Negatively Catalyzed Gasification Characteristics of Metallurgical Coke and its Implication for Ironmaking Process

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Boric acid as a negative catalyst can decrease the coke reactivity, and increase coke strength after reaction which is essentially important for high efficient utilization of coke and stable operation of blast furnace. CO2 gasification was conducted to investigate the gasification characteristics and kinetics of H3BO3 treated metallurgical coke with different loading amount and loading method. After 2.0 wt% H3BO3 sprayed, the thickness of coke pore walls increased from 132.41 μm to 162.34 μm, and the porosity decreased from 46.76% to 42.16%. Gasification reaction was suppressed obviously by introducing 0.5 wt% H3BO3. This effect is slightly increased with further addition of H3BO3. As characterized by reactivity index, reactivity of coke without H3BO3 was 9.72 × 10−3 min−1 at 1473 K, while it decreased to 7.19 × 10−3 min−1 when 2.5 wt% H3BO3 loaded. Unreacted core model was used to establish the corresponding kinetic relationship and analyze the rate-limiting step in gasification process. Internal diffusion resistance reduced as temperature increased, and rose alongside carbon conversion rate. Results from reactivity and strength analysis proved that a certain amount of H3BO3 sprayed onto coke surface can significantly improve the coke strength after reaction and reduce the generations of coke fine.

KEY WORDS: metallurgical coke; negative catalytic; kinetics; reaction resistance; implication.

1. Introduction

Energy is always the key issue for iron and steel making process which takes more than 15% energy consumption in the whole process industry in China.1) The blast furnace (BF) ironmaking system accounts for about 70% of total energy consumption of steel industry, making it the central focus of energy conservation.2) Coke serves as the main energy carrier and the most important raw materials for blast furnace. Even though part of coke functions such as energy resources, reductant and carburizer can be replaced by coal injection, its role as column skeleton is found to be irreplaceable by any materials after more than 200 years’ industry practice.3) High efficient utilization of various coke resources is a key challenge for BF ironmaking to minimize its energy consumption and maximize production efficiency. With increasing demands for higher coke quality, one of the key requirements is to design cokes with an appropriate reactivity, strength and other properties for both current and emerging ironmaking technologies, i.e., low temperature blast furnace, nitrogen-free blast furnace, etc.

With the gradual shortage of high-quality coking coal, the quality of metallurgical coke gets worse with higher reactivity and lower strength after reaction. An important property of coke for use in BF is the suitability of cold strength and thermal strength. The thermal strength is often expressed by coke reactivity index (CRI) and coke strength after reaction (CSR). There is no direct relationship between CRI and the cold strength of coke, but it affects CSR indirectly. For coke with more pores and more cracks, there is more chance for CO2 and H2O to contact with carbon, making a higher CRI. At the same time, some minerals in coke, alkali metals and Zn adsorbed in BF can catalyze the gasification reaction of coke to varying degrees. The consumption of carbon gasification causes an increase in pores and a thinning of the pore walls, making a lower CSR. Studies have shown that the higher the CRI, the greater the gasification amount of coke.4,5) On the one hand, the heat level in BF reduces and the fuel ratio increases. On the other hand, the strength of coke is weakened, and a large amount of coke fine is generated. The gas permeability of the column in furnace gets worse due to the coke fine accumulated in the part with low gas flow velocity, which is harmful for the blast furnace operation and may increase the total energy consumption.6,7)
The gasification characteristics and kinetics of coke inside blast furnace have been a hot topic in the field of high efficient utilization of fossil fuels for a long time. Various factors have been confirmed to influence coke gasification. Xu et al. found the crystalline structure of carbon played a vital role on gasification reactivity, while the gasification rates are also significantly influenced by pore structures. Xu et al. analyzed the influence of iron minerals on the CO₂ gasification of ferro-coke. With the increase of iron amount, the strength of ferro-coke strongly decreases and the influence of hematite, limonite, and olivine hematite on strength decreases slightly in that order. Reid et al. studied the effects of minerals on coke reactivity by coke analogue. The individual effects of different minerals were determined. Previous study convinced that different minerals may have significant discrepancy when it comes to the catalytic ability on coke gasification. The main positive catalytic minerals are pyrite, gypsum, iron, troilite, magnetite, lime and hematite, while the main negative catalytic minerals are kaolinite, quartz, potash feldspar and soda feldspar. Because of the proposal of future low temperature BF with high reactivity coke, a lot of researches have been done regarding the positive catalytic effect of minerals, while the understanding about negative catalysts is far from complete.

It is reported that the use of high reactivity coke in a commercial scale blast furnace increased the reaction efficiency and decreased the temperature of the thermal reserve zone. In addition, increasing iron oxide reduction efficiency would greatly reduce direct reduction in the high temperature zone. As a result, the high reactivity coke helps to increase gas utilization efficiency, decrease direct reduction degree and fuel rate. Normally, high reactivity coke has lower strength after reaction, which is unfavorable for the BF production. The existing way to improve the strength after reaction of high reactivity coke is to increase the proportion of coking coal in the coking process. However, this leads to an increase in coking costs and the emission of harmful gases. A new technique which is called “coke passivation technology” by using a negative catalyst and selecting a proper adding method was proposed to ensure the appropriate CRI and CSR of coke in recent years. This technology was found to be able to decrease coke reactivity and increase coke strength, which finally decreases the energy consumption in BF. An in-depth understanding about coke gasification mechanism, especially under the condition of negative catalyst, is significant to increase the coke utilization efficiency and decrease energy consumption in ironmaking process as well as other coke-related industrial processes.

Roseoe and Thomas found that BO₃⁻ can bind to C atoms around the lattice and block channels for diffusion, thereby reducing coke reactivity. Audrieen and Walker found that the gasification rate of natural graphite doped with B in CO/CO₂ at 1 988 K decreased, but the activation energy of the whole reaction did not change. Boration reaction increases the reaction order of Langmuir-Hinshelwood model (C + CO₂ = 2CO), but reduces the reaction rate constant. Mi and Li treated coke with a 0.5 wt% boric solution. The results showed that the passivation effect was more obvious when directly acting boride on coke surface than blending them in coal, especially for high reactivity coke. Zhu et al. developed a special coke passivator named as ZBS, and the industrial test results indicated an increased pig iron production and reduced fuel consumption, mainly metallurgical coke.

The reactions between carbon and gas molecular (CO₂, H₂O) is key in coke gasification process. The common models for studying gasification kinetics are random pore model (RPM), volume model (VM) and grain model (GM), which place emphasis on the apparent chemical reaction. However, the detailed gasification process of carbon materials is not analyzed step by step. Guo et al. analyzed the gasification kinetics of metallurgical coke with CO₂ and H₂O, which takes external diffusion, internal diffusion, and interfacial chemical reaction into consideration. Results showed that the diffusion of gas in porous coke is more pronounced at high temperatures (> 1273 K), Lundgren et al. compared the properties between coke before and after reaction in experiential BF at LKAB company. They proved that the control step of the coke gasification process during the CRI/CSR test is chemical reaction (reaction is slow when temperature is low), while it has changed to diffusion (chemical reaction is fast at high temperature, the gas diffusion is slow conversely) in industrial BF. That is to say, the deterioration of metallic coke in BF occurs more on the surface. As the reaction progresses, the unreacted core gradually shrinks to disappear, and the transformation behavior is consistent with the unreacted core model (URCM). Xu et al. used the URCM to characterize the gasification mechanism and kinetics analysis of coke, while they assumed the mechanism remained constant during the whole process, and the only k₀ was obtained by fitting dX/dt with X.

Reducing gasification of coke in BF is considered to be an effective way to increase coke strength for both low quality coke and high reactivity coke, which becomes the key concerns of both ironmaking and cokemaking. Experimental and industrial studies have shown that B-based negative catalyst is suitable for the inferior coke, which is beneficial to areas lack of caking coal. Applying negative catalyst directly to the coke is more effective than adding them to blending coal before cokemaking, which helps to reduce the consumption of catalysts. However, the inhibition mechanism and kinetics of B-based negative catalyst have not been fully studied. The present studies are devoted to investigating the effect of boric acid on metallurgical coke gasification and exploring its best application in industrial production. The reaction rate and kinetics of CO₂ gasification for coke loaded with H₃BO₃ were compared with different loading methods and loading amounts. And negative catalytic mechanism of H₃BO₃ on coke gasification was also proposed. This study is expected not only to contribute new insights into the understanding of negative catalytic characteristics of H₃BO₃ on CO₂ gasification reaction of high reactivity metallurgical coke, but also to guide the application of negative catalyst H₃BO₃ in cokemaking and ironmaking process.
2. Experimental

2.1. Raw Materials and Analysis Method

A high reactivity metallurgical coke was collected from a steel plant in China. Samples were cut to the sizes of φ23–25 mm. The results of the strength, proximate, ultimate and ash component analysis of coke are shown in Table 1. Mineral Catalytic Index (MCI) is also calculated using Eq. (1). After coke was dried at 448 K for 0.5 h, it was subjected to catalysts loading treatment. The boric acid was dissolved in deionized water at 343 K, and its mass concentration was set to 0.5–2.5 wt%. To be more suitable for use in coking production, two methods: spraying and soaking were selected as the loading methods. 10 ml H₃BO₃ solution (3 mg/ml–15 mg/ml) is sprayed on the coke surface uniformly. The solution is also used to soak samples for two minutes. And 2 h of drying at 448 K is taken to eliminate the influence of moisture before gasification test. Spraying can more effectively save water and reduce sewage in steel production.

The morphology of metallurgical coke and H₃BO₃ were observed using Scanning Electron Microscopy (SEM) (FEI Quanta-450) at 15 kV, with a Energy Dispersive Spectrometer (EDS). Intrinsic major phases of coke and H₃BO₃ was investigated by a DMAX-RB X-ray diffractometer (XRD). Cu Kα (λ = 1.54051 Å, 40 kV, 30 mA) radiation was selected as the X-ray source. Record the diffraction intensity in the range of 10° ≤ 2θ ≤ 90° at 0.02°/step. In order to avoid the difficulty of sample preparation and the influence of pressure on experimental measurement, image analysis via imageJ was used to evaluate the microstructure of metallurgical coke before and after treated. As many pictures as possible were chosen for data statistics to reduce experimental error.

\[
\text{MCI} = A_{\text{ad}} \times \\
\text{Fe}_2\text{O}_3 + 1.85\text{K}_2\text{O} + 2.2\text{Na}_2\text{O} + 1.6\text{CaO} + 1.91\text{BaO} + 0.83\text{MgO} + 0.9\text{MnO}_2 - \\
\text{SiO}_2 + 0.41\text{Al}_2\text{O}_3 + 2.5\text{TiO}_2
\]

................................. (1)

2.2. Apparatus and Operation

The coke reaction index and coke strength after reaction tests were carried out in a program controlled high temperature reaction furnace, with 50 g φ23–25 mm spherical coke under CO₂ for 2 hours at 1 373 K. The mass loss of coke sample was expressed as experimental coke reactivity index (exp-CRI), and the experimental coke strength after reaction (exp-CSR) is measured based on the residue. Exp-CSR is defined as the weight percentage of coke larger than 10 mm in size after 600 revolutions at 20 rev/min in a type 1 tumbler rotating. While for the gasification tests, one φ23–25 mm spherical coke approximately 6 g was placed in a hanging basket made by MoO, and it will react with CO₂ under 1 173 K–1 473 K for 2 hours. Figure 1 shows the schematic diagram of program controlled high temperature reaction furnace for reactivity and gasification test. N₂ was introduced for 30 min in advance to exhaust air, and it was replaced by 5 L/min CO₂ after the desired temperature was reached and no evident weight loss was observed. The metallurgical coke was put in after the temperature and airflow were kept constant. Only the gasification process was calculated and analyzed in this paper.

![Fig. 1. A schematic diagram of program controlled high temperature reaction furnace, mainly including high temperature furnace, weighing balance, data processing center, gas distribution system. (Online version in color.)](image-url)
2.3. Kinetics Analysis

The coke gasification is a typical two-phase reaction between porous solid and gas. According to the theory of unreacted core model, gasification reaction consists of three parts: external diffusion, internal diffusion and interfacial chemical reaction. Figure 2 shows the schematic diagram of coke gasification reaction (gas-solid reaction) process. For the gas-solid reaction of spherical particles, there is

\[ A_{(g)} + B_{(s)} = gG_{(g)} + sS_{(s)} \] .......................... (2)

The following assumptions were made for URCM to guarantee the continuous and stable gas-solid reaction: 1) solid reactant B (carbon) is dense and the particle shape remains unchanged during reaction; 2) gasification reaction is a first-order irreversible reaction at the interface of gas-solid phase, which has the characteristics of interfacial chemical reaction; 3) movement rate of the reaction interface is smaller than diffusion rate of the production layer. The reduced product S is porous layer, providing diffusion channel for the gaseous reaction.

The carbon conversion rate can be analyzed by the following equation:

\[ X = \frac{\Delta W}{W_{(0)}} \times 100\% \] .......................... (3)

where \( X \) is the carbon conversion rate, %; \( \Delta W \) represents the mass loss of coke by gasification, mg; \( W_0 \) the initial mass of coke sample, mg; \( \alpha \) the initial fixed carbon content of coke, mass%. According to Guo et al., when the resistances of external diffusion, internal diffusion and chemical reaction are all present, the contribution of these three factors to gasification rate should be considered simultaneously.

Rate of external diffusion:

\[ v_E = \frac{4\pi \rho_B}{bM_B} \frac{dn}{dt} = \frac{4\pi \rho_B}{bM_B} \frac{\Delta W}{W_{(0)} \cdot 100\%} \frac{1}{\rho_B} \frac{1}{bM_B} \] .......................... (4)

Rate of internal diffusion:

\[ v_I = \frac{4\pi \rho_B}{bM_B} \frac{dn}{dt} = -\frac{4\pi D_{\text{eff}}}{bM_B} \frac{\Delta W}{W_{(0)} \cdot 100\%} \frac{1}{\rho_B} \frac{1}{bM_B} \] .......................... (5)

Rate of interfacial chemical reaction:

\[ v_{rea} = -\frac{4\pi r_i^3 \rho_B}{bM_B} \frac{dn}{dt} = -\frac{4\pi r_i^3 \rho_B}{bM_B} \frac{\Delta W}{W_{(0)} \cdot 100\%} \frac{1}{\rho_B} \frac{1}{bM_B} \] .......................... (6)

The completion time of each individual process is calculated:

\[ t_E = \frac{n_1 \rho_B}{bM_B} \frac{1}{3}, t_I = \frac{n_i \rho_B}{bM_B} \frac{1}{3}, t_R = \frac{n_R \rho_B}{bM_B} \frac{1}{3} \] .......................... (7)

\( C_{AB} \) is the initial CO2 concentration, mol/m3; \( k \) is the mass transfer coefficient of external diffusion, m/s; \( r_0 \) is radius of spherical particle, m; \( r_i \) is radius of unreacted core, m; \( \rho_B \) is the molar concentration of coke, mol/m3. \( D_{\text{eff}} = D_{\text{eff}}/\tau \) is the effective gas diffusion coefficient in residual multi-space ash layer, m2/s, \( \tau \) is the tortuosity coefficient. \( k \) denotes the interfacial reaction rate constant, m/s. The following relationship exists between reactant consumption and conversion rate:

\[ X = -\frac{4}{3} \pi r_i^3 \rho_B \frac{4}{3} \pi r_i^3 = 1 - \left( \frac{r_i}{r_0} \right)^3 \] .......................... (8)

The total reaction time of gasification reaction is

\[ t = t_E X + t_I [1 - (1 - X)^{2/3} + 2(1 - X)] + t_R [1 - (1 - X)^{3/2}] \] .......................... (9)

The right side of Eq. (9) indicates the contributions of external diffusion, internal diffusion, and interfacial chemical reaction, respectively. Since the gas flow rate of CO2 in this experiment is large enough, the influence of external diffusion on gasification rate can be excluded. When the gasification reaction is controlled by the internal diffusion and chemical reaction, there is:

\[ \frac{bC_{AB}}{n_1 \rho_B} \frac{1}{6D_{\text{eff}}} \frac{[1 - 3(1 - X)^{2/3} + 2(1 - X)]}{[1 - (1 - X)^{3/2}]} \] .......................... (10)

Make

\[ F = 1 - \frac{n_1}{n_0} \] .......................... (11)
Then the above formula can be converted into:

\[
\frac{I}{F} = t_t (3F - 2F^2) + t_R 
\]

The time \( t_t \), \( t_R \) represent the contributions of internal diffusion and interfacial chemical reaction, which can be obtained from the change of carbon conversion rate.

3. Results and Discussion

3.1. Structure of Metallurgical Coke before and after Treatment

The morphology of metallurgical coke and boric acid was observed by SEM, shown in Fig. 3. The pores of metallurgical coke are well developed and evenly distributed, making coke very vulnerable to deterioration. In addition, the pore wall is thin with a large number of closed pores distributed around, which is beneficial for pore growth during gasification. The porous coke reacts strongly with \( \text{CO}_2 \) in the cohesive zone of BF, and the pore walls become thinner, making the strength of the coke sharply decrease after gasification. It is easy to generate coke fine and affect the gas permeability in BF. It can be seen from Fig. 3(B), the particle size of \( \text{H}_3\text{BO}_3 \) (around 20 \( \mu \text{m} \)) is close to mesopores in coke. \( \text{H}_3\text{BO}_3 \) may exist in pores of coke in the form of particles and flakes after spraying and soaking. It can also form a snowflake-like, network-like carbide, which not only shields the reaction gas contacted with carbon for gasification in BF but also increases the strength of coke. Figure 3(C) is the energy spectrum of local minerals in coke, and oxides of Si, Al and Ca are main composition in addition to carbon. The X-ray diffraction pattern of boric acid (Fig. 3(D)) indicates that the purity of \( \text{H}_3\text{BO}_3 \) is high enough and it can be used for investigation of catalytic effect on the gasification of metallurgical coke.

After \( \text{H}_3\text{BO}_3 \) loading, pore morphology of peripheral coke changed obviously, seen from Fig. 4. The choice of ‘2.0 wt%’ \( \text{H}_3\text{BO}_3 \) as a research example was to avoid experimental error caused by the highest (2.5 wt%) and the lowest (0.5 wt%) concentration. On the other hand, ‘2.0 wt%’ was

![Fig. 3. The characteristics of samples: (A) and (B) morphology of metallurgical coke and boric acid, respectively; (C) local energy spectrum of metallurgical coke; (D) X-ray pattern of boric acid. (Online version in color.)](image)

![Fig. 4. Morphology of metallurgical coke before and after treatment: (A) coke without treatment; (B) 2.0 wt% \( \text{H}_3\text{BO}_3 \) soaked coke; (C) 2.0 wt% \( \text{H}_3\text{BO}_3 \) sprayed coke. (Online version in color.)](image)
chosen in order to better highlight the impact of negative catalysts on structure characteristics, loading method and gasification kinetics of metallurgical coke. The micron-sized catalyst particles can penetrate into pores after soaking, while they are mainly attached to the surface during spraying to block pores. This indicates that the spray mainly acts on the surface of the coke, and the negative catalyst can penetrate into the interior when soaked. The results of pores size distribution in metallurgical coke were obtained by Image J, as shown in Fig. 5. Affected by the particle size of H$_3$BO$_3$, pores $>$ 241 μm significantly increased, with 121–180 μm pores reduced. The addition of negative catalyst significantly reduces the porosity of coke from Fig. 5(b). Further comparison shows that, the effect of spraying is more obvious under the same conditions. The thickness of pore walls increased from 132.41 μm to 162.34 μm, and porosity decreased from 46.76% to 42.16% with 2.0 wt% H$_3$BO$_3$ sprayed. The effect of spraying is more concentrated, mainly on the surface of coke. On the contrary, H$_3$BO$_3$ particles enter coke pores under soaking. In general, negative catalyst sprayed on coke surface not only directly reduces the contact area between carbon and CO$_2$, but also prevents the diffusion of CO$_2$ into the coke, thereby inhibiting the gasification of coke in BF and increasing the strength of coke after reaction.

3.2. Characteristics of Metallurgical Coke Gasification

3.2.1. Influence of Catalyst Loading Amount on CO$_2$ Gasification

High reactivity coke treated with negative catalyst was selected for CO$_2$ gasification studies and Fig. 6 shows the carbon conversion rate curves of coke loaded with various amounts of H$_3$BO$_3$ by spraying. Temperature has a significant effect on gasification, and the change in carbon conversion $\Delta X$ between 1 273 K and 1 373 K is the greatest, which means that there is a substantial change in the gasification process. At 1 273–1 373 K, the resistance of temperature on interfacial reaction was lower, while that of internal diffusion is higher. When 0.5 wt% loaded, the gasification reaction of coke was significantly inhibited. As the loading amount of catalyst increased from 0.5 wt% to 2.5 wt%, the negative catalytic effect gradually deepened over the same time period. Compared with the catalyst content, the presence of negative catalyst has more obvious influence on coke gasification. Within the scope of this experiment, the negative catalytic effect of H$_3$BO$_3$ has not yet reached a limit.

The reactivity index $R_s$ was used to quantify the gasification reactivity of coke, which is defined as:

$$R_s = \frac{0.5}{t_{50}}$$

where $t_{50}$ (min) indicates the time required for 50% carbon conversion rate. Take gasification of coke at 1 473 K as an example. As shown by $R_s$, the coke reactivity without H$_3$BO$_3$ was $9.72 \times 10^{-3}$ min$^{-1}$ at 1 473 K, while it decreased to $8.42 \times 10^{-3}$ min$^{-1}$ when 0.5 wt% H$_3$BO$_3$ was loaded. Further loading H$_3$BO$_3$ from 0.5 wt% to 2.5 wt%, $R_s$ only decreased by $1.23 \times 10^{-3}$ min$^{-1}$ to $7.19 \times 10^{-3}$ min$^{-1}$. Such considerable reduction in coke reactivity could be attributed to the localized deposition of H$_3$BO$_3$ particles on coke surface, forming clusters to a certain extent. H$_3$BO$_3$ showed negative catalytic effect in the way of blocking
accessible active sites on the coke surface. The surface area and porosity analyses confirmed such speculation, where porosity calculated by Image J decreased 4.6% and thickness of pore walls increased 29.93 μm, along with increasing the H₃BO₃ loading from 0 to 2.0 wt% by spraying (Fig. 5). The temperature in the blast furnace gradually rises from top to bottom and the gasification become stronger if there is CO₂. It can be seen from Fig. 6 that the effect of negative catalyst is more obvious at high temperature, and the protective effect of the partially gasified coke is stronger, which is beneficial for the gas permeability of column in BF.

3.2.2 Influence of Catalyst Loading Method on CO₂ Gasification

Figure 7 shows exp-CRI and exp-CSR of metallurgical coke with different catalyst amounts in CO₂ at 1 373 K by two loading methods. Exp-CSR went up as exp-CRI went down with the increase of negative catalyst concentration. And spray and soak have similar effects on exp-CRI, the same as exp-CSR. In actual production, coke with low reactivity and high post-reaction strength is more preferred, so the effect of spraying is superior to that of soaking on the whole. The exp-CRI gradually decreases from 52.29% of untreated coke to 46.12% of 2.5 wt% H₃BO₃ sprayed coke. As for exp-CSR, the spraying method showed obvious advantages when the concentration of H₃BO₃ exceeded 1.0 wt%. Previous research shows the 1 kg coke can be saved per ton iron when the CRI is reduced by 1%. The CSR is improved which strengthens the skeleton function of coke in the BF. And the gas permeability index of the column is increased to further increase the coal injection amount.

There are two main reasons for the inhibitory effect of negative catalyst on CO₂ gasification with coke. On the one hand, boric acid adheres to the surface of coke, prevents contact between coke and CO₂, resulting in the reduced reaction rate; on the other hand, the atomic structure of B is similar to C, and CO₂ preferentially reacts with B due to its high reactivity. In spraying, H₃BO₃ particles had an increased chance of adhering to coke surface. The newly generated interface has much lower free energy, which thereby resists the contact with CO₂. At the same catalyst loading level, the amount of H₃BO₃ attached to the coke surface by spraying is more than that of soaking. It is indicated that coke passivation technology is very effective in improving the thermal performance of medium-strength coke (CSR~30%), and difference in strength properties depend on the pore structure of coke. More mesopores and less micropores lead to lower strength, and these pores need to be filled with more negative catalyst to effectively prevent the coke and CO₂ gasification reaction. Pores of high-strength coke are less, and the possibility of negative catalyst entering into coke is small, so its effect is relatively poor. For medium-strength coke, less negative catalyst is needed due to the less mesopores and more micropores. In general, the availability of medium-reactive and medium-strength coke in BF is considerable, high reactivity coke increases the gas utilization efficiency, and reduces the fuel ratio. Medium-strength coke can use a small amount of negative catalyst as much as possible to improve the gas permeability of the furnace.

3.3 Kinetics Analysis of Coke CO₂ Gasification

3.3.1 Apparent Reaction Kinetics

The experimental data at different temperatures were combined with isothermal thermodynamics study, and the kinetic parameters of reaction process were calculated according to URCM. The formula is plotted as t/F versus (3F−2F²), the slope and the intercept are the complete reaction time of internal diffusion and chemical reaction, tᵢ and tᵣ respectively. Substitute them into Eqs. (5) and (6), the effective diffusion coefficient Dᵢ and coke gasification reaction rate constant kᵣ were obtained. According to the Arrhenius formula:

\[ \ln kᵣ = \frac{Eₐ}{RT} + A \]  \hspace{1cm} (14)

\[ \ln Dᵢ = \frac{Eᵢ}{RT} + A' \]  \hspace{1cm} (15)

The corresponding apparent activation energy Eₐ and effective diffusion activation energy Eᵢ can be obtained. The specific values of 2.0 wt% loaded metallurgical coke are shown in Fig. 8.

It can be seen the negative catalytic effect of H₃BO₃ is
mainly manifested in internal diffusion. H$_3$BO$_3$ particles adsorbed on the coke surface is partially filled into the pores to prevent CO$_2$ diffusing into the inner of coke at low temperature. After reaching to high temperature region, B converted into the corresponding carbide, forming a shielding protective film on the surface of coke. What’s more, the negative catalyst enriched on the surface of coke, blocking the contact between coke and CO$_2$. The results of activation energy $E_a$ and $E_I$ indicated that gasification between CO$_2$ and coke treated with negative catalyst is more difficult compared with ordinary high reactivity coke in BF. In addition, the spray works better and is easier to handle during the cokemaking process. The boron compounds were inhibitors of oxidizing gases, which can adsorb stable complexes at the active sites in carbon structure, and make the active sites disappear. Further atomic simulation research is undergoing to verify this effect.

3.3.2. Step by Step Analysis of Kinetics Process

In order to further analyze the control steps of suppressed coke reaction, the internal diffusion mass transfer resistance $\eta_I$ and chemical reaction resistance $\eta_R$ were calculated respectively.

\[
\eta_I = \frac{\eta}{nD_{eff}} = \frac{\eta}{(1 - X)^{1/3} - 1}, \quad \eta_R = \frac{1}{k_{rea}(1 - X)^{2/3}}
\]

Taking the metallurgical coke sprayed by 2.0 wt% H$_3$BO$_3$ as representative, the total resistance and relative resistance of each step under different temperature and carbon conversion rates were obtained, as shown in Fig. 9. $\Sigma \eta$ is the total resistance of coke gasification reaction.

Figure 9(a) shows the change laws of chemical reaction rate constant $k_{rea}$ and effective diffusion coefficient $D_{eff}$ with temperature during gasification between coke and CO$_2$. Both showed a significant increase with increasing temperature. However, when the temperature raised from $1373 \text{ K}$ to $1473 \text{ K}$, $k_{rea}$ increases multiply, while $D_{eff}$ hardly changes. The increase of temperature in BF leads to a higher gasification rate of coke, and the coke is seriously degraded with a low strength after reaction. The negative catalyst acts significantly at high temperatures ($>1373 \text{ K}$), especially inhibiting the internal gasification of coke. As seen from Fig. 9(b), internal diffusion resistance $\eta_I$ reduced as temperature increased, and rose alongside carbon conversion rate. The influence of internal diffusion on gasification was smaller at
temperatures near 1 373 K. This may be due to the ash layer was continuously thickened as the reaction progressed, and the distance CO2 passing through lengthened. Same law for the chemical reaction resistance $\eta$. To better show the relative change of $\eta_c$ and $\eta_b$, the proportion of $\eta$ to total gasification reaction resistance $\Sigma \eta$ was drawn in Fig. 10. Coke gasification after treated by $\text{H}_3\text{BO}_3$ was mainly controlled by interface chemical reaction and internal diffusion at the early stage. Internal diffusion became the main control step with carbon conversion closing to 1. $\eta/\Sigma \eta$ reached a minimum (0.588) at 1 373 K when 20% carbon conversion, and it decreased by 0.177 from 1 173 K to 1 373 K. When the temperature went up to 1 473 K, it increased to 0.631. The pore diameter on the surface became larger due to the expansion of coke as the temperature increased, and the number of pores also increased, making the resistance of CO2 through ash layer decreased, which resulted in the relative lower $\eta/\Sigma \eta$. On the other hand, $D_{\text{eff}}$ increased faster than $k_{\text{rea}}$ by comparing the activation energy $E_\alpha$ and $E_\beta$ of the catalyst loaded coke gasification (Fig. 8(b)). When temperature continued to rise to 1 473 K, $k_{\text{rea}}$ doubled and $D_{\text{eff}}$ remained almost unchanged (Fig. 9(a)). The gasification process became significantly affected by internal diffusion. What’s more, the influence of coke expansion was no longer obvious. Under the same temperature, the thicker ash layer due to carbon loss increased the $\eta/\Sigma \eta$. The kinetic calculation results show that among the entire temperature range of the gasification reaction in BF, the addition of negative catalyst makes the limiting part of the gasification process the internal gas diffusion, which indicates that $\text{H}_3\text{BO}_3$ on the coke surface can prevent coke internal gasification, avoid the growth of pores and the destruction of pore wall. Finally, coke strength is guaranteed to reduce coke ratio and increase the amount of coal injected.

3.4 Guidance for Industrial Operation of BF and Further Research

According to the results of previous experiments and industrial tests, the negative catalysts do have a certain influence on improving the use of coke in BF, whether they are added before and after cokemaking. There are three main ways in which the negative catalysts act: (i) decrease the reaction interface area and the number of active sites. For example, $\text{P}^{+5}$, halogen elements and some B compounds are inhibitors of oxidizing gases, which can form stable complexes in carbon structure, reducing the active sites. While the positive catalysts (Na, K etc.) can produce interlayer compounds, and cracks generated by volume expansion of minerals provide sufficient active sites for the reaction; (ii) affect or block the diffusion process of gas reactant. The $\text{Mo}_2\text{O}_7^{2-}$ can combine with C atoms around the crystal lattice and block the diffusion channel, thereby suppressing the reaction speed. Ti has the same suppression effect. In addition, the formation of interlayer compounds decreases the stacking height of carbon hexagonal lattice, which hinders the diffusion of CO2 (iii) influence the optical composition of coke during the cokemaking process. The negative catalyst increases the diameter of microcrystalline layer in carbon structure during cokemaking, indicating that oxygen released during coal pyrolysis can be captured, which is beneficial to the growth of anisotropic phase. The degree of anisotropy and carbonization of microscopic component can increase the activation energy of coke gasification reaction, decrease the reaction rate finally.

In addition to the direct influence of $\text{H}_3\text{BO}_3$ on coke gasification reaction, there are also some indirect effect of $\text{H}_3\text{BO}_3$ when using in BF. First, alkali metal plays a significant positive catalytic effect on the reaction between coke and CO2. The coke with boric acid treatment can significantly improve its alkali resistance and reduce its reactivity. Secondly, due to the high alkalinity of its own mineral components, reactivity of some cokes is high, and boron has a shielding effect on the alkali metal contained in itself. Finally, researches showed that the degradation of coke in the BF was not only attacked by alkali metal and alkaline earth metal, but also by the iron in BF. The effect of iron on coke degradation is mainly the scouring of molten iron and the promotion of coke gasification reaction. The addition of boracic acid weakens the erosion of iron on coke.

Under the existing technical conditions of coke production, negative catalytic treatment technology is a good way to save investment and quickly improve the thermal properties of coke. Improving the quality of coke and reducing its use is an important method to ensure the economic benefit of blast furnace ironmaking. From the the results of present study, it can be concluded that the small amount of $\text{H}_3\text{BO}_3$ will decrease the coke reactivity and increase its strength after reaction at high temperature. It works by preventing CO2 from diffusing into coke and substituting C atom reacting with CO2 preferentially. Corresponding carbonized material can be generated at high temperature in BF, forming a protective film on the coke surface to suppress gasification reaction. This trend will be considered desirable in BF operations since a good gas and liquid permeability is guaranteed with the protected coke. This will maximize the efficiency of energy use in the context of gradual shortage of high-quality coking coal, and it also provides a guarantee for increasing the amount of coal injected into BF at the same time.

On the other hand, when treated with the same concen-
tration of $\text{H}_3\text{BO}_3$ solution, the effect of spraying is better as compared to that of soaking. From the perspective of economic benefits, it can not only conserve the use of new water and reduce the generation of sewage in treatment process, but also save negative catalysts in a targeted manner. Further research is required to consider the suitability of $\text{H}_3\text{BO}_3$ use based on the overall nature of the ironmaking system. The removal of B element from BF should be carefully studied to figure out its influence on other complicated high temperature reactions, such as the viscosity of slag, etc. In addition, the optimum addition amount of boric acid as a negative catalyst should also be studied in detail to ensure whether the benefits of reduced use of high quality coking coal are balanced with the investment of boric acid introduction as an additive. Last but not least, the environmental impact of $\text{H}_3\text{BO}_3$ addition should be placed at the top of the list.

4. Conclusion

In this paper, the unreacted core model was used to study the negative catalyzed CO$_2$ gasification of metallurgical coke with $\text{H}_3\text{BO}_3$. The effects of catalyst loading amount and loading method were compared. The following conclusions were obtained:

(1) The $\text{H}_3\text{BO}_3$ particles mainly adhere to the pore surfaces of metallurgical coke, which reduces the porosity and increases the thickness of pore walls, thereby preventing CO$_2$ from diffusing into the coke and suppressing the coke gasification reaction. And coke thermal strength in BF is maintained and the generations of coke fine is reduced finally. Therefore, the gas permeability in the blast furnace can be improved, and the production efficiency can be increased while reducing the coking cost.

(2) Compared with the content of negative catalyst, the presence of $\text{H}_3\text{BO}_3$ has more important influence on coke gasification. $R_s$ without $\text{H}_3\text{BO}_3$ was 9.72 $\times 10^{-3}$ min$^{-1}$ at 1473 K, while it decreased to 8.42 $\times 10^{-3}$ min$^{-1}$ when 0.5 wt% $\text{H}_3\text{BO}_3$ was loaded. Further loading $\text{H}_3\text{BO}_3$ from 0.5 wt% to 2.5 wt%, $R_s$ just decreased by 1.23 $\times 10^{-3}$ min$^{-1}$. This indicates that the addition of a small amount of negative catalyst can improve the use of high reactivity coke in BF and reduce the cost of coking.

(3) The negative catalytic effect of spraying is better than that of soaking on exp-CRI and exp-CSR. The exp-CRI gradually decreases from 52.29% of untreated coke to 46.12% of 2.5 wt% $\text{H}_3\text{BO}_3$ sprayed coke. The increase in coke strength after reaction has a significant effect on reducing the use of coke in BF and increasing the amount of coal injected.

(4) Spraying works better because $\text{H}_3\text{BO}_3$ particles have an increased chance of adhering to the coke surface. The newly generated interface has much lower free energy, which thereby resisting the contact with CO$_2$ to protect the carbon inside the coke from gasification. In addition, spraying is good for water saving. Further research is required to determine the most appropriate addition ratio based on environmental and economic benefits through industrial production practices.

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