Shrinkage Character in the Forming Semi-Coke

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Abstract

A mini coke oven has been used to study the shrinkage crack character in the process of semi-coke formation. The results show that the section of coke cake has clearly layered, from the inner to outward, divided into loose honeycomb semi-coke layer, small honeycomb semi-coke layer, compact semi-coke layer, cracks layer. The colour of loose honeycomb semi-coke layer and small honeycomb semi-coke layer is dark black, and its porosity about 44.8%.The colour of the compact semi-coke layer is bright black, and its porosity about 34.0%. The colour of cracks layer is silver gray, and its porosity about 46.0%. The pyrolytic plastic layer area of static and dynamics state difference, the static state pyrolytic plastic layer area is an obturation flat elliptic area, wrapped in the middle of semi-coke; the dynamic state pyrolytic plastic layer area is a placket oblate gasbag, wrapped by semi-coke from the outside. The shrinkage rate of semi-coke increases with temperature increasing, the relationship between shrinkage and temperature can be described as $Y=-7 X^2 \times 10^{-5}+0.14X-56.26$ (600℃-850℃). The thickness of semi-coke decreases, with temperature increasing, crack increases and clump decrease. Fit adding humidity of coal, the crack of semi-coke decreases and the clump increases.

Keywords: Regression model; Pulverized coal; Ignition temperature; Prediction.

1. Introduction

China hold large reserves of low rank coal resources, such as lignite, long flame coal, non-caking coal and weakly caking coal [1]. Low rank coal production proportion in the total coal utilized [1-3]. Using solid heat carrier retorting pulverized coal technology[4-7], not only obtained semi-coke, coal gas and tar products, but also a partial solution to the problem of pulverized coal utilization, which is one of the effective ways to use coal with high added value. Semi-coke is widely used in foundry coke, calcium carbide, ferroalloy, ferrosilicon, silicon carbide and other areas of production. A more in depth study of semi-coke and semi-coke process have become a hot spot in recent years.

In addition, with the development of industry and the increase in the vehicle as well as a large number of coal-fired power generation, more and more nitrogen oxide, carbon dioxide and methane are emitted into the atmosphere causing air pollution. It caused a wide range of concern. In order to control nitrogen oxide, carbon dioxide and methane emissions, extensive research had been done, to seek an economic and efficient reducing agent transforming carbon dioxide and nitrogen oxides into the resources and N2. Semi-coke has aroused keen interest because of its efficient deoxidation capacity and cheap price. In addition as a reducing agent, the semi-coke can be as a catalyst or catalyst carrier in carbon dioxide - methane reforming and NOx removal process [8-12].

Semi-coke is irregular porous body containing cracks and defects, the carbon as a main component. Semi-coke is made by charging coal into hot ovens, usually in the temperature range 350-500 ℃. Layers of plastic coal are formed parallel to the heated oven surfaces and these move progressively towards the

oven center as carbonisation proceeds. Coke oven gas from the pyrolysing coal into the plastic mass results ultimately in the porous structure of coke. Thus shrinkage occurs on transforming coal to coke. Differential shrinkage of various layers after resolidification of the plastic coal to form semi-coke, causes stresses to be set up which, if they exceed the breakage stress of the material, cause fissures to form. It is this network of fissures which controls the mean size of the coke lumps produced and influences their breakage in subsequent use [13]. However, even today to date, the mechanism of the semi-coke fissure formation did not have a complete understanding.

In this paper, we describe the results of a series of laboratory scale coke oven experiments that were designed to investigate the nature of the fissure formation process. The objectives are to obtain the shrinkage fissure characters in the process of semi-coke formation, to provide a theoretical basis for the preparation of the catalyst of nitrogen oxide reduction and $CO_2 – CH_4$ reforming.
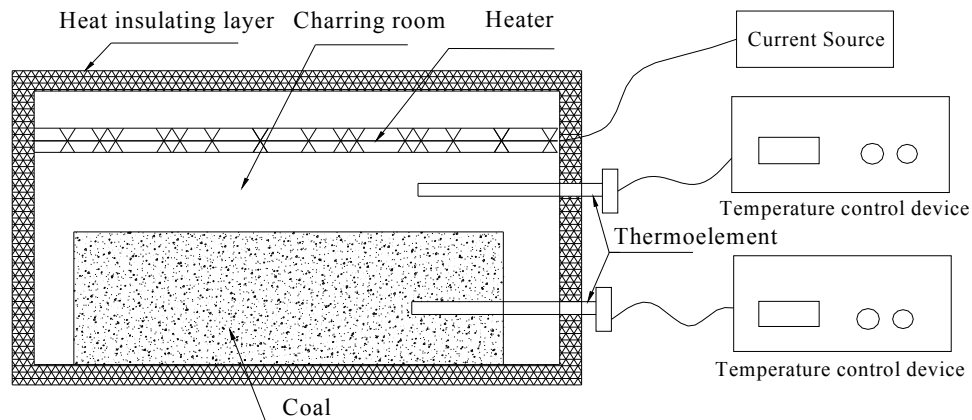
2. Experimental

Fig. 1. Schematic diagram of experiment apparatus

To examine the coke fissures an experimental coke oven was devised whose construction simulated the main parameters of industrial coking (Fig. 1). The temperature of the flue walls was adjusted by a fully automatic programming system. A charge box, made from steel and insulating-board, was packed with air-dried coal sized. A thermocouple was placed at the center of the half oven width to measure the average final carbonization temperature.

To examine the fissure network, five coal types were used. Their analyses and characteristics are summarized in Table 1.

Before transfer into the oven, the feed coals were ground to 80% minus 2 mm and adjusted to 10% moisture by addition of water. First, a rack made of chromium-nickel steel (later used for withdrawing the coke) was introduced into the oven. Then tilling of the oven began, during which the charge was compressed as evenly as possible to arrive at an initial bulk density of 800 kg/m^3. The charge amounted to 1470-155 g of damp coal. Cokes were carbonised at 5 °C/min to final temperatures of 750 and 850 °C, measured at the centre of the half oven width for coal. Once the desired temperature in the centre of the oven was attained, heating was stopped and the charge box was taken out and quenched immediately by means of quartz sand. After cooled，the samples were analyzed.

Table 1 Proximate analyses of samples

| Sample	Proximate analysis w/%			Blended ratio, w/%
	A_d	V_{daf}	FC_{daf}	
Xiongfeng	9.97	25.20	74.80	35
Jinyang	14.38	26.86	73.14	25
Jinfen	10.26	31.56	68.44	10
Changsheng	11.92	19.20	80.80	15
1/3coking coal	9.58	34.10	65.90	15
Blended Coal	11.34	26.69	73.31	

3. Results and discussion

3.1 The heating rate of coal in coking chamber

Temperature conditions in a coal charge during coking depend on the location towards heating walls of a coke oven. In general, temperature distribution in a coal charge during coking process is mainly connected with the location towards heating walls and with the time of coking. Three zones have been distinguished in relation to their position toward heating walls of coking chamber: zone 1- close to the heating wall, zone 2 - the middle area and zone 3 - close to the bottom. The temperature field in a coal charge during coking in a coke oven has been intensively studied. The heating rate of coal in coking chamber has been shown in Fig. 2. It is obvious, that the temperature is one of the most important parameters of coking process. As one can see in Fig. 2, coal heated in a coking chamber has a non-uniform distribution of a temperature. The heating rate of the coal charge strongly decreased from the heating walls to the central axis of the coke oven. The coal charge close to the chamber wall is heated quickly. The highest heating rate of coal is about 450℃/h within 1h, then heating rate become gradually stationary is about 65℃/h. Whereas in the central part of an oven chamber the heating rate is much lower. The heating rate of coal is in the central part of an oven chamber is 120℃/h. This means that the coke close to chamber walls is kept in the high temperature almost three times longer than that in the central part of coking chamber. Such different temperature conditions of coking process have to affect properties of resultant semi-coke [14].

3.2 semi-coke layer

To analyse the fissure network, photographs were taken of the coke cake, which are shown in Fig. 3. It is obvious, as one can see in Fig. 3, cross-section of coke cake forms an obvious layer-belt. Out from the center of coke cake, it can be divided into loose honeycomb semi-coke layer, small honeycomb semi-coke layer, compact semi-coke layer and fissures layer. The porosity of layer climb up and then decline. The color of loose honeycomb semi-coke layer is atrous. The color of fine honeycomb semi-coke layer is black and the porosity is 44.8%. The color of compact semi-coke layer is glossy black and the porosity is 34.0%. The color of fissures layer is silver gray and the porosity is 46.0%. It is mainly because of: 1) the coal heated, the coal starts to rapidly expand, pore size and porosity increase; 2) upon further heating, liquid plastic mass generation enters pore, and bond-breaking reactions that occur in the coal structure at the same time, which lead porosity decreases. During further heating, coal resolidification, some volatiles leave from pores, pore size of semi-coke changed very little, porosity increases. The fissure would be widened and enlarged; no further larger fissures would develop.
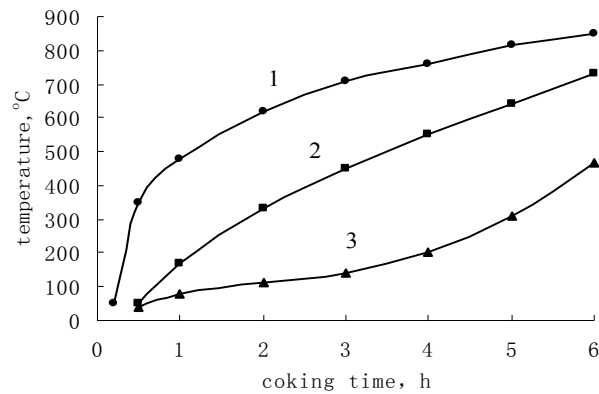
1 The coal temperature close to the chamber wall, 2 Coal temperature close to the coking chamber center, 3 The coal temperature of box bottom

**Fig. 2.** Temperature distribution in a coal charge during coking process

Fig. 3. Photographs of coke cake in 850^0C

3.3 The characteristics of plastic mass bag of coke cake

The coal to semi-coke transformation takes place as follows (Fig. 4): the heat is transferred from the heat brick walls into the coal charge (Fig. 4 A), the coke cake heated become soft. From about 375 ℃ to 475 ℃, the coal decomposes to form plastic mass bag in the middle of coal charge. At about 475℃ to 600℃, there is a marked evaluation of tar, and aromatic hydrocarbon compounds, followed by resolidification of the plastic mass into coke cake with cavity(Fig. 4 B). This is characterized by contraction of the coke mass. During the plastic stage, the plastic layers move from each wall towards the center of the oven tapping the liberated gas and creating in gas pressure build up which is transferred to the heating wall. Once, the plastic layers have met at the center of the oven, the entire mass has been carbonized.

The study found that plastic mass bags can be formed when coal is heated (Fig. 4). But the pyrolytic plastic layer area of static and dynamics state are difference, the static state pyrolytic plastic layer area is an obturation flat elliptic area, wrapped in the middle of semi-coke(Fig. 4 B); the dynamic state pyrolytic plastic layer area is a placket oblate gasbag, wrapped by semi-coke from the outside(Fig. 4 C).
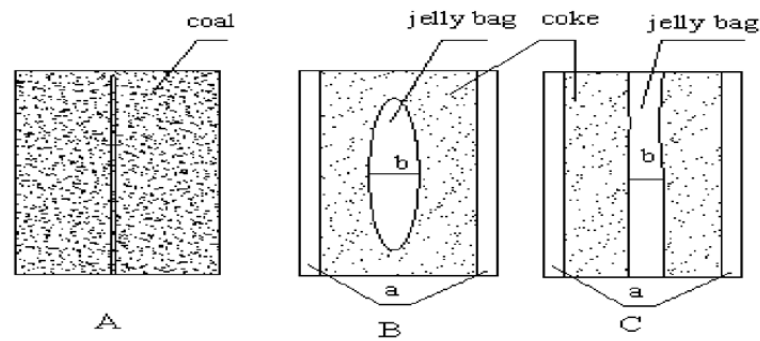
a-The gap of coke and chamber wall; b- Jelly bag
Fig. 4. the diagrammatic sketch of shrinkage of coal to semi-coke

Total shrinkage of semi-coke consists of outer contraction and inner contraction. The amount of outer shrinkage is a, the amount of inner shrinkage b (Fig. 4). Differential shrinkage of various layers after resolidification of the plastic coal to form semi coke, causes stresses to be set up. Thermal stress arises in the coke layer because of the variation of temperature in the layer when the shrinkage of the layer is restrained by the adjacent relatively low-temperature coke layer. If the thermal stress exceeds the strength of the coke, coking fissures in coke are generated fissures to form.

3.4 Shrinkage vs temperature

Since thermal stress is generated because of shrinkage in the coke, heating conditions which affect the variation of the temperature field in the coke is one of the main factors governing fissure formation. The shrinkage rate of semi-coke increases with temperature increasing, the relationship between shrinkage and temperature is shown in Fig. 5. After the data fitting [15-17], the relationship between shrinkage and temperature can be described as:

$Y=-7\times10^{-5}X^2+0.14X-56.26$ (600℃-850℃)

Where Y is shrinkage rate of semi-coke, %; X is semi-coke temperature, ℃.

In addition, it is found that it was possible to prevent the formation of fissures in the briquette by properly controlling the heating pattern. According to the Soule's theory [13], the fissuring mesh size is inversely proportional to the temperature gradient. Therefore, the more rapid the heating conditions and the higher the temperature gradient, the greater is the number of fissures in the coke.

4. Conclusion

A mini coke oven has been used to study the shrinkage character in the process of semi-coke formation. The results of the investigations could be summarized as follows:

1) The section of coke cake has clearly layered, from the inner to outward, divided into loose honeycomb semi-coke layer, small honeycomb semi-coke layer, compact semi-coke layer and fissures layer. The colour of loose honeycomb semi-coke layer and small honeycomb semi-coke layer is dark black, and its porosity about 44.8%.The colour of the compact semi-coke layer is bright black, and its porosity about 34.0%. The colour of cracks layer is silver gray, and its porosity about 46.0%.

2) The pyrolytic plastic layer area of static and dynamics state are difference, the static state pyrolytic plastic layer area is an obturation flat elliptic area, wrapped in the middle of

semi-coke; the dynamic state pyrolytic plastic layer area is a placket oblate gasbag, wrapped by semi-coke from the outside.

3) The shrinkage rate of semi-coke increases with temperature increasing, the relationship between shrinkage and temperature can be described as $Y=-7\ X^2\times10^{-5}+0.14X-56.26$ (600℃ -850℃).
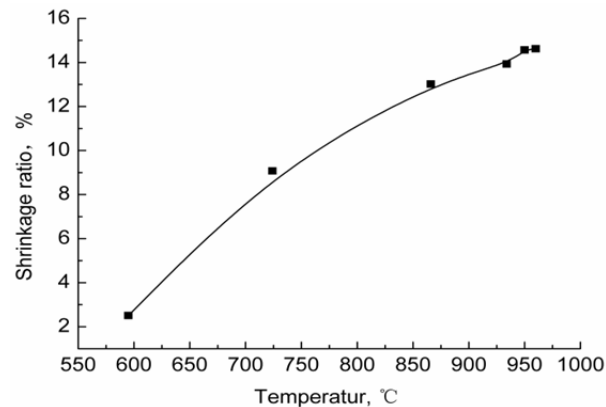

Fig. 5. The relation of the Shrinkage percentage of semi-coke and the temperature

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