Metallurgical Coke Structures

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The structure of coke affects its reactivity and strength, which directly influences its performance in the blast furnace.

coke quality coke structures characterization molecular model

1. Introduction

The blast furnace (BF) is a high-efficiency shaft furnace. The high heat utilization rate and production efficiency make the BF route the dominant ironmaking process globally [1]. About 70% of the hot metal used in producing crude steel comes from the BF route [2][3][4]. Coke is an indispensable burden in the blast furnace, and its performance shows a substantial impact on the ironmaking process [5]. The coke plays the role of the skeleton, which ensures the gas and liquid penetration through the blast furnace. The Coke reactivity index (CRI) and the coke strength after reaction (CSR) are the most widely used indexes to indicate the coke degradation potential in a blast furnace. A coke with good quality shows a lower CRI and a higher CSR.

To cut CO_2 emissions during BF ironmaking process, many methods have been developed for substituting part of the coke, such as the application of ferro coke [6][7] and biomass coke [8][9], injection of pulverized coal or biomass, or natural gas, etc. [10][11][12][13][14]. Oxygen-enriched blast technology is another well-used method to decrease the coke ratio by increasing the production rate of hot metal through enhancing the combustion intensity of coke and pulverized coal [15][16]. However, these methods result in higher requirements of coke quality, especially the coke strength. The coke quality should be adequate to ensure a continuous production of hot metal in the BF [17].

Coke shows different deterioration degrees in different parts of the blast furnace. During the movement from the top to the lower part of the furnace, most lump cokes break into smaller particles consumed in the hearth. In this process, the structures of the coke change significantly [18]. It is well known that the reactivity [19][20] and the strength of coke [21][22][23][24] are closely related to its structures. Therefore, it is essential to characterize the coke structures comprehensively. It should be noted that the properties of the parent coal and coking condition also influence the coke properties. Currently, there is no specific test for coals to guarantee high-quality coke products. Instead, multitudes of empirical laboratory tests have been developed to investigate aspects of the physical, chemical, and thermoplastic behavior of individual coals and blends [25]. Some researchers summarized some models for predicting the metallurgical coke quality based on maceral composition and properties of coals. However, the models were not satisfactory when applied to coals or blends of different geological histories [26]. Generally, in terms of coal properties, coke quality is primarily influenced by coal rank, coal type (reactive and inert macerals), and its inherent ability to soften, become plastic, and re-solidify into a coherent mass when heated [25]. As a general comment on model replication, they cannot be used beyond the conditions under which they were derived [27]. It is more acceptable to conclude the relations between coke structure and the properties.

Many studies discussed the relationship between coke structures and properties, but there is a lack of systematic discussion on characterization methods of coke structures.

2. Relations between Coke Structures and Properties

The most important properties of coke are the reactivity and the strength. To measure the reaction characteristics of coke under high temperature conditions, the reactivity index (CRI), and coke strength after reaction (CSR) are proposed. CRI refers to the ability of the coke to react with carbon dioxide at 1100 °C. CSR refers to the strength of the coke after the reaction with carbon dioxide. CRI and CSR are two critical indicators of the thermal performance of coke. It is believed that a good quality metallurgical coke should have low CRI and high CSR. If the CRI is too high, the starting temperature of the reaction between the coke and CO_2 will decrease. In other words, the reaction may start at the upper part of the blast furnace, resulting in the generated CO escaping from the top of the blast furnace. The cold/hot compressive strength of the coke is measured by two flat plates in room/high temperature conditions. One of the plates moves to compress the coke sample till the coke is destroyed. When the coke is used in a giant blast furnace, the compressive strength should be sufficient to support the iron-containing burdens. The following subsections introduce the relations between coke structures and the coke properties.

2.1. Coke Structure and Reactivity

The main factors influencing the reactivity of coke include the pore structures, the mineral types and contents, and the inherent properties of the carbon matrix. Guo et al. [28] analyzed the porosities, pore wall thicknesses, and pore size distributions of 10 types of cokes to find the relations between these parameters and CRI. The reactivity of the coke was mainly affected by the content of pores with a size between 60 and 120 μm. These pores were important channels for the diffusion of the reaction gas into the coke. The coke with a larger pore wall thickness showed a lower CRI. Fott et al. [29] found a similar phenomenon in that the effective diffusion rate of CO_2 in the ultra-micropores and macropores of the coke was relatively small. In these pores, the reaction only occurred in a small local area.

There are two primary sources of minerals that affect coke’s reactivity: the inherent minerals in the coke matrix and the extrinsic minerals that are enriched in the blast furnace. A large number of studies have pointed out that the minerals in the coke matrix showed different promotion effects on the reactivity of the coke [30][31][32][33][34]. Generally, the cations of the minerals played a critical role in the promotion effects. The catalytic effect in descending order were $K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Fe^{2+} > Al^{3+} > Si^{4+}$. To study the impact of the specific types of the minerals, a so-called coke analogue was developed for simulating the industrial coke. Reid et al. [30] used the coke analogue to simulate the metallurgical coke with a particular type of mineral. It was found that K^+ showed the most potent catalytic effect. Due to the strong catalytic effect, alkali elements are regarded as detrimental for the blast furnace [35][36]. The influence of alkali elements in the blast furnace on coke reactivity has been a hot topic [37]. The impact of Zn has also been extensively studied [38][39]. The extrinsic minerals enriched in the blast furnace are not within the scope. In general, the appearance of these alkali and Zn elements could strongly accelerate the degradation of the coke.

Coke is a brittle material with a developed pore system composed of pore walls, pores, and cracks. The basic unit of the coke pore wall is the microcrystallite structure [40]. Ignoring the influence of the pore structures and the mineral effect, the inherent property of the coke matrix is the decisive factor that determines the reactivity of the coke. The two crucial intrinsic properties of the coke matrix are microcrystallite and optical characteristics. The method of determining the microcrystallite parameters, such as the average stacking height (Lc) of crystalline, the average size (La) of crystalline layer, and the average spacing (d_{002}) of crystalline, are introduced in 2.2. Zhang et al. [41] evaluated 30 different metallurgical cokes and found that d002, Lc, and La were in the ranges of 3.46–3.51 Å, 28.95–42.18 Å, and 41.40–53.05 Å, respectively. The interlayer spacing of cokes showed a neglectable difference. It was found that when the mineral effect was not strong, the CRI decreased with the increasing Lc and La. During the CO_2 gasification reaction, the isotropic texture in the coke reacted more quickly than the anisotropic texture [42][43][44][45]. The higher value of the ∑ISO of the coke is, the higher CRI of the coke will be. OTI is another index but describes the same optical phenomenon of the coke matrix. Generally, the coke with a higher value of OTI shows lower CRI.

2.2. Coke Structure and Strength

The direct forces that cause the degradation of the coke in the blast furnace are the friction and collision between the bulk burden materials, such as iron ore sinter, iron ore pellet, and cokes. The coke strength can be comprehensively indicated by cold compressive strength, CSR, and hot compressive strength. The pore structures play an essential role in determining the strength of the coke. Mihashi et al. [46] found that the matrixes of different cokes showed similar strength. Young et al. [22] used the 3-dimensional discrete element method to simulate the compressive cracks of coke. It was found that porosity is the main factor affecting the strength of the coke. A uniform pore distribution and less porosity contributed to the coke's higher cold compressive strength. Saito et al. [23] used the rigid bodies–spring model to analyze the relations between the pores and the cold compressive strength. He found that slight roundness and large distorted pores might cause stress concentration and significantly reduce the strength of coke. Gornostayev et al. [24] found a similar result by directly observing the coke using a scanning electron microscope. The elliptical, elongated, and flattened pores, compared with circular pores, showed a lower ability to resist load pressure. The high cold compressive strength of coke could not guarantee its high CSR. The CSR presents a good negative correlation with the CRI [21][47][48]. The factors that affect the CRI of the coke inevitably affect the CSR of coke. The aim of measuring hot compressive strength is to simulate the load borne by the coke in an actual blast furnace. Haapakangas et al. [49][50] used the Gleeble thermomechanical simulator to evaluate the coke hot compressive strength at 1000 °C, 1600 °C, and 1750 °C. It was found that the coke was brittle at 1000 °C but partially plastic at 1600 °C and 1750 °C. The high-temperature treatment above the temperature of the coking furnace may cause further graphitization. The non-graphitizing carbons became harder, and the graphitizing carbons became softer at temperatures between 1000 °C and 2000 °C. The low coke compressive strength at high temperature was considered to be due to the high graphitization degree of the coke. Fang et al. [51] investigated the relations between temperature, carbon loss of the coke, and hot compressive strength. It was found that the hot compressive strength was significantly decreased with the increasing carbon loss of the coke and the temperature. However, the effects of individual factors affecting coke hot strength were not illustrated. Guo et al. [52] studied the influence of the pore structure features on the hot compressive strength of coke. It showed that in the temperature between 1000 °C and 1300 °C, the temperature presented a limited influence on the strength. The coke with a higher hot compressive strength showed a smaller pore size with a more uniform distribution. The following chapter introduced the relevant characterization methods of the coke structures.

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