Fractal description and adsorption-desorption behaviour of coke treated by benzene pyrolysis carbons

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Abstract: For explaining why benzene pyrolysis carbons could inhibit coke deterioration in blast furnace, the adsorption-desorption data of coke sample treated by benzene pyrolysis carbons were obtained to establish adsorption-desorption isotherms and to fit fractal description model with Frenkel-Halsey-Hill equation. The SEM photographs of coke revealed that the pores of the infiltrated coke were almost filled with pyrolysis carbon particles. The fitted curves showed that the types of isotherms were similar to 'type II' of IUPAC classification, and the hysteresis loops belonged to type H3 which represents a typical multilayer adsorption. Model tests indicated that the pore structure of the coke samples have obvious fractal feature and the fractal dimensions of coke sample treated by benzene pyrolysis carbons were smaller than that of original coke sample. So, it explained that benzene pyrolysis carbons can effectively inhibit coke deterioration by infiltrating into the pore structure of coke and reducing pore roughness.

Keywords: coke; inhibition deterioration; benzene pyrolysis carbons; adsorption-desorption; fractal description.

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1 Introduction

Coke is used in metallurgy, chemistry industry and has strong influence on energy efficiency and quality of hot metal (Li et al., 2014; Tony et al., 2013). In blast furnace, coke is used as energy material, reductant and mechanical permeable skeleton. With the reduction in coke rate and the increase of coal injection, the skeleton of coke becomes weaker and causes coke to be deterioration (Zorin and Stakheev, 2015; Shigeno et al., 1998).

Chemical vapour infiltration (CVI) is a technology to fill the pores or discrepancies existing in ceramic matrixes or carbonaceous materials by reactant gases diffused into a porous substrate and deposited (Zhang and Huttinger, 2002). The technology is widely used to reinforce the composite material or to change the reactivity of substrates. One of the representative applications is filling the pores existing around a carbon fibre with thermally deposited carbon from hydrocarbons (Shigeno et al., 1997).

Another application of CVI is for metallurgy coke, improvement of characteristics of coke, such as coke reaction index (CRI) and coke strength after reaction (CSR), has been studied (Koyano et al., 2011; Bogolova et al., 2011; Zhang et al., 2012). Increase in CSR and decrease in CRI can inhibit deterioration of coke and open the possibility of use of lower-quality coke in a blast furnace.

In the previous researches (Zhang et al., 2012, 2013), the effect of benzene pyrolysis carbons on coke by CVI technology and the kinetics of inhibition reaction to coke deterioration by benzene pyrolysis carbons were discussed respectively. In this article, the CRI and CSR of coke samples were tested to verify the improvement of characteristics of coke samples through the apparatus described in Nippon Steel Corporation (NSC) method, and the adsorption-desorption data of coke samples were obtained to set up the mathematical model with Frenkel-Halsey-Hill (FHH) equation. Model tests showed that coke samples have obvious fractal feature and the value of dimensions, D, are all between 2 and 3. The change of D indicated that benzene pyrolysis carbons could reduce the surface and the internal hole number of coke samples with pore roughness decreased. It could explain theoretically why benzene pyrolysis carbons could effectively inhibit coke deterioration.

2 Experiments

2.1 Materials

The original coke sample was provided by Anyang Iron and Steel Group Corporation. The infiltration coke was re-treated by benzene pyrolysis carbons under the optimum reaction conditions described in the literature (Zhang et al., 2012). So, coke samples used are categorised into four groups:

a original coke

b infiltration coke

c oxidised coke

d coke oxidised after infiltration, respectively.

Nitrogen was used as adsorption and desorption gas in the experiments.

2.2 Experiment methods

The coke samples were scanned by *Quanta 200* scanning electron microscope to investigate changes of coke surface morphology.

The CRI and CSR were tested through the apparatus described in NSC method in the previous research (Zhang et al., 2012). The adsorption-desorption data of coke samples were measured using low-pressure nitrogen adsorption-desorption experiment at temperature (77K) by NOVA4200e apparatus. The CRI, CSR and the specific surface area, S_{BET}, were listed in Table 1. The S_{BET} were calculated using BET method.

Table 1 Properties of coke samples

Samples	*CRI/wt %*	*CSR/wt %*	$S_{BET}/m^2\cdot g^{-1}$
Original coke	33.41	61.73	0.89
Infiltration coke	21.23	72.45	0.26
Oxidised coke	-	-	22.0
Coke oxidised after infiltration	-	-	8.60

3 Result and discussion

3.1 Effect of enhancement in CSR and decrease in surface area

The CSR listed in Table 1 showed that the infiltrated coke had about 10.72% enhancement of CSR than that of the original coke, which illustrated that benzene pyrolysis carbons could infiltrate into the pores of coke. Thereby the resistance against oxidation of coke is enhanced.

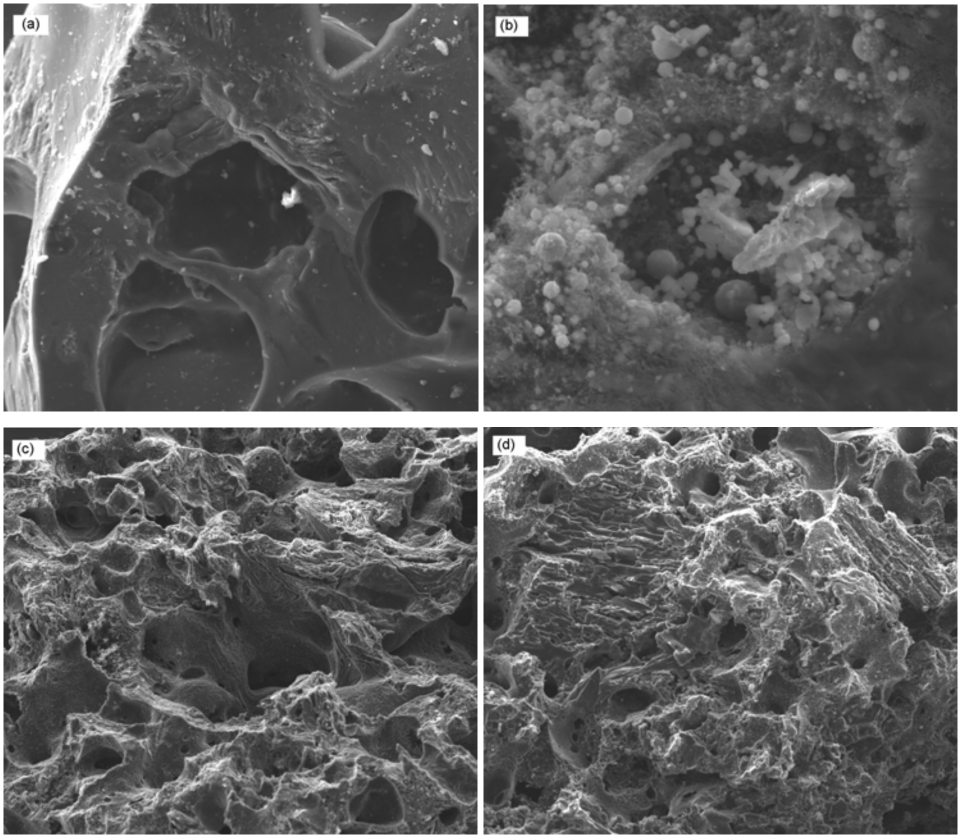
Compared with original coke, the infiltrated coke had a less surface area (0.26 $m^2\cdot g^{-1}$) than that of the original coke (0.89 $m^2\cdot g^{-1}$) listed in Table 1, which can reduce the reaction contact area as well as the reaction active sites between coke and carbon dioxide. Hence, infiltration of benzene pyrolysis was benefit to inhibit coke deterioration for improving thermal properties of coke.

3.2 Surface morphology analysis

The SEM photographs of original coke and infiltrated coke were shown in Figure 1(a) and 1(b), respectively. Comparison revealed that the original coke has larger and more clearly visible pore than infiltrated coke which has pyrolysis carbons infiltrated into the pores. The pores filled with many pyrolysis carbons caused a reduction in the pores volume and a decrease in reactivity of coke. It contributed to inhibit the deterioration of coke and enhance the skeleton of coke.

Photograph of oxidised coke and coke oxidised after infiltration were shown in Figure 1(c) and 1(d), respectively. It showed that the reaction between coke and carbon dioxide distinctly affects the physical structure of cokes. The coke oxidised after infiltration presented a closed structure with the pores in semi-closed state and less open porosity than that of the oxidised coke, which helped to decrease significantly the reaction area. Consequently, the coke oxidised after infiltration had a strong ability to resist the loss reaction with carbon dioxide and enhance the permeable skeleton role of coke.

Figure 1 SEM photographs of coke samples, (a) original coke (b) infiltration coke (c) oxidised coke (d) coke oxidised after infiltration



3.3 Adsorption-desorption behaviour of coke samples

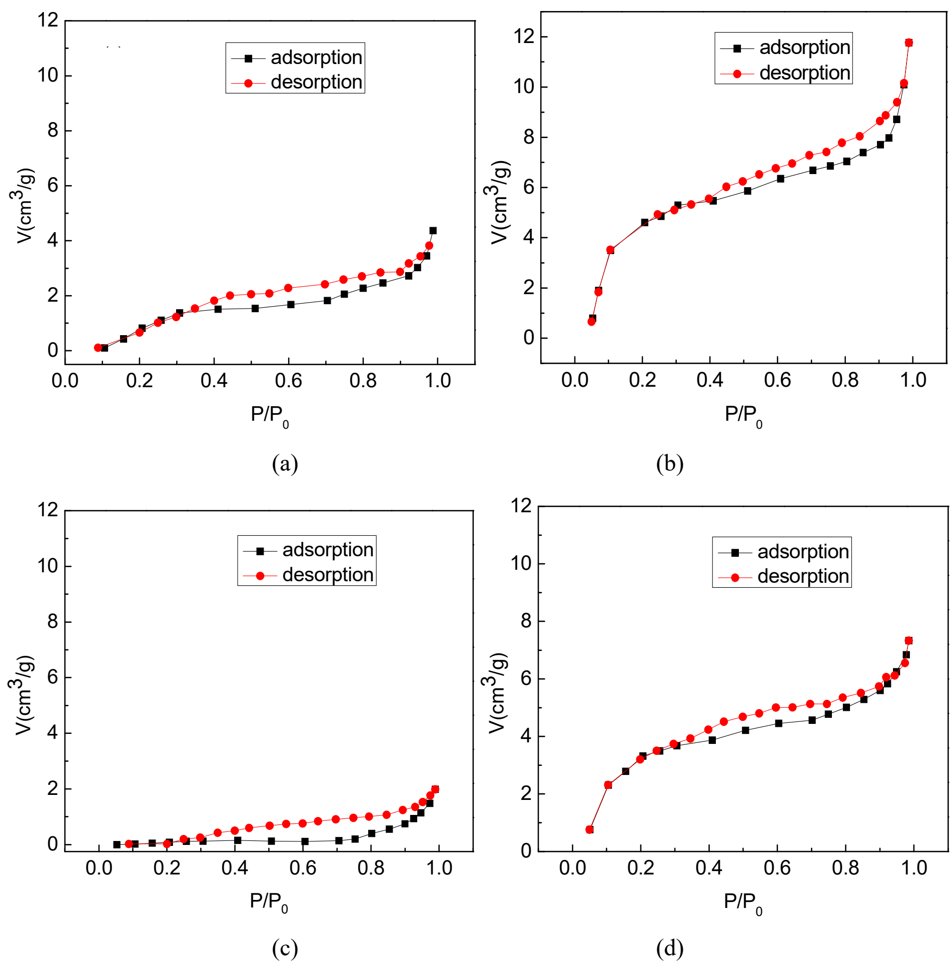
The adsorption-desorption data of nitrogen under the different equilibrium relative pressure P/P_0 were measured for different coke samples, respectively. The N_2 adsorption-desorption isotherms of different coke samples were described in Figure 2. The V is plotted against the relative equilibrium pressure, P/P_0. Where, V is volume of adsorbed nitrogen, $cm^3 \cdot g^{-1}$; P is equilibrium pressure, kPa; P_0 is the saturation pressure of the pure adsorptive nitrogen at the temperature of the measurement, kPa. It was found that the volume of adsorbed nitrogen increased in the order of oxidised coke > original coke > coke oxidised after infiltration > infiltration coke at the same or similar relative pressure, P/P_0.

The shapes of all the adsorption curves are all similar to so called ‘type II’ among the six types of the curves categorised IUPAC classification (Sing, 1982; Dou et al., 2011). And the types of hysteresis loops belong to type H3, which represents a typical multilayer adsorption in the pore structure of coke samples.

The ‘type II’ isotherm is a normal form of isotherm obtained by coke samples which are macroporous adsorbent. The isotherm represents unrestricted adsorption. Usually, at 0.2 of P/P_0 the beginning of middle section of isotherm is often used to indicate the stage at which monolayer coverage is complete and multilayer adsorption begins. Above 0.2 of P/P_0, the hysteresis loop is applied to all samples, the lower curve is of the adsorption and the upper one is of the desorption.

The isotherm of infiltration coke [Figure 2(c)] was compared with that of original coke [Figure 2(a)] to estimate the effect of infiltration on the properties of coke. And likewise, the isotherm of coke oxidised after infiltration [Figure 2(d)] was compared with that of oxidised coke [Figure 2(b)].

Figure 2 Adsorption-desorption isotherms of N_2 in coke samples, (a) original coke (b) infiltration coke (c) oxidised coke (d) coke oxidised after infiltration (see online version for colours)



The adsorption in micropores is a direct consequence of the overlap in the adsorption field from adjacent walls of micropores at low pressure. Comparison of the isotherm of infiltration coke [Figure 2(c)] and that of original coke [Figure 2(a)] revealed that the first half hysteresis loop of infiltration coke rose trend slowly, with the slope smaller than that of the original coke sample. It indicated that the adsorption volume in infiltration coke was smaller than that in original coke. The adsorption volume of nitrogen could measure changes in the size and the volume of pore in coke samples, the more of the adsorption volume, the bigger of the pore volume (Samadi-Maybodi and Vahid, 2011; Nakai et al., 2012). The original coke sample has large pore size and many mesopores while the infiltrated coke sample has many pyrolysis carbons infiltrated into the pores, which resulted in smaller size and volume of the pore. The pores filled with pyrolysis carbons greatly reduce volume and specific surface area (listed in Table 1) as well as the reaction area between coke and carbon dioxide, which resulted in enhancement of CSR. It also suggested that reduction in reactivity was a consequence of decrease in the surface area. It contributes to improve CSR and enhance skeleton of coke to inhibit the deterioration of coke.

Similarly, comparison with the oxidised coke [Figure 2(b)] and the coke oxidised after infiltration [Figure 2(d)], the isotherms exhibited the similar phenomena to that of original coke and infiltration coke. The adsorption of nitrogen for the oxidised coke is higher than that of the coke oxidised after infiltration. It can be explained by the fact that the coke oxidised after infiltration presented a closed structure with the pores in semi-closed state and less open porosity than that of the oxidised coke.

In conclusion, the isotherms explained the fact that the infiltration coke had the strong ability to resist loss reaction and enhance the permeable skeleton of coke, which was in accordance with the result in the literature (Zhang et al., 2012).

3.4 Adsorption-desorption models and fractal description of coke samples

A fractal dimension is an index for characterising fractal patterns or sets by quantifying their complexity as a ratio of the change in detail to the change in scale (Robert, 1990). Fractal dimensions were first applied as an index characterising complicated geometric forms for which the details seemed more important than the gross picture (Albers and Alexanderson, 2008). Although the adsorption and desorption isotherm can well describe the properties of coke samples, but it could not describe the fractal description for pore structure of the coke samples. So, the data in Figure 2 were fitted according to FHH equation (1) to prove changes of pore structures in coke samples (Shi et al., 2009; Cheng et al., 2016).

$$\ln V = (D-3)\ln\left(\ln\left(P_0/P\right)\right) + A \tag{1}$$

where V is volume of adsorbed nitrogen, $cm^3 \cdot g^{-1}$; P is equilibrium pressure, kPa; P_0 is the saturation pressure of the pure adsorptive nitrogen at the temperature of the measurement, kPa. D is fractal dimension, and A is an equation parameters. The confidence intervals for D, A and the correlation coefficient, r, were listed in Table 2, respectively.

The changes of D indicated that the infiltrated material can transform the surface structure of the samples (Ping et al., 2007). It can be seen from Table 2 that the D of coke samples were all between two and three, the obvious changes of the D indicated that the change of pore structures in coke samples. The D of infiltration coke was less than that of the original coke samples. It showed that the infiltration coke reduced the surface area and pore numbers of coke samples with pore roughness decreased.

Table 2 Values of *D*, *A* and *r* of coke samples according to equation (1)

Samples	*Processes*	*D*	*A*	*r*
Original coke	Isothermal adsorption	[2.663, 2.667]	0.2508	0.9923
	Isothermal desorption	[2.688, 2.694]	0.6222	0.9740
Oxidised coke	Isothermal adsorption	[2.803, 2.807]	1.634	0.9796
	Isothermal desorption	[2.816, 2.824]	1.729	0.9721
Infiltration coke	Isothermal adsorption	[2.185, 2.189]	–2.363	0.9885
	Isothermal desorption	[2.217, 2.221]	–1.800	0.9953
Coke oxidised after infiltration	Isothermal adsorption	[2.778, 2.782]	1.274	0.9821
	Isothermal desorption	[2.751, 2.756]	1.420	0.9751

Also, in the process of isothermal desorption, the values of fractal dimension of coke oxidised after infiltration was less than that of the original coke sample, which illustrated that original coke sample has relatively high specific surface areas.

It proved that benzene pyrolysis carbons can infiltrate in pore structure of coke samples and inhibit the reactions of coke with carbon dioxide. It also explained that benzene pyrolysis carbons can effectively inhibit coke deterioration reaction by infiltrating into the pore structure of coke, reducing pore roughness and making pore to be smoother.

4 Conclusions

The SEM photographs of the infiltrated coke suggested that benzene pyrolysis carbons can infiltrate in pore structure of coke samples and inhibit the reactions of coke with carbon dioxide.

The adsorption-desorption isotherms of coke samples are similar to type II of IUPAC classification and the hysteresis loops belonged to type H3. The adsorption of nitrogen at low pressure increases in the order of oxidised coke > coke oxidised after infiltration > original coke > infiltration coke at the same P/P_0. The fact suggested that the infiltrated coke has pyrolysis carbons infiltrated into the pores which contribute to inhibit the deterioration of coke and improve the properties of coke.

The values of fractal dimension *D* of coke samples are all between 2 and 3, the obvious changes of the *D* indicated that the benzene pyrolysis carbons could reduce the surface area, the hole number and the pore roughness of coke samples, so that it inhibit coke deterioration for improving the thermal properties of coke.

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