Influence of carbonization conditions on micro-pore structure of foundry formed coke produced with char

Jun Qiao; Jianjun Wu; Jingru Zu; Zhiyuan Gao; Guoli Zhou

Abstract: There are few studies on coke’s micro-pore structure in recent years, however, micro-pore structure of foundry coke determines its macroscopically quality index and reactivity in cupola furnace. Effect of such factors on micro-pore structure were investigated under different carbonization conditions with certain ratio of raw materials and material forming process in this article as charging temperature (A); braised furnace time (B); heating rate of the first stage (C) and the second stage (D) and holding time of ultimate temperature (E). Research showed that charging temperature was the most influential factor on the coke porosity, pore volume, pore size and specific surface area. It is suggested that formation of plastic mass and releasing rate of volatile during carbonization period are two main factors on microstructure of foundry coke while charging temperature contributes most to the above factors.

Keywords: foundry formed coke; carbonization conditions; micro-pore structure

0 Introduction

Foundry formed coke is a dedicated fuel in cupola furnace. The product, with the characteristics of block degree, uniform, high strength, low porosity, low ash, low sulfur and high rate into the furnace, can make the operation stably in furnace, and improve the quality of castings. Developing the technology in foundry formed coke is an effective means to solve the shortage of high quality coking coal resources, protect the environment and use energy source rationally.

The coke whose raw materials are non/weakly caking coal, additives and adhesive, is produced after comminution, batching, mixing kneading, code-forming and carbonization. The quality of foundry coke will be determined by carbonization conditions with the same material granularity, material ratio and molding pressure. The formed coke’s micro-pore structure its macroscopically quality index and reactivity in cupola furnace. In recent years, people has done a lot of research on the formula of foundry formed coke, however, research of the influence of carbonization conditions on micro-pore structure are relatively few. In this paper, we studied the influence of carbonization conditions on micro-pore structure by changing carbonization conditions on laboratory research, explore the variation of the coke’s micro-pore structure under different carbonization conditions, and provide a theoretical foundation of formed coke’s further study.

1 Test portion

1.1 Experimental raw material

Semi-coke, made of long-flame coal in Yulin Shanxi province, was the primarily raw material in this experiment, and added some proper adhesive as auxiliary materials.
1.2 Experimental plan

Based on thermogravimetric analysis in earlier period and actual industrial production situation, we used the method of orthogonal test to investigate the effects of charging temperature(A); braised furnace time (B); heating rate of the first stage(C)and the second stage(D)and holding time of ultimate temperature (E) on micro-pore structure. Each factor drewed up 4 levels as follows, Ai: 450 °C, 500 °C, 550 °C, 600 °C; Bi: 6 h, 7 h, 8 h, 9 h; Ci: 0.5 °C/min, 0.8 °C/min, 1.0 °C/min, 1.5 °C/min; Di: 0.8 °C/min, 1 °C/min, 1.5 °C/min, 2 °C/min; Ei: 0 h, 0.5 h, 1 h, 1.5 h.

2 Result and discussion

Because of carbonization conditions were different, the regularity of foundry formed coke’s pore size distribution was not strong. Consequently, the results of this experiment were processed by intuitive analysis and variance analysis to find the influence law of various factors to the coke’s pore structure.

2.1 Intuitive analysis and variance analysis of formed coke porosity

Formed coke porosity was calculated by true density and false density. Table 1 shown its results of the analysis of pore structure under different carbonization conditions.

<table>
<thead>
<tr>
<th>Test number</th>
<th>True density (g/cm³)</th>
<th>False density (g/cm³)</th>
<th>Pore volume (cm³/g)</th>
<th>Specific area (m²/g)</th>
<th>Average pore diameter (μm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6287</td>
<td>1.1653</td>
<td>0.2442</td>
<td>1.2849</td>
<td>0.5155</td>
<td>28.45214</td>
</tr>
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<td>2</td>
<td>1.6398</td>
<td>1.1768</td>
<td>0.2399</td>
<td>1.2632</td>
<td>0.5321</td>
<td>28.235151</td>
</tr>
<tr>
<td>3</td>
<td>1.6243</td>
<td>1.1717</td>
<td>0.2378</td>
<td>1.2411</td>
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<td>0.5437</td>
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<td>5</td>
<td>1.5989</td>
<td>1.1396</td>
<td>0.2521</td>
<td>1.1967</td>
<td>0.5845</td>
<td>28.725999</td>
</tr>
<tr>
<td>6</td>
<td>1.6013</td>
<td>1.1411</td>
<td>0.2519</td>
<td>1.1755</td>
<td>0.5216</td>
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<tr>
<td>7</td>
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<td>1.1356</td>
<td>0.2551</td>
<td>1.1544</td>
<td>0.5653</td>
<td>28.967286</td>
</tr>
<tr>
<td>8</td>
<td>1.6015</td>
<td>1.1288</td>
<td>0.2615</td>
<td>1.1622</td>
<td>0.5368</td>
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<tr>
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<td>1.1159</td>
<td>0.2713</td>
<td>0.8679</td>
<td>0.6954</td>
<td>30.269325</td>
</tr>
<tr>
<td>10</td>
<td>1.6075</td>
<td>1.1158</td>
<td>0.2741</td>
<td>0.9757</td>
<td>0.8195</td>
<td>30.587869</td>
</tr>
<tr>
<td>11</td>
<td>1.5993</td>
<td>1.1185</td>
<td>0.2688</td>
<td>1.1065</td>
<td>0.5837</td>
<td>30.063153</td>
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<tr>
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<tr>
<td>13</td>
<td>1.6018</td>
<td>1.1384</td>
<td>0.2541</td>
<td>0.9408</td>
<td>0.6189</td>
<td>28.929954</td>
</tr>
<tr>
<td>14</td>
<td>1.5877</td>
<td>1.1211</td>
<td>0.2621</td>
<td>1.0984</td>
<td>0.5945</td>
<td>29.388424</td>
</tr>
<tr>
<td>15</td>
<td>1.6106</td>
<td>1.1265</td>
<td>0.2668</td>
<td>1.1332</td>
<td>0.5812</td>
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<tr>
<td>16</td>
<td>1.5993</td>
<td>1.1234</td>
<td>0.2649</td>
<td>1.1543</td>
<td>0.5363</td>
<td>29.756769</td>
</tr>
</tbody>
</table>

The intuitive analysis and variance analysis results of carbonization conditions on the porosity of formed coke were shown in Table 2, Table 3, and the porosity change tendency along with various levels was shown in Figure 1.
From Table 2, Table 3 and Figure 1, we could find that formed coke porosity had been affected most by charging temperature into the furnace, followed by holding time of ultimate temperature, then influence of braised furnace time and heating rate of the first stage and the second stage on formed coke porosity was relatively not obvious. The formed coke porosity decreased slightly after the first to rise with charging temperature from 450 °C to 600 °C; the formed coke porosity increased after the first to decrease when holding time of ultimate temperature had increased to 1.5 h from 0 h.

2.2 Intuitive and variance analysis on the pore volume of formed coke

The intuitive analysis and variance analysis results of carbonization conditions on the volume of formed coke were shown in Table 4, Table 5, and the pore volume change tendency along with various levels was shown in Figure 2.
From Table 4, Table 5 and Figure 2, we could find that the pore volume of formed coke had been affected most by charging temperature into the furnace, followed by holding time of ultimate temperature, then influence of braised furnace time and heating rate of the first stage and the second stage on the pore volume of formed coke was relatively not obvious. Pore volume decreased slightly after the first to rise with charging temperature from 450 ℃ to 600 ℃; the pore volume of formed coke increased after the first to decrease when holding time of ultimate temperature had increased to 1.5 h from 0 h.

### 2.3 Intuitive and variance analysis on the average pore diameter of formed coke

The intuitive analysis and variance analysis results of carbonization conditions on the average pore diameter of formed coke were shown in Table 6, Table 7, and the average pore diameter change tendency along with various levels was shown in Figure 3.
Table 6 The intuitive analysis of carbonization condition on average pore diameter of formed coke

<table>
<thead>
<tr>
<th>Factor</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>k1</td>
<td>0.532</td>
<td>0.604</td>
<td>0.539</td>
<td>0.612</td>
<td>0.613</td>
</tr>
<tr>
<td>k2</td>
<td>0.552</td>
<td>0.617</td>
<td>0.618</td>
<td>0.568</td>
<td>0.582</td>
</tr>
<tr>
<td>k3</td>
<td>0.718</td>
<td>0.567</td>
<td>0.591</td>
<td>0.619</td>
<td>0.613</td>
</tr>
<tr>
<td>k4</td>
<td>0.583</td>
<td>0.598</td>
<td>0.637</td>
<td>0.585</td>
<td>0.577</td>
</tr>
<tr>
<td>Range</td>
<td>0.186</td>
<td>0.05</td>
<td>0.098</td>
<td>0.051</td>
<td>0.036</td>
</tr>
</tbody>
</table>

Table 7 The variance analysis of carbonization condition on average pore diameter of formed coke

<table>
<thead>
<tr>
<th>Factors</th>
<th>Square of deviance</th>
<th>Degree of freedom</th>
<th>F ratio</th>
<th>F critical value</th>
<th>Significant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.085</td>
<td>3</td>
<td>17</td>
<td>9.28</td>
<td>*</td>
</tr>
<tr>
<td>B</td>
<td>0.005</td>
<td>3</td>
<td>1</td>
<td>9.28</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.022</td>
<td>3</td>
<td>4.4</td>
<td>9.28</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.007</td>
<td>3</td>
<td>1.4</td>
<td>9.28</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.005</td>
<td>3</td>
<td>1</td>
<td>9.28</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>0.01</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Table 6, Table 7 and Figure 3, we could find that the average diameter of formed coke had been affected most by charging temperature into the furnace, followed by heating rate of the first stage, then influence of holding time of ultimate temperature, braised furnace time and heating rate of the second stage on the average diameter of formed coke was relatively not obvious. Average diameter decreased slightly after the first to rise with charging temperature from 450 °C to 600 °C; the average diameter of formed coke was overall showing an upward tendency when heating rate of the first stage increased to 1.5 °C/min from 0.5 °C/min.

2.4 Intuitive and variance analysis on the specific area of formed coke

The intuitive analysis and variance analysis results of carbonization conditions on the specific area of formed coke were shown in Table 8, Table 9, and the specific area tendency along with various levels was shown in Figure 4.
Table 8 The intuitive analysis of carbonization condition on specific area of formed coke

<table>
<thead>
<tr>
<th>Factor</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>1.229</td>
<td>1.073</td>
<td>1.18</td>
<td>1.09</td>
<td>1.139</td>
</tr>
<tr>
<td>K2</td>
<td>1.172</td>
<td>1.128</td>
<td>1.103</td>
<td>1.118</td>
<td>1.11</td>
</tr>
<tr>
<td>K3</td>
<td>0.943</td>
<td>1.159</td>
<td>1.092</td>
<td>1.142</td>
<td>1.045</td>
</tr>
<tr>
<td>K4</td>
<td>1.082</td>
<td>1.066</td>
<td>1.049</td>
<td>1.075</td>
<td>1.132</td>
</tr>
<tr>
<td>Range</td>
<td>0.286</td>
<td>0.093</td>
<td>0.131</td>
<td>0.067</td>
<td>0.094</td>
</tr>
</tbody>
</table>

Table 9 The variance analysis of carbonization condition on specific area of formed coke

<table>
<thead>
<tr>
<th>Factors</th>
<th>Square of deviance</th>
<th>Degree of freedom</th>
<th>F ratio</th>
<th>F critical value</th>
<th>Significant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.187</td>
<td>3</td>
<td>11.333</td>
<td>4.76</td>
<td>*</td>
</tr>
<tr>
<td>B</td>
<td>0.024</td>
<td>3</td>
<td>1.455</td>
<td>4.76</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.036</td>
<td>3</td>
<td>2.182</td>
<td>4.76</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.011</td>
<td>3</td>
<td>0.667</td>
<td>4.76</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.022</td>
<td>3</td>
<td>1.333</td>
<td>4.76</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>0.03</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Table 8, Table 9 and Figure 4, based on the intuitive analysis and variance analysis of specific area and the changement of specific area with various levels, we found that mutual influence of carbonization on formed coke specific area was obvious. Charging temperature affected the specific area mostly, the specific area first decreased and then increased with the increase of charging temperature.

Figure 4 Influence of carbonization condition on specific area of formed coke

2.5 Theoretical Explanation

From the above-mentioned analysis, we found charging temperature had been the most important factor in carbonization conditions on the coke porosity, pore volume and average diameter. It could be explained as follows: when the briquette had been put into the furnace, because of opening the furnace door and in-material, large amount of heat escaped from the furnace. The actual temperature in the furnace might be only 380 °C, or even lower after
closing the furnace door. Moreover, the briquette and mould were also required to absorb a lot of heat with the furnace to achieve a new balance. Hence the temperature continued to reduce over a period of time. At this moment, the actual temperature was lower than 390 °C which only asphalt could be fully softened in molten state and a lot of volatile matter released, however, liulin coking coal and balougou gas coal had not started to soften and melt. With the charging temperature raised from 450 °C to 550 °C, the temperature of braise furnace was also higher, volatile of asphalt released more and quicker, which brought on the formation of some big pores and cracks, and also resulted in the decrease of softening melting materials and the shortage of flow plastic mass which impacted the process of coke forming. This explained the formed coke porosity also improved while braised furnace temperature raised from 450 °C to 550 °C. But if we increased it to 600 °C, after putting briquette into the furnace and closing the door, furnace temperature was in the range of 450 °C to 550 °C in process of mould, briquette and furnace re-balancing. Further more, this temperature range was just the mass loss areas of liulin coking coal and balougou gas coal, which accounted for the softening and melting of liulin coking coal and balougou gas coal at this temperature. Together with the softened and melt asphalt, briquette had entered the glial precursor stage ahead at this time, which slowed down cracks and pores' formation caused by substantial precipitation of the asphalt volatile. Replaced by the relatively release of plastic mass co-formed form asphalt, liulin coking coal and balougou gas coal, it was helpful to the process of coking. Accordingly, formed coke porosity has a certain drop with charging temperature raised from 550 °C to 600 °C, but still bigger than 500 °C into the furnace. It shown that liulin coking coal and balougou gas coal in advance to enter the stage of plastic mass had slowed down the formation of big pores and cracks, but the asphalt on the effects of porosity are the most important. If the temperature increases further, briquette may get softened, cracked and collapsed quickly in high temperature.

Influence of holding time of ultimate temperature was only next to charging temperature on the porosity and pore volume of formed coke. It could be understood that volatile had not precipitated completely at the temperature of 1100 °C. It was helpful to the precipitation of the remaining volatile and the coke polycondensation completely staying at the ultimate temperature for a while. Therefore, formed coke porosity had a certain decline when holding time raised from 0 h to 1 h. The coke porosity would increase in the condition of raising holding time to 1.5 h. It was because that formed coke had continued to stay in high temperature after the completion of coke, which had resulted in the continuation of coke pyrolysis condensation, the fracture of some bridge bonds(such as C-H) and the appearance of a few new cracks. The porosity would increase slightly.

Influence of heating rate of the first stage was only second to charging temperature on the average diameter of formed coke. The weight loss rate of mix materials mainly occurs before 700 °C, consequently, the heating rate before 700 °C determined the pyrolysis rate of asphaltum and coking coal and the separating rate of volatile under the same braised temperature in the process of carbonization. The slower the heating rate was, the more sufficient the pyrolysis process was. The longer the coke stayed in the stage of plastic mass, the slower and the evener the volatile precipitated, the number of small pores would be larger and the cracks would be less.
3 Conclusions

We had studied on the influence of the carbonization on the formed coke pore structure with certain ratio of raw materials and material forming process, and drawn the conclusions as follows:

(1) The porosity and pore volume of formed coke is affected most by charging temperature into the furnace, followed by holding time of ultimate temperature, then influence of braised furnace time and heating rate of the first stage and the second stage on the pore volume of formed coke is relatively not obvious.

(2) The average diameter of formed coke is affected most by charging temperature into the furnace, followed by heating rate of the first stage, then influence of braised furnace time, heating rate of the second stage and holding time of ultimate temperature on the pore volume of formed coke is relatively not obvious.

(3) Effect of charging temperature is significant on the specific area of formed coke when the interaction of various factors is very obvious.

Reference: