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Gasification Reaction Characteristics of Ferro-Coke at Elevated Temperatures

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Abstract: In this paper, the effects of temperature and atmosphere on the gasification reaction of ferro-coke were investigated in consideration of the actual blast furnace conditions. Besides, the microstructure of the cokes was observed by scanning electron microscope (SEM). It is found that the weight loss of ferro-coke during the gasification reaction is significantly enhanced in the case of increasing either the reaction temperature or the CO_2 concentration. Furthermore, compared with the normal type of metallurgical coke, ferro-coke exhibits a higher weight loss when they are gasified at the same temperature or under the same atmosphere. As to the microstructure, inside the reacted ferro-coke are a large amount of pores. Contrary to the normal coke, the proportions of the large-size pores and the through holes are greatly increased after gasification, giving rise to thinner pore walls and hence a degradation in coke strength after reaction (CSR).

Keywords: ferro-coke, gasification reaction, microstructure, weight loss

Introduction

In recent years, facing increasingly stringent environmental regulations, steel companies around the world have been working hard to seek various means to reduce energy consumption and pollution. It is well acknowledged that the ironmaking process regarding the BF-BOF process accounts for the largest part in terms of energy use and pollutant emission. However, recent studies in relation to metallurgical coke show that the improvement of the coke reactivity contributes to the increase of the reduction efficiency inside blast furnace (BF) as well as the decrease of the energy consumption [1–3]. Great breakthrough was made in Japan regarding increasing the reactivity of coke by adding Ca- and Fe-based catalysts [4–6]. Sun et al. [7] selected steel slag as the catalyst charged into the coal blends so as to manufacture high-reactivity coke. Cui et al. [8] analyzed some problems involved during the ferro-coke (derived from the addition of iron ore fines) production in the laboratory and discussed the characteristics of the obtained ferro-coke products. Zhang et al. [9] paid attention to the influence of the variety of iron ore fines charged into the coking blends on the properties of ferro-coke products.

It is found that the ferro-coke obtained when iron ore fines is added into coking coal possesses not only high CRI but also the ability of metallic iron. Unfortunately, few studies in relation to the high-temperature performance of ferro-coke to date can be found. It is expected that the replacement of conventional metallurgical coke with ferro-coke creates the possibility of increasing the addition of weakly-caking coal and low grade iron ore fines by a large amount. Therefore, it is of vital importance to clarify the gasification reaction characteristics of ferro-coke.

In the present work, the weight loss of ferro-coke at various temperatures and atmospheres was measured during the gasification reaction. In addition, the weight loss of the normal coke free from the addition of iron ore fines was also determined so as to allow for the comparison with the ferro-coke. On the other hand, the observation of the ferro-coke microstructure was carried out to analyze the metallurgical performance of ferro-coke. Besides, it is noted that the ferro-coke employed in this paper was obtained by adding 10 % iron ore fines into coking coke blend in the coke oven with the capacity of 40 kg.

Experimental

Sample preparation

All the raw materials involved in this work including the ferro-coke and the normal type of metallurgical coke were from a steel company in China. The proximate

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Table 1: Proximate analysis of the normal coke and ferro-coke mass %.

Coke type	Proximate analysis/weight percent		
	Ash	Volatile matter	Fixed carbon
Normal coke	12.90	1.44	85.66
Ferro-coke	21.94	1.28	76.78

analysis regarding these two types of coke is demonstrated in Table 1 (These data are a dry basis.). It can be seen that due to the addition of iron ore fines, the gangue content is absorbed into the blend, thereby resulting into a rise in the ash content by 10 % while a fall in the fixed carbon by 8 %.

Experimental procedure

The gasification reaction of two types of coke of interest was conducted in the programmable reduction furnace schematically shown in Figure 1. The first step was to size the coke mass in the range 20–25 mm (average diameter) and insert them in a drying oven at 100 ± 5 °C for up to 2 h. Then the temperature inside the programmable reduction furnace was raised to the predetermined ones (900, 1,000, 1,100, and 1,200 °C were selected). Once the predetermined temperature was reached, a mixture of gas with a certain composition (three compositions used in this paper were 100 % CO_2, 50 % CO_2 + 50 % N_2, and 30 % CO_2 + 70 % N_2 respectively) together with two pieces of coke was directed into the furnace. Moreover, the gas flow was maintained at a rate of 5 L/min and the holding time was 1 h. When the gasification reaction finished, CO_2 was cut off and pure N_2 was delivered into the furnace to cool down the apparatus.

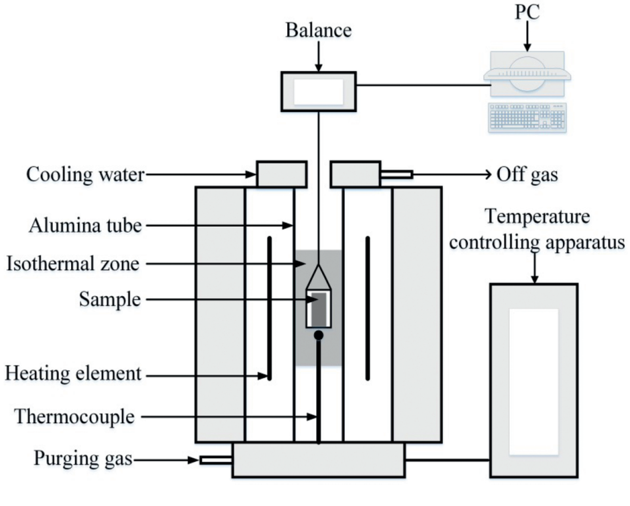

Figure 1: Schematic diagram showing the programmable reduction furnace.

The weight loss during the gasification reaction can be calculated by the following formula.

$$\eta = \frac{(m_0 - m_1)}{m_0} \times 100 \qquad (1)$$

where η is the weight loss of coke after the gasification reaction, m_0 the mass of unreacted coke, m_1 the mass of reacted coke.

Results

Influence of temperature on the gasification reaction

The authors in reference [10] investigated, in the presence of pure CO_2, the influence of temperature controlled in the range of 1,000–1,300 °C on the weight loss of three various types of coke due to the reaction between carbon and CO_2. They claimed that within the same holding time, the weight loss of coke exhibited a positive correlation with temperature, which meant that the higher the temperature, the more the weight loss. In the present work, the weight loss over time concerning the normal coke and ferro-coke at various temperatures was graphically presented in Figures 2 and 3. Taking into account the fact that, in the case of the gasification reaction of the normal coke, a slight weight loss was expected at the temperature 900 °C and 1,000 °C, this paper hence only conducted the experiment involving the reaction temperature 1,100 °C and 1,200 °C. The results indicate that regardless of the type of coke used in the experiment, the relationship between the temperature and the weight loss of coke during the gasification reaction is consistent with the conclusion given by reference [10]. In Figure 3, it can be easily seen that the weight loss of ferro-coke at 900 °C is undoubtedly insignificant. In contrast, when the temperature rises to 1,000 °C or more, the weight loss of ferro-coke goes up greatly. In general, the gasification reaction at 1,000 °C proceeds at an unsatisfying rate. However, it is noteworthy that at this temperature the weight loss of ferro-coke reaches the value of 16 %, which means that the addition of iron ore fines into the coking coal blends is favorable to enhancing the gasification reaction of coke, thereby promoting the carbon solution-loss reaction. With regards to the situation both at 1,100 °C and 1,200 °C, the weight loss for ferro-coke corresponding to 19.35 % and

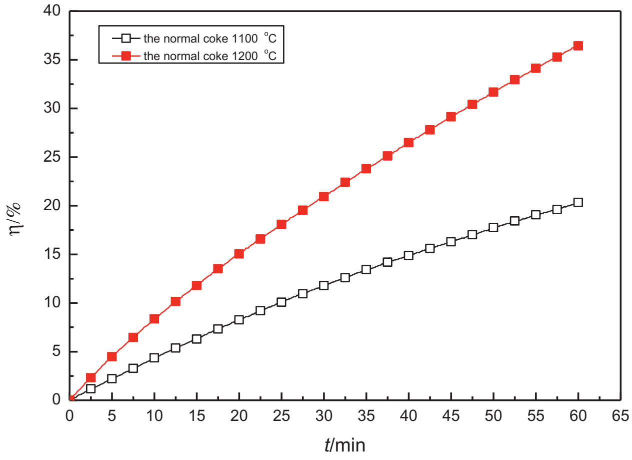

Figure 2: Weight loss of the normal coke at various temperatures.

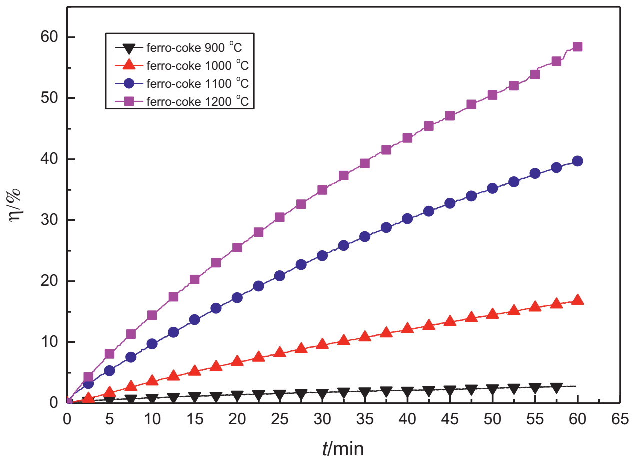

Figure 3: Weight loss of ferro-coke at various temperatures.

22.01 % respectively is higher than that for the normal coke. This can also be explained by a higher CRI the ferro-coke possesses.

Influence of atmosphere on the gasification reaction

In order to figure out the atmosphere dependence of the gasification reaction of coke, three different atmospheres in this work were selected including 100 % CO_2, 50 % CO_2 + 50 % N_2, and 30 % CO_2 + 70 % N_2. Figures 4 and 5 correspond to the curves depicting the weight loss of the normal coke and ferro-coke respectively. It is noted that these two types of coke were both heated up to 1,100 °C under various atmospheres. Apparently, the rise in the concentration of CO_2 leads to a drastic increase in the weight loss regardless of the type of coke. In order to differentiate the ferro-coke with the normal coke, Figure 6

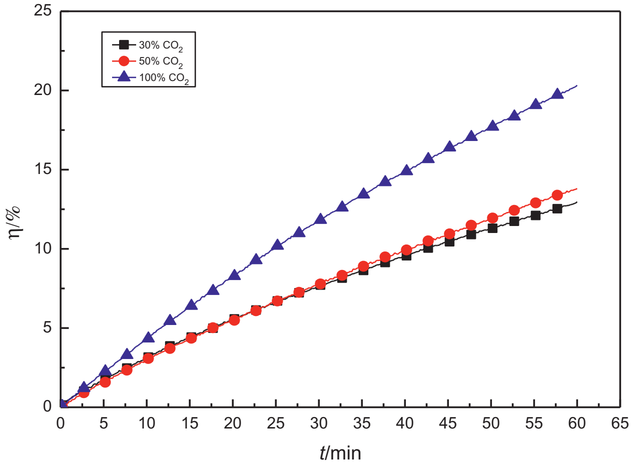

Figure 4: Weight loss of the normal coke at various atmospheres.

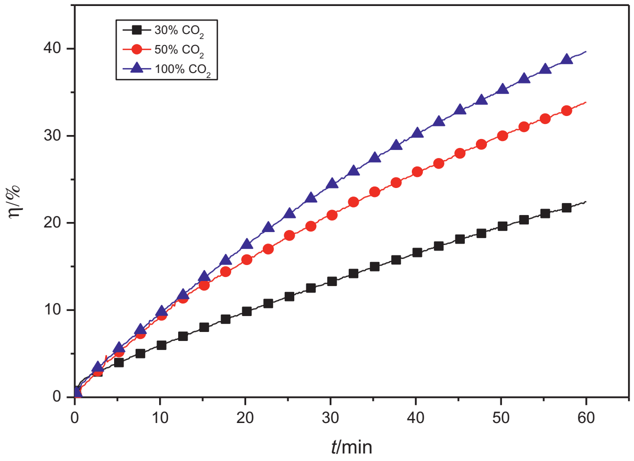

Figure 5: Weight loss of ferro-coke at various atmospheres.

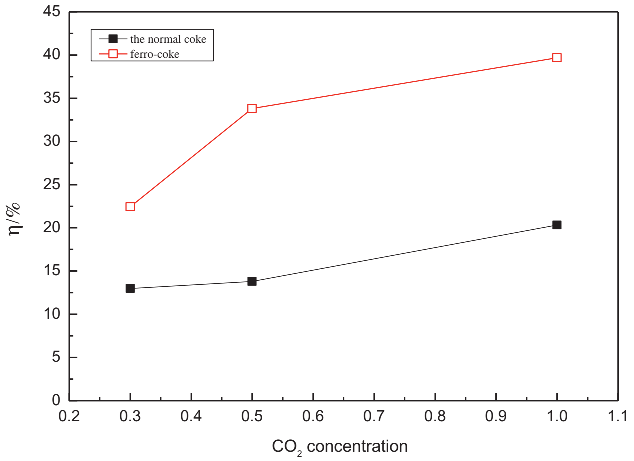

Figure 6: Comparison of weight loss ratio of normal coke and ferro-coke under various atmospheres.

presents the weight loss curve for two types of coke when the reaction temperature and atmosphere were identical. It can be seen that the weight loss of ferro-coke is higher than that of the normal coke. The weight losses of ferro-coke are increased by 9.47 %, 20.01 %, and 19.35 % respectively compared with the normal coke. On the other hand, the CSR of ferro-coke is known to be lower than that of the coke charged into BF. Therefore, ferro-coke is capable of acting as a supplementary material for nut coke, which can be charged in combination with iron ores, thus making full use of its excellent reactivity.

Microstructure observation of cokes

The micro-morphology of the two types of coke in this paper before and after the gasification reaction was observed by means of FEI Quanta 250 SEM. The samples were obtained through the grinding and polishing of the pre-selected side.

The characteristics of pores distributed in the coke sample were evaluated according to Figure 7, in which the normal coke is deficient in the amount of pores, especially those with a large size, while small- and middle-size pores dominate. Besides, the relatively thick pore wall is also the feature of the normal coke sample. It is also noted that the strength of the normal coke is positively affected by such structures as a uniform distribution of a large number closed pores, a dense microstructure, and few amounts of surface cracks. However, this kind of structure featuring a lack of CO_2 effective diffusion paths reduces the coke reactivity. Contrary to the normal coke, the ferro-coke is characterized by a sufficient porosity and an irregular distribution of pores. Moreover, the presence of abundant large-size pores and surface cracks is favorable to the formation of a loose structure. This kind of structure yet is susceptible to generating the large pores with thin walls as well as through holes during the gasification reaction, thus reducing the coke strength.

Figure 8 presents the SEM images of ferro-coke when treated at 1,100 °C. It can be found that in the case of 30 % CO_2, an obvious separation line describing the degree of reaction is observed. In the lower left of the

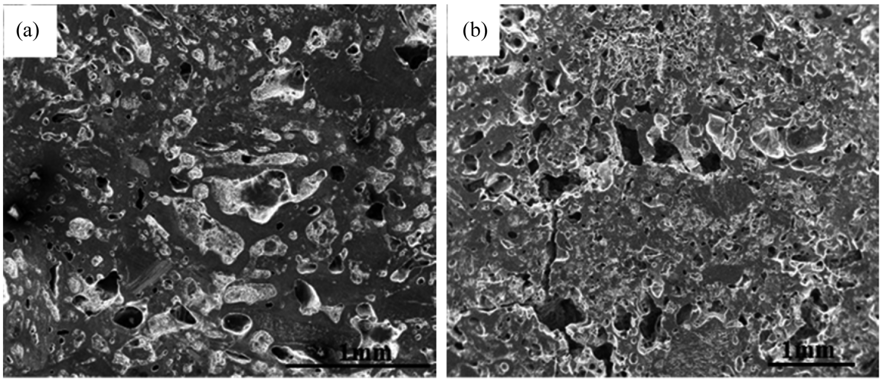

Figure 7: SEM images of coke sample before the gasification reaction: (a) normal coke; (b) ferro-coke.

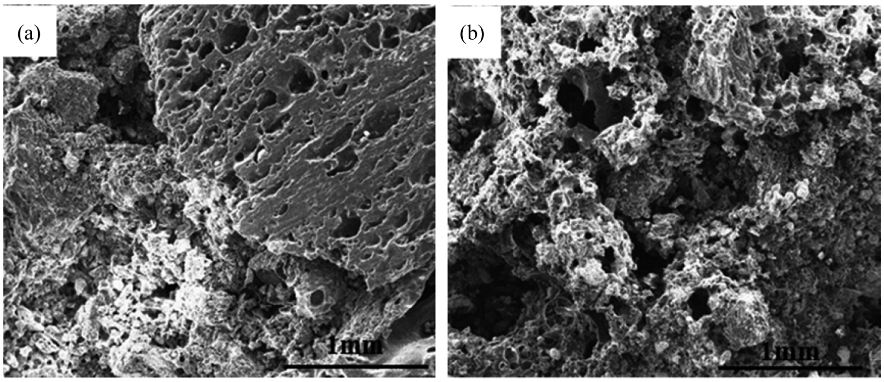

Figure 8: SEM images of ferro-coke sample after the gasification reaction: (a) 30 % CO_2; (b) 50 % CO_2.

image, it is speculated that a complete reaction occurred, destroying the pore-structure, and thus severely corroding the ferro-coke inside. While in the upper right of the picture, the number of micro-pores or small-size pores is to some extent increased, thereby resulting into a large porosity. In addition, the original pores in part were converted into large through holes due to the reaction between ferro-coke and CO_2, and thus as a result, CO_2 was ready to diffuse into the ferro-coke internal structure, further reacting with the ferro-coke so as to enlarge the size of pores continually. As the reaction proceeded, the strength of ferro-coke was reduced. As to the case of 50 % CO_2, no obvious separation line similar to the case of 30 % CO_2 is seen. This can be explained by the fact the gasification reaction reached a throughout state. Besides, the ferro-coke inside was seriously destroyed by the reaction with CO_2, thereby leading to noticeable thin pore walls. Figure 8(b) also reveals the evolution of the form of pores including the enlargement, penetration, and corrosion of pores. All of these reasons are responsible for the formation of a great number of surface cracks, thus reducing CSR accordingly.

In Figure 9, back scattered electron images of ferro-coke are showed. It can be readily seen that prior to the gasification reaction of ferro-coke, metallic iron is present within the structure, which means that during the carbonization process of coking coal part of iron oxides was reduced to the metallic iron which was subsequently evenly distributed in the matrix of resultant ferro-coke. The existence of metallic iron after the gasification reaction further provides the evidence that the catalytic nature of Fe for the carbon solution-loss reaction.

Discussion

It is widely believed that Fe in the form of metallic state and oxidized state [$(Fe_{(1-X)}O)$ and Fe_3O_4] is capable of acting as an effective catalyst in the CO_2/CO mixture. Moreover, the effectiveness of the Fe as a catalyst is intensified when the iron oxide is gradually reduced. The relevant research [11] reveals the oxygen-transfer mechanism of catalytic Fe is as follows.

$$Fe_mO_n + CO_2 -> Fe_mO_{n+1} + CO \tag{2}$$

$$Fe_mO_{n+1} + C -> Fe_mO_n + CO \tag{3}$$

Hermann and Huttinger [12] bearing in mind that eq. (3) was the catalytic reduction reaction considered it as the rate-determining step. The Fe_mO_n acts as the oxygen carrier and promotes the oxygen transfer, which contributed to the gasification of coke.

Zhang etc. [9] pointed out, during the coking process the iron oxides were mostly reduced into metallic iron, which accounted for the phenomenon that the application of ferro-coke was able to increase the BF reaction rate while reduce the energy consumption. They also maintained that the metallic iron had a positive effect on catalyzing the gasification reaction of coke. According to Electron Cyclic Donor-Acceptor Catalyzing Theory (ECDAT), the presence of metallic iron is favorable to the restoration of the carbon molecular orbits from a distorted state to original symmetric balanced state, thus accelerating the gasification reaction [13].

Other researchers claimed that, the addition of iron ore fines into the coking coal blends produced such coke that the tendency to reacting with CO_2 was enhanced while CSR was decreased. The SiO_2-rich particle contained in iron ore, they believed, exhibited an expansion coefficient which failed to match that of coke. As a result, cracks generated from the center resulted into a loose structure of coke, increasing the contact area with CO_2 gas, thereby speeding up the rate of carbon solution-loss reaction [14].

In the paper, the reason accounting for the CRI improvement of ferro-coke can be summarized as follows. Except for the catalytic function of Fe, the flow of the

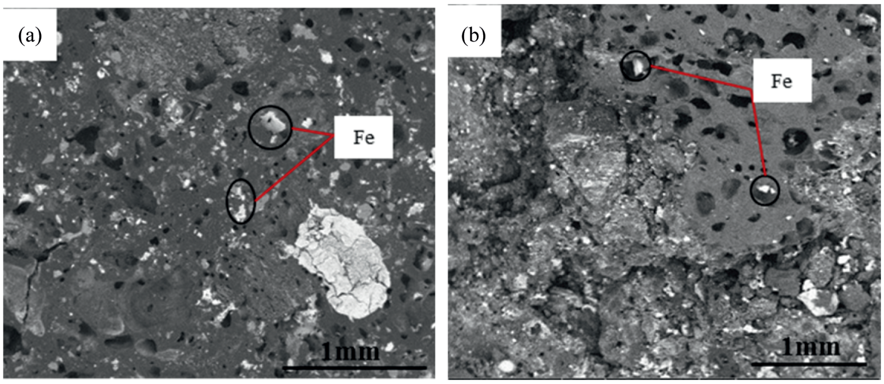

Figure 9: Back scattered electron images of ferro-coke: (a) unreacted; (b) reacted.

liquid substance generated in the coke-making process was inhibited by the charged iron ore fines, thus resulting into an incomplete carbonization process. Accordingly, the number of active particles was increased, which improved the resultant ferro-coke CRI. On the other hand, when the reaction between coke and CO_2 occurred in the temperature range from 900 °C to 1,200 °C, the rapid reaction almost depleted the CO_2 in the entrance of the pores, thus hindering the reaction occurring inside the coke. Under such circumstances, the diffusion of CO_2, the size of coke pores, and the flow rate as well as concentration of CO_2 were of critical importance to the gasification reaction. From Figure 8 (b), it can be seen that the diffusion of CO_2 was positively affected by the pores of ferro-coke, and hence the gasification reaction happening in the regions located inside the coke was intensified.

Conclusions

By investigating the high-temperature characteristics of ferro-coke gasification reaction and the microstructure of ferro-coke, following conclusions are derived.

(1) The weight loss of ferro-coke increases as the reaction temperature is raised, and particularly 1,200 °C reaction temperature gives rise to a weight loss of 58.44 %. Compared with the normal coke, given the identical reaction temperature, the weight loss of ferro-come up to 20 % is higher. The improvement of CRI for ferro-coke indicates that the addition of iron ore fines into the coking coal blends derives some substances capable of catalyzing the gasification reaction of ferro-coke.

(2) The weight loss of ferro-coke increases with CO_2 becoming increasingly concentrated. Given the same reaction atmosphere, ferro-coke has a higher weight loss than the normal coke. This result once signals the presence the substance capable of catalyzing the gasification reaction.

(3) The observation of the microstructure of coke samples shows that the ferro-coke prior to the gasification possesses a relatively large number of pores and a loose structure. Therefore, after the reaction, the number of large-size pores is increased, so is the through holes. In addition, the thickness of pore walls is reduced, and the gasification reaction is enhanced, thereby giving rise to a low CSR.

(4) The back scattered electron images of ferro-coke graphically display the distribution of Fe. The metallic iron had a positive effect concerning catalyzing the gasification reaction of coke. Ferro-coke is capable of acting as a supplementary material for nut coke, which can be charged in combination with iron ores, thus making full use of the feature of excellent reactivity.

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