

Influence of Temperature and CO₂ on High-Temperature Behavior and Microstructure of Metallurgical Coke

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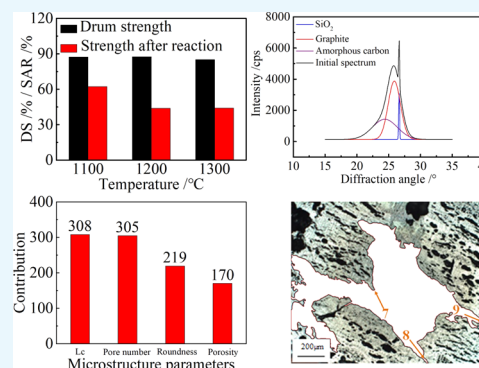
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ABSTRACT: Metallurgical coke is an important raw material for blast furnaces. Specifically, temperature and CO₂ significantly affect its metallurgical behavior. In this study, the influence of temperature and CO₂ on the high-temperature behavior of three metallurgical coke samples, used in blast furnaces of different volumes, was investigated. The carbon structure and pore structure of the coke samples were analyzed. The results indicated that as the temperature increased from 1100 to 1500 °C, the weight loss ratio increased 10-fold and the drum strength decreased to approximately 80% in Ar. Under a CO₂ atmosphere, as the temperature increased from 1100 to 1300 °C, the reactivity index increased from 20 to 70%, and the strength after reaction exhibited the lowest value of 40% at 1250 °C. When the temperature increased from 1100 to 1500 °C, the stacking height of the layer structure L_c of the coke samples increased to ~5.5 nm. Under the influence of CO₂ and temperature, the L_c of the coke samples increased to approximately 4 nm between 1100 and 1300 °C. Furthermore, CO₂ slightly affected the carbon structure. The changes in pores under the influence of CO₂ and temperature were greater than those under the influence of temperature between 1100 and 1300 °C. Typically, the strength of coke is high when the pore number, roundness, and porosity are low. The strength and microstructure parameters of the coke samples were correlated via multiple regression. The results of the multiple regression showed that the carbon structure and pore number had the highest impact on coke strength, followed by roundness and porosity.



1. INTRODUCTION

Metallurgical coke is an important raw material for blast furnace smelting. The main functions of coke in a blast furnace are heat source, reducing agent, and carburizing agent and support. Among these functions, the role of support is irreplaceable.¹ Coke reacts differently from top to bottom in a blast furnace, and its behavior also changes.² Specifically, in a cohesive zone and below, coke is affected by temperature, CO₂, slag, iron, and gas flow.³ As the only bulk material in the lower part of blast furnace, the high-temperature reaction behavior of coke in such a complex environment significantly affects the stability of the blast furnace.⁴ Currently, it is generally considered that coke with low coke reactivity index (CRI) and high coke strength after reaction (CSR) exhibits better thermal performance.⁵ CRI and CSR are determined via Nippon Steel coke reactivity tests. These tests are widely used to characterize high-temperature properties of coke. Specifically, these high-temperature properties are obtained by reacting coke with 100% CO₂ at 1100 °C.^{6,7} However, the reaction conditions of this test are quite different from the environment in the blast furnace. During a practical application, the high-temperature index of coke does not match the operation of the blast furnace.^{8,9} Therefore, it is necessary to systematically examine the reaction behavior of

coke under different conditions, clarify the reaction behavior and reaction mechanism of coke under complex conditions of a blast furnace, and lay a foundation for fully utilizing coke.

The coke in a blast furnace can reveal the state of coke after the reaction in different regions of the blast furnace. Therefore, many scholars have examined coke in blast furnaces. By using scanning electron microscopy and X-ray diffraction (XRD), the behavior of coke from the lower part of the blast furnace can be studied.^{10,11} Specifically, the particle size, graphitization degree, and minerals of coke were analyzed. The results indicated that graphitization of coke significantly affects the formation of tuyere coke powder and reveals the effect of blast furnace conditions on the mineral and reactivity of tuyere coke.^{12,13} Tuyere coke reveals the state of coke in a blast furnace and provides a reference for theoretical research. However, tuyere coke is expensive because it is difficult to

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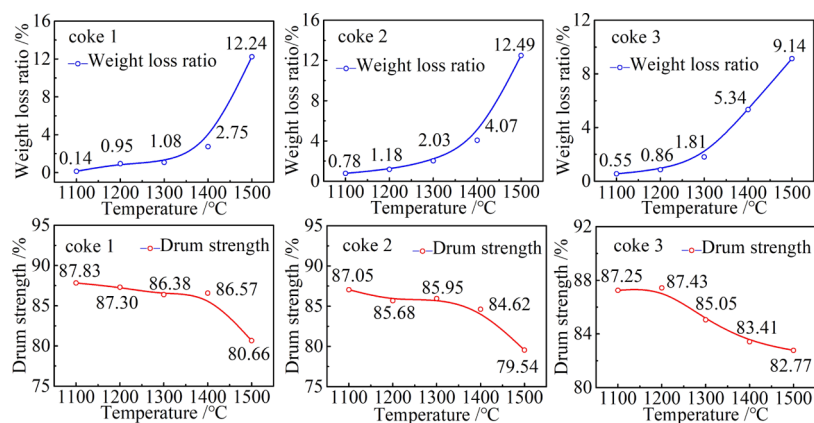


Figure 1. Influence of temperature on weight loss ratio and drum strength.

obtain from the blast furnace. Hence, simulating the conditions of blast furnaces and studying the reaction behavior of coke in the laboratory is a more widely used research method. The thermal history of coke in a blast furnace can be estimated by the changes in the coke mineral and carbon structure.^{14,15} Temperature has always affected the behavior of coke in blast furnaces. After annealing at 1000–1600 °C, the carbon structure of metallurgical coke changes significantly.¹ Minerals in coke change as the temperature increases.^{7,16} The gasification of coke and CO₂ is one of the main reasons for the changes in coke behavior. The reaction temperature, gas composition, and particle size affect the gasification reaction rate of coke.¹⁷ Furthermore, the specific surface area of coke changes with the volume fraction of CO₂.¹⁸ The changes in the coke structure and pore due to the gasification reaction lead to changes in the coke strength after gasification.¹⁹ After the reaction of coke with CO₂, the change in big pores is much more complicated than that in small pores.²⁰ The minerals in coke, such as Ca and Fe, enhance the gasification. Specifically, Ca has a higher influence on the gasification of coke.^{21,22} In addition to temperature and gasification reaction, the interaction between slag/iron and coke significantly affects the operation of the blast furnace.^{23,24} Slag fills the pores of coke, and coke reacts with components in slag.²⁵

Based on previous studies, the reaction behavior of coke under different reaction conditions has been gradually understood. However, under complex conditions, the degree of action and mechanisms of different factors are not clear. Therefore, it is necessary to compare the reaction behavior and microstructure changes of coke under single-factor and multi-factor conditions and link the microstructure with the reaction behavior. To develop a systematic method for predicting coke properties in the future, the changes in temperature and CO₂ should be considered. In this study, three different coke samples from different blast furnaces were selected. The changes in weight loss ratio, drum strength, carbon structure, and pore structure from 1100 to 1500 °C were examined under the effect of temperature. The changes in the reactivity index (RI), strength after reaction, carbon structure, and pore structure from 1100 to 1300 °C under the effect of CO₂ and temperature were studied. The differences in the behaviors and microstructures under different conditions were compared. The relationship between coke strength and microstructure was established using multiple regression. Hence, this study serves as a reference for understanding coke degradation and predicting the quality of coke.

2. RESULTS AND DISCUSSION

2.1. Influence of Temperature on the High-Temperature Behavior of Coke.

Under the influence of temperature, coke undergoes a change in weight and strength. Hence, weight loss ratio was used to characterize the change in weight, and drum strength was used to characterize strength. Annealed coke was weighed to calculate the weight loss ratio by using the following equation after annealing.

$$\text{WLR} = \frac{m_0 - m_1}{m_0} \times 100 \quad (1)$$

where WLR denotes the weight loss ratio, m_0 denotes the weight before annealing, and m_1 denotes the weight after annealing.

A few samples were removed before drumming for the next analysis. The drum strength was evaluated after the samples were tumbled in an I-Type drum (600 revolutions at 20 rpm) by using the following equation

$$\text{DS} = \frac{m_a}{m_b} \times 100\% \quad (2)$$

where DS denotes the drum strength, m_a denotes the weight after drumming (samples above 10 mm), and m_b denotes the weight before drumming.

The weight loss ratio and drum strength under the influence of temperature are shown in Figure 1. The main reason that leads to weight loss in coke under high-temperature treatment is the reaction between the minerals and carbon. The WLR of coke 1 and coke 2 increased slowly from 1100 to 1400 °C and increased rapidly to approximately 12% at 1500 °C. This implies that volatilization of volatiles and reaction of low melting point minerals occurred below 1400 °C. The main reaction of minerals in coke 1 and coke 2 occurred between 1400 and 1500 °C. For coke 3, the main reaction occurred between 1300 and 1500 °C, and its WLR was 9.14% at 1500 °C, which was less than that of coke 1 and coke 2.

Given the thermal stress and reaction in coke, the microstructure changes, and this can cause variations in coke strength. The DS of the three types of coke decreased as the temperature increased. For coke 1 and coke 2, the main change in DS occurred between 1400 and 1500 °C. The DS of coke 3 decreased uniformly to 82.77% from 1200 to 1500 °C. Thus, it was observed that the weight loss ratio and drum strength are inversely proportional.

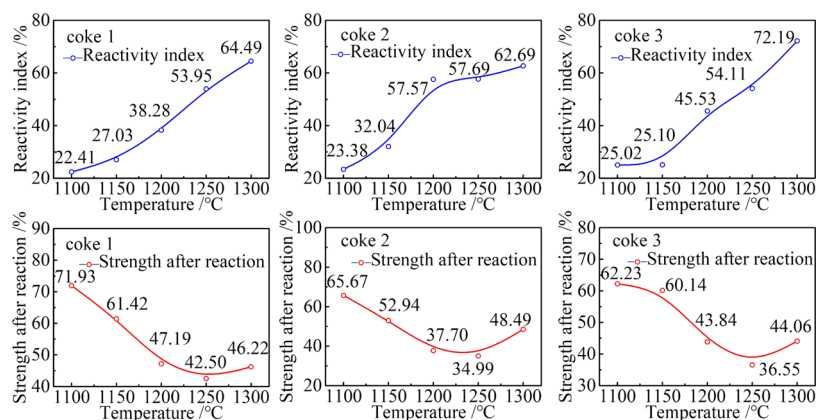


Figure 2. Influence of CO₂ and temperature on RI and strength after reaction.

The results indicated that WLR is the lowest and RS is the highest in coke 3 at 1500 °C. The curves of coke 3 exhibited the evenest changes. Coke 3 is different from coke 1 and coke 2 mainly because it exhibits the most stable high-temperature behavior. This implies that coke for big blast furnaces requires stable behavior at high temperatures.

2.2. Influence of CO₂ and Temperature on the High-Temperature Behavior of Coke. Under the influence of CO₂ and temperature, coke exhibits changes in weight and strength. Hence, RI was used to characterize the changes in weight and strength after drum strength was used to characterize strength. The reacted samples were weighed to calculate the RI using the following equation

$$RI = \frac{m_2 - m_3}{m_2} \times 100\% \quad (3)$$

where RI denotes the RI, m_2 denotes the weight before the reaction, and m_3 denotes the weight after the reaction.

A few samples were removed before drumming for the next analysis. The strength after the reaction was evaluated after the reacted coke was tumbled in an I-type drum (600 revolutions at 20 rpm) using the following equation

$$SAR = \frac{m_A}{m_B} \times 100\% \quad (4)$$

where SAR denotes the strength after reaction, m_A denotes the weight after drumming (samples above 10 mm), and m_B denotes the weight before drumming.

Under the influence of CO₂ and temperature, the main reasons for changes in coke behavior correspond to thermal stress and gasification. The RI and strength after the reaction are shown in Figure 2. The RI of the three coke samples increased with an increase in temperature. This implies that high temperatures can promote coke gasification. For coke 3, the RI was 72.19% at 1300 °C, which was higher than that of coke 1 and coke 2. This indicates that coke 3 exhibits the strongest ability to react with CO₂ at high temperatures.

After the effect of CO₂ and temperature, the weight of coke increased significantly. However, the changing trend of SAR was not similar to that of RI. The SAR values of the three coke samples decreased by approximately 40% at 1250 °C and increased by approximately 45% at 1300 °C. This implies that in a pure CO₂ atmosphere, coke gasification leads to the highest degradation temperature. Coke gasification is a complex process. During gasification, coke is simultaneously influenced by temperature and CO₂. Therefore, coke behavior

is affected by several factors such as the reaction between the carbon matrix and CO₂ and the effect of temperature on the carbon matrix.

The results indicated that the SAR range of coke 3 was the lowest. For blast furnaces, the strength of coke at high temperatures is very important. This implies that the ability of coke to react with CO₂ is not a significant index. Hence, the most important index corresponds to the strength after the reaction. Specifically, stable strength is required in coke for large blast furnaces at high temperatures.

A comparison between temperature and CO₂ can aid in observing the behavior of coke under different conditions. The weight loss of the reacted coke in the CO₂ atmosphere was much higher when compared to that in the Ar atmosphere. This indicates that when compared to the effect of CO₂ and temperature, the influence of temperature on weight loss can be ignored between 1100 and 1300 °C. However, the weight loss after annealing can increase by approximately 10% at 1500 °C, and it cannot be ignored at 1500 °C or higher. At 1100, 1200, and 1300 °C, the strength of the samples that reacted with CO₂ was much lower than that of the annealed coke samples. This implies that the effect of coke gasification at high temperatures on the strength of coke is more significant than the effect of temperature. However, at higher temperatures, the effect of temperature is more evident and cannot be ignored. Coke strength can be affected by multiple factors. However, the changes in the microstructure of coke, such as the carbon structure and pore structure, correspond to the underlying reasons.

2.3. Influence of Temperature and CO₂ on the Carbon Structure of Coke. The carbon structure is always represented by the crystalline size of graphite in the coke. The stacking height of the layer structure L_c is typically used to characterize the crystallinity of graphite.^{26,27} The stacking height L_c can be calculated by using the Scherrer equation

$$L_c = \frac{0.8\lambda}{B \cos \theta} \quad (5)$$

where λ denotes the wavelength of X-ray radiation (nm), B denotes the full width of half-maximum intensity of the 002 peak (degrees), and θ denotes the diffraction angle of the 002 peak (degrees).

2.3.1. Influence of Temperature on the Carbon Structure of Coke. Peak fitting was used to distinguish between the peaks in the XRD spectrum. There are two types of carbon in coke: graphite and amorphous carbon. Figure 3 shows the XRD

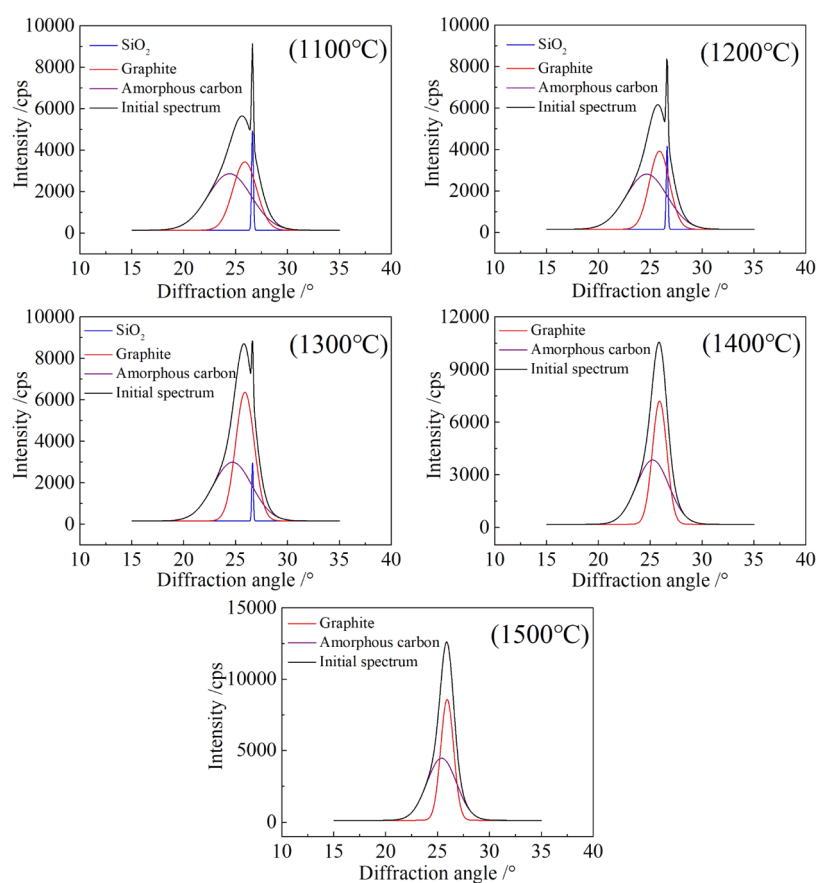


Figure 3. XRD patterns of coke 1 under the influence of temperature.

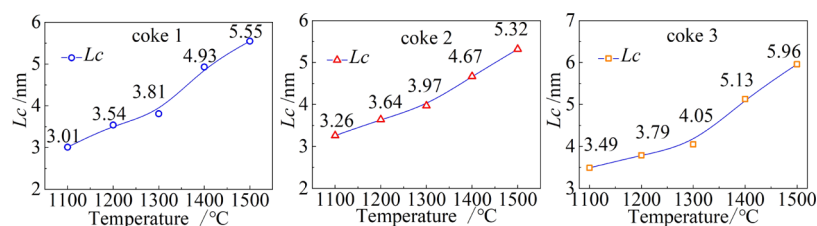


Figure 4. Influence of temperature on Lc values.

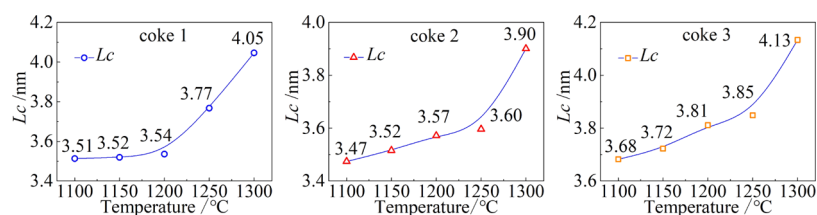


Figure 5. Influence of CO₂ and temperature on Lc values.

patterns of the 002 carbon peaks of coke 1 annealed at 1100, 1200, 1300, 1400, and 1500 °C. The XRD patterns of coke 2 and coke 3 were similar to those of coke 1.

After peak fitting, the XRD spectrum can be deconvoluted into three peaks below 1400 °C, namely, peaks for SiO₂, graphite, and amorphous carbon. The SiO₂ peak disappeared at 1400 °C. It was observed that the width of 002 carbon peaks became narrower as the temperature increased. This implies that the degree of ordering of carbon layers increased.

Lc values were calculated using eq 5. The influence of temperature on Lc values is shown in Figure 4. With respect to

the effect of temperature, the Lc values of the three types of coke increased as the temperature increased. Specifically, the Lc values of coke 1 changed from 3.01 to 5.55 nm; the Lc values of coke 2 changed from 3.26 to 5.32 nm; and the Lc values of coke 3 increased from 3.49 to 5.96 nm. The difference in the Lc values of the three types of coke was not evident.

2.3.2. Influence of CO₂ and Temperature on the Carbon Structure of Coke. Between 1100 and 1300 °C, the XRD spectrum can be deconvoluted into three peaks via peak fitting. The 002 carbon peak became narrower as the temperature

increased. The influence of CO₂ and temperature on Lc values is shown in Figure 5. Specifically, the Lc value of coke 1 increased from 3.51 to 4.05 nm between 1100 and 1300 °C, and the Lc value of coke 2 increased from 3.47 to 3.90 nm. Similar to coke 1 and coke 2, the Lc value of coke 3 increased from 3.68 to 4.13 nm. Under the effect of CO₂ at high temperatures, the Lc values increased as the temperature increased.

The Lc values at the same temperature in different atmospheric conditions did not change significantly. It was observed that CO₂ slightly affected graphitization. Hence, the main reason for the enlargement in graphite crystal corresponded to the increase in temperature.

2.4. Influence of Temperature and CO₂ on the Pore Structure of Coke. Figure 6 shows different types of pores

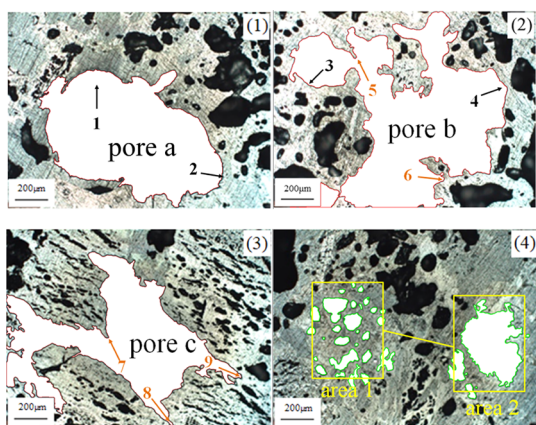


Figure 6. Different kinds of pores from coke 1 annealed at 1100 °C: (1) pore a; (2) pore b; (3) pore c; and (4) area 1 and area 2.

from coke 1 annealed at 1100 °C. As shown in Figure 6, the size of the pores is larger than 5 μm, and the number, shape, and size of the pores varied. For instance, the sizes of pores a, b, and c were almost the same. The performances of the three

pores were almost the same, and the pores were characterized solely by porosity. In practical applications, the ability to resist the stress of the three pores is different. The compression strength of the circle is the strongest. This implies that as the roundness of the pores increases, the resistance to stress increases. As shown in positions 1 and 2, the shape of pore a is closest to the circle, and it exhibits the least points of stress concentration. Thus, pore a exhibits the strongest resistance to stress. Pore b exhibits certain arc-shaped edges such as positions 3 and 4. However, it also has more points of stress concentration, such as positions 5 and 6, which lead to weaker resistance to stress. Pore c has the highest number of points of stress concentration, namely, positions 7, 8, and 9, and it has the weakest resistance to stress. This shows that the pore structure cannot be evaluated only by the porosity. In photo (4), the pore number in area 1 is greater than that in area 2. However, it can be estimated that area 1 has stronger resistance to stress. This indicates that high pore number does not result in a lower intensity. As mentioned above, pores that can influence the strength of coke cannot be characterized by a single index. It is necessary to discuss different aspects of the pores.

In this study, the pore number was used to characterize the number, the roundness was used to define the shape, and the porosity was used to express the size of the pores. The pore number can be calculated by using the following equation

$$P_n = \frac{n_{op}}{n_{oa}} \quad (6)$$

where P_n denotes the pore number, n_{op} denotes the number of observed pores, and n_{oa} denotes the number of observed areas.

The roundness can be calculated as follows

$$R = \frac{\sum_1^n R_{pore(n)}}{n_{op}} \quad (7)$$

where R denotes the roundness and $R_{pore(n)}$ denotes the roundness of a single pore.

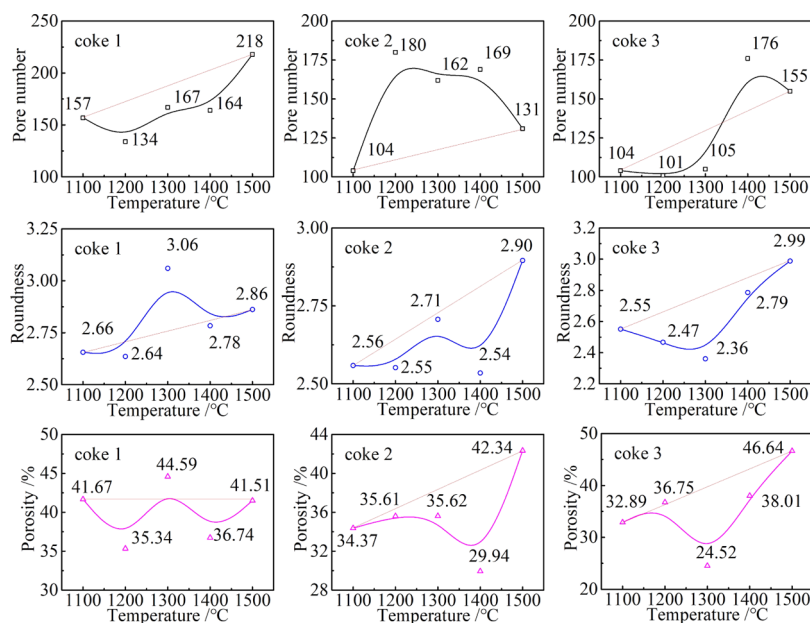


Figure 7. Influence of temperature on the pore structure of cokes.

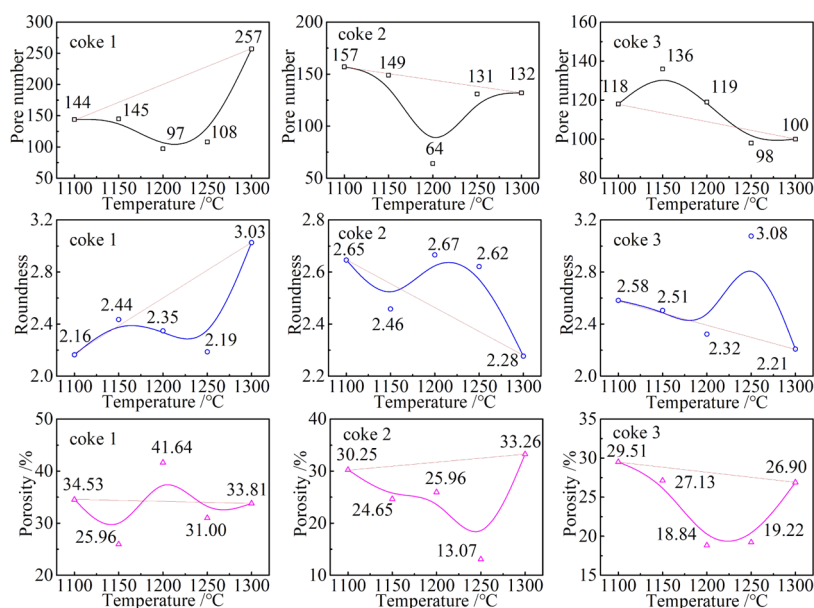


Figure 8. Influence of CO₂ and temperature on the pore structure of cokes.

$$R_{\text{pore}(n)} = \frac{l^2}{4\pi S} \quad (8)$$

where l denotes the perimeter of pore and S denotes the area of pore.

The porosity can be calculated by the following equation

$$P = \frac{A_h}{A_o} \times 100\% \quad (9)$$

where P denotes the porosity, A_h denotes the area of the hole, and A_o denotes the area of the observed image.

2.4.1. Influence of Temperature on the Pore Structure of Coke. The influence of temperature on the pore structure of coke is shown in Figure 7. For coke 1, when compared to the pore structure parameters at 1100 °C, the pore number and roundness at 1500 °C increased, while the porosity almost did not change. The pore number, roundness, and porosity of coke 2 increased at 1500 °C when compared to those at 1100 °C. The pore number and roundness for coke 3 increased at 1500 °C when compared to the pore structure parameters at 1100 °C. Hence, the strength of coke is the highest when the values of pore number, roundness, and porosity are minimal.

2.4.2. Influence of CO₂ and Temperature on the Pore Structure of Coke. The influence of CO₂ and temperature on the pore structure of coke is shown in Figure 8. The pore number and roundness for coke 1 increased at 1300 °C when compared to the pore structure parameters at 1100 °C, and the porosity remained almost unchanged. The pore number and roundness for coke 2 decreased and the porosity increased at 1300 °C when compared to the pore structure parameters at 1100 °C. For coke 3, the pore number and roundness decreased and the porosity increased at 1300 °C when compared to the pore structure parameters at 1100 °C.

The variation in pore structure under the effect of temperature was smaller than that under the effect of CO₂ and temperature. Furthermore, it is observed that gasification at high temperatures has an evident effect on the changes in pores. Under the effect of temperature and CO₂, the variation in pore structure was not regular, and it was difficult to explain

the mechanism of strength variation. Therefore, other methods should be used to determine the internal relationship.

2.5. Multiple Regression of Strength and Microstructure. To clarify the effect of microstructure on strength, multiple regression was conducted on coke strength and microstructure. In the process of comprehensive analysis, the two indicators have different dimensions and orders of magnitude because of the different properties of the indicators. If the original index value is directly used for analysis, then it can potentially highlight the role of indicators with higher values in comprehensive analysis and can relatively weaken the role of indicators with lower values. Therefore, to ensure the reliability of the results, it was necessary to standardize the original data. In this study, a z-score standardization method was used.

Multiple regression analysis was performed using Python. Before multiple regression, collinearity analysis between various parameters was performed. The results of the analysis are presented in Table 1. As shown in the table, there is no strong collinearity between the parameters. Therefore, multiple regression can be performed.

Table 1. Collinearity between Parameters

parameter	strength	Lc	pore number	roundness	porosity
strength	1.00	−0.64	−0.05	−0.38	0.06
Lc	−0.64	1.00	0.27	0.35	−0.14
pore number	−0.05	0.27	1.00	0.43	0.26
roundness	−0.38	0.35	0.43	1.00	0.22
porosity	0.06	−0.14	0.26	0.22	1.00

Among the 30 rows of data, 24 rows of data were selected for data training and 6 rows of data were used for data validation. Figure 9 shows a comparison between the predicted and actual data. As shown in the figure, the predicted value is close to the actual value, thereby indicating that the regression results can predict the impact of various microscopic parameters on strength. The contribution of Lc is 308 and that of pore number is 305. Thus, both indicators exhibit a higher degree of influence on the strength. The contribution of

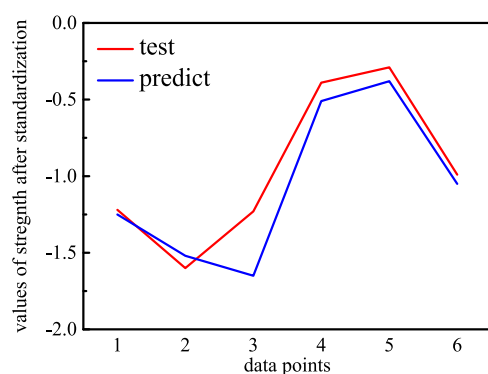


Figure 9. Comparison of forecast data and actual data.

roundness is 219, and thus, it had a moderate impact on the strength. The contribution of porosity is 170, thereby indicating the least impact on strength. This shows that the effect of changes in temperature on the strength of coke cannot be ignored in a blast furnace. In previous studies, with respect to pores of coke, the relationship between porosity and strength of coke was examined more thoroughly. However, the results of this study indicate that the effect of number and shape of pores should not be ignored.

3. CONCLUSIONS

In this study, three different coke samples were selected to examine the influence of temperature on the weight loss ratio and drum strength between 1100 and 1500 °C. Furthermore, the influence of CO₂ on the RI and strength of coke after reaction between 1100 and 1300 °C was examined. The carbon structure and pore structure under different conditions were investigated. The following observations and conclusions were made.

- (1) An increase in temperature leads to an increase in weight loss of coke. When compared to temperature, the CO₂ and temperature significantly increase the weight loss of coke. The strength of coke decreased as the temperature increased without CO₂. Under the effect of CO₂, the strength increased after a rapid decrease, and it was the lowest at 1250 °C. The change range of coke 3 was the lowest. This implies that coke for large blast furnaces requires stable behavior at high temperature.
- (2) The Lc values increased to approximately 6 nm at 1500 °C under the effect of temperature. When compared to temperature, the Lc values changed slightly with the addition of CO₂ at the same temperature. Furthermore, Lc exhibited a strong correlation with temperature, and CO₂ had a slight effect on the carbon structure of coke.
- (3) The variation range of the pore parameters is higher with the addition of CO₂ when compared to that of temperature. The strength of coke is the highest when the values of pore number, roundness, and porosity are the smallest.
- (4) The results of the multiple regression showed that the contribution of the coke carbon structure and pore number on the strength were 308 and 302, respectively. This was followed by the contribution of roundness (219) and porosity (170). The carbon structure and pore number exhibited the highest impact on coke strength, and this was followed by the impact of roundness and porosity.

4. MATERIALS AND METHODS

4.1. Materials. Three types of metallurgical coke samples with high CSR are obtained from three different operating blast furnaces as listed in Table 2. Cokes 1, 2, and 3 were

Table 2. Industrial Analysis of Three Cokes

coke	A_d	V_{daf}	$S_{t,d}$	M_t	CRI	CSR	M_{40}	M_{10}
1	12.79	1.28	0.85	0.2	25.7	63.2	89.3	6.4
2	13.08	1.25	0.96	0.3	27.5	61.4	87.4	6.8
3	12.94	1.20	0.96	0.2	24.2	65.7	88.8	6.1

selected from 2000, 3000, and 4150 m³ blast furnaces, respectively. The A_d (ash), V_{daf} (volatile), $S_{t,d}$ (S), and M_t (moisture) of the three coke samples were approximately 12, 1.25, 0.9, and 0.2%, respectively.

Specifically, the crushing strength (M_{40}) and abrasion resistance (M_{10}) were obtained according to GB/T 2006–2008. The CRI and CSR were tested according to GB/T 4000–2017. Furthermore, M_{40} , M_{10} , CRI, and CSR were approximately 88, 6.5, 25, and 63%, respectively. There were slight differences in the indices of the three coke samples.

4.2. METHODS

Before the experiment, the raw coke was broken in the range of 23–25 mm and dried at 170 °C for 2 h in a draft-drying cabinet. The experimental process is illustrated in Figure 10.

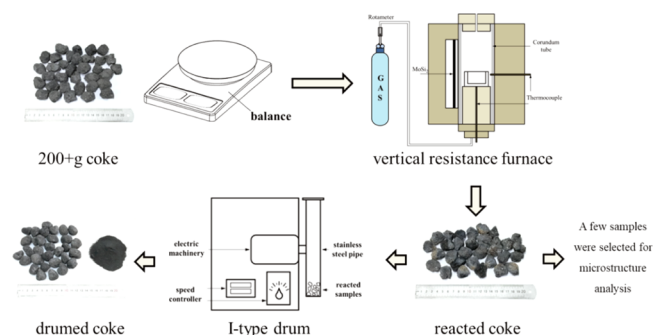


Figure 10. Schematic diagram of the experiment.

First, more than 200 g of lump coke was weighed. Second, the samples were charged into a corundum crucible and placed at the bottom of a vertical resistance furnace. The internal diameter of the furnace was 90 mm. The heaters were fabricated using MoSi₂. A thermocouple on the furnace wall was used to measure the temperature of the furnace body, and a thermocouple at the bottom of the furnace was used to measure the temperature of the samples. The gas entered the bottom of the furnace. The samples were preheated to the set temperature at a rate of 10 °C/min in an Ar atmosphere.

Then, the samples were annealed at a set temperature (1100, 1200, 1300, 1400, and 1500 °C) with 100% Ar flow. The samples for CO₂ were reacted at a set temperature (1100, 1150, 1200, 1250, and 1300 °C) with 100% CO₂ flow. After the reaction, the coke samples were gradually cooled to room temperature in an Ar atmosphere and weighed. Finally, the reacted coke was charged into an I-type drum (600 revolutions at 20 rpm). The dried samples were then weighed.

The carbon structure was analyzed using XRD. The treated samples were tested using XRD (Almelo, The Netherlands), which was operated under the following conditions: Cu K α

radiation with a tube current and a voltage of 40 mA and 40 kV, respectively, scanning range of 5–90°, and scanning speed of 0.05°/s. Some reacted coke was fixed with epoxy resin and polished for optical microscopy (Leica) analysis to observe the pores of the coke samples. Optical microscopy photographs of 20 pots per sample were obtained. An image analysis software, Image pro plus 6.0, was used to analyze the pore structure of the coke samples.

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