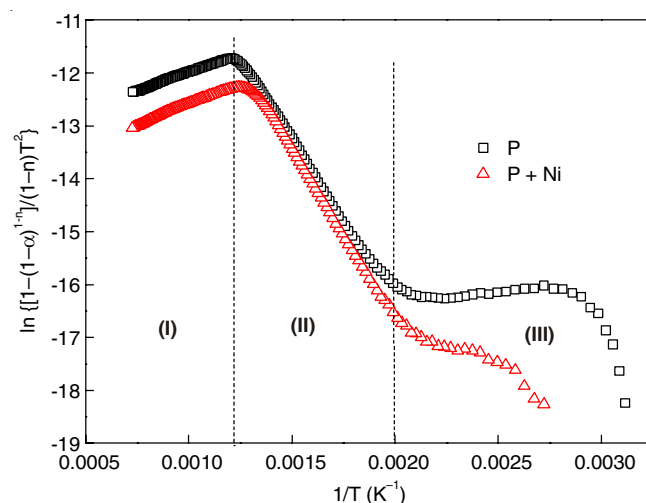


Fig. 6.  $\ln\{[1-(1-\alpha)^{1-n}]/(1-n)T^2\}$  vs.  $1/T$  curves of pitch with or without addition of nickel

TABLE-5  
TEMPERATURES ( $T_i$ ,  $T_f$  AND  $T_{max}$ ), ACTIVATION ENERGY AND COKE VALUE OF PITCH WITH OR WITHOUT ADDITION OF NICKEL ELEMENT

| Sample | $T_i$ (°C) | $T_f$ (°C) | $T_{max}$ (°C) | $E_a$ (KJ/mol) | CV (%) |
|--------|------------|------------|----------------|----------------|--------|
| P      | 206.2      | 543.45     | 383.1          | 48.619         | 40.27  |
| P + Ni | 216.7      | 519.05     | 385.3          | 52.964         | 47.20  |

Similarly, the pitch with addition of nickel the pyrolysis process was also treated using eqn. 11. The test results are shown in Fig. 6 and Table-4, including reaction order 4.7 for 222-560 °C, linear correlation coefficient 0.997 (Table-4), apparent activation energy 52.964 KJ/mol (Table-5) and termination temperature 519.05 °C.



Fig. 7 shows the DTG curves was a first-order differential TG curve, the starting temperature and peak temperature were obtained by analysis software installed instruments in Table-3. In addition, according to the actual carbon anode preparation conditions, the coke value at 1100 °C can be directly read as shown in Table-3 through the test results, also better reflected the actual situation.

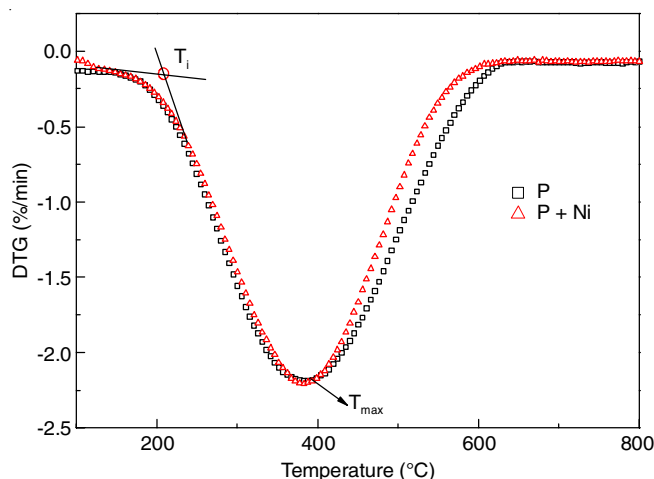


Fig. 7. DTG vs. T curves of pitch with or without addition of nickel

Experimental results show that the addition of nickel can raise the reaction starting temperature, delay the pyrolysis process, lower the reaction termination temperature, shorten the temperature range of volatile escape, increase the apparent activation energy of the pyrolysis process and increase the coke value by 6.93 %.

From the above results, the increase of nickel contents may be the main reason for the great improvement of carbon anode residual in CO<sub>2</sub> and air because it increased the apparent activation energy, increased the resistance of volatile escape, delayed the pyrolysis process, reduced the emission of volatile, maintained more fully pyrolysis process, increased the coke value, reduced the carbon anode porosity and increased the bulk density.

At the same time, the similarly trend is consistent with the finding in the literature [5]: after adding MgO particles into asphalt, the MgO particles promotes the tight charring layer generation on the asphalt surface and the layer hinders carbon particles and volatiles from releasing out of asphalt.

## Conclusion

The following conclusions are obtained from the analysis of the experimental results:

- With the increase of nickel content, especially low concentrations, the results show that the bulk density of carbon anode can be improved, the residual rate and chalking rate of carbon anode can also be significantly improved and the additional consumption of the carbon anode can be reduced.
- With the increase of nickel content, the XRD diffraction of carbon anodes and pitch cokes show that the crystallite height were refined, the carbonization degree were increased.
- With the addition of 500 ppm nickel, apparent activation energy of pitch pyrolysis process can be increased to 52.964 KJ/mol, the reaction starting temperature can be raised, the reaction termination temperature can be dropped, the coke value can be increased by 6.93 %.

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