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Microstructure and Melting Loss Behavior of Blast Furnace Incoming Coke and Radial Tuyere Coke

Hongliang Wu ^{1,2}, Laihao Yu ¹, Shengchao Chang ¹, Yingyi Zhang ^{1,*}  and Jialong Yang ^{1,*}

¹ School of Metallurgical Engineering, Anhui University of Technology, Maanshan 243002, China

² Maanshan Iron & Steel Co., Ltd., Maanshan 243003, China

* Correspondence: zhangyingyi@ahut.edu.cn (Y.Z.); jialongyang@126.com (J.Y.)

Abstract: As an indispensable raw material in blast furnace ironmaking, coke plays an important role, which is also the key to low-carbon smelting and reducing ironmaking carbon emissions, so it is necessary to study its quality, degradation behavior, and microstructure evolution. In this work, the pore structure and micromorphology of the blast furnace incoming coke (IC) and tuyere coke (TC) were analyzed comprehensively by comparative research methods. The results showed that the microcrystalline structure of TC was more orderly than that of IC. In addition, the order degree of the coke microcrystalline structure increased first and then decreased in the radial direction and reached the highest value at the distance of 1–2 m from the tuyere. The porosity of radial TC increased obviously. The pore wall became thinner, and the pore size of the original micropores in TC expanded. Simultaneously, large numbers of micropores were also generated, and cracks appeared, resulting in the specific surface area and pore volume of TC becoming higher than that of IC. Moreover, the graphite structure inside TC increased, and the crystal structure became larger. In the radial direction, with an increase in temperature, the number of amorphous structures in coke decreased, the ordering increased, and the graphite structure continued to grow. However, along the direction of the furnace core, a decrease in temperature led to the stagnation of amorphous structure content and a decrease in graphitization degree.

Keywords: incoming coke; tuyere coke; micropore structure; tuyere sampling; microstructure



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1. Introduction

Coke, as the basic energy of blast furnace ironmaking, provides the heat, reductant, and carburizing agent required in the whole ironmaking process and also acts as the skeleton supporting charge in the furnace, which is one of the reasons why coke cannot be replaced for a long time [1–3]. Although the operating system and smelting process of blast furnaces have been continuously improved in recent years, material failure is always easy to occur in a high-intensity environment such as high air temperature, high air volume, and oxygen-rich injection [4–6]. For example, in this environment, coke not only suffers from the physical effects given by the outside world, such as impact, extrusion, and wear, but also bears the chemical effects, such as melting loss, gasification, alkali metal corrosion, and slag iron penetration. Thus, the requirements for coke quality are becoming higher and higher [7].

Coke quality is related to its structure. According to the coke structure, the quality of coke can be judged, and the coking process can also be reflected [8]. As the basis for studying the properties of coke, the structure of coke can be divided into three categories according to the type: pore structure, microcrystalline structure, and optical structure, and relevant scholars have conducted numerous studies on various structures [9–11]. The pore structure of coke mainly refers to pore distribution, size, shape, and wall thickness, which depend on the nature of the coal coking process. In addition, these factors will directly affect the performance of coke. Li et al. [12] explored the relationship between

the pore structure and thermal performance of coke. They found that the reactivity of coke was not only related to the porosity but also related to the average pore diameter and pore wall thickness, which was positively correlated with the average pore diameter and negatively correlated with the pore wall thickness. Therefore, improving the porosity and pore structure can enhance the strength of coke after the reaction. Pusz et al. [13] also reported that after the coke reacted with CO_2 , the pore wall of coke was greatly eroded, the pore diameter was expanded, the pore wall was significantly thinner, and the connection between the pores was obvious. As an important factor determining the performance of coke, it is also a good choice to strengthen the pore structure by improving the quality of coke smelting.

The microcrystalline structure of coke is similar to that of graphite crystal, with high density and orderly stacking of the lamellar structure. Therefore, the research on the microcrystalline structure of coke is mainly carried out through a comparative analysis with that of graphite crystal structure. At present, the bonding of sp^2 hybrid carbon in coke can be determined, but the bonding of sp^3 and sp hybrid carbon has not been completely determined [14]. The microcrystalline structure of coke affects the coke performance from the chemical molecular level, which is the core factor in coke deterioration. Thus it is of far-reaching significance to clarify the evolution of microcrystalline structure in a blast furnace to guide the production and application of coke. Fan et al. [15] used XRD methods to characterize the microcrystalline structure of coal char at different temperatures and heating rates and found that the stacking height (L_c) of coke micro lamellar structure increased significantly with the increase of reaction temperature. In contrast, the microcrystalline size (L_a) was relatively stable, indicating that the microcrystalline lattice in the inner part of coal char was mainly bonded and polycondensated in the longitudinal direction. The main direction of studying coke performance is starting from the microstructure of coke to seek the connection between micro and macro and using the changes in microstructure to reveal the impact on macro [16–18].

The optical structure of coke can generally be divided into isotropic and anisotropic. In contrast, the anisotropic structure can be divided into fine, medium, and coarse-grained mosaic structures, as well as fibrous and flaky structures, which will affect the performance of coke in different ways [19]. As one of the main types of coke microstructure, the optical structure has a decisive influence on the macroscopic properties and has become an important means to evaluate the quality of coke. Cheng et al. [20] measured the optical structure content and comprehensive properties of coke at different temperatures. The results showed that the optical structure had different depth effects on the initial reaction temperature, average melt loss rate, and post-reaction strength of coke under the same melt loss rate. The relationship between them usually presented a parabolic trend. Pusz et al. [21] compared the percentage of embedded structures in coke with the double reflectivity of coke to study the relationship between reflectivity and optical structure content and found that the content of embedded structures in coke was positively correlated with its double reflectivity and the double reflectivity increased with an increase in anisotropy. Guo et al. [22] conducted an experimental study on the relationship between the optical structure of coke and its cold and hot strength, revealing that the cold and hot strength was related to the content of the optical structure in coke, and the strength after reaction increased with an increase in mosaic structure volume fraction.

Although there are many studies on the microstructure analysis of coke at present, there are few studies on the influence of the microcrystalline structure on coke properties. Therefore, this work analyzed the internal microstructure characteristics of coke and the evolution law at the molecular level and revealed the essence of coke performance changes from the microscopic perspective. In addition, this work also used a variety of characterization means to compare the distribution and microstructure of coke at different positions in the radial direction of the blast furnace tuyere plane so as to explore the ways and factors that affect the metallurgical properties of coke. At the same time, combined

with the macro behavior of coke, this study revealed the microcrystalline structure behavior law and degradation status of incoming coke and radial tuyere coke in a blast furnace.

2. Materials and Methods

2.1. Raw Materials

The metallurgical properties of coke at high temperatures can be measured by thermal simulation, but it is difficult to simulate the actual reaction conditions of a blast furnace in the laboratory due to the complex conditions such as high temperature, extrusion, and co-existing reduction and oxidation atmosphere in the blast furnace. In order to understand the performance of coke truly and effectively in the tuyere area of a blast furnace at about 1100 °C, an offline sampling method was used to obtain tuyere coke (TC) at various positions in the radial direction of the tuyere plane and corresponding batches of incoming coke (IC). The performance indexes of radial TC and IC were compared and analyzed, which can be helpful for the study of coke degradation in a blast furnace and the real-time analysis of furnace conditions.

The radial TC was fully representative of the research on the deterioration of tuyere plane coke, and the TC sampler was autocratic equipment for this purpose. Before sampling, the blast furnace duct of the tuyere was removed, and the sampling rod was pushed into the tuyere by a hydraulic device of the sampling machine itself. The sampling rod and the upper cover of the sampling rod always provided a high-pressure water flow for cooling throughout the sampling process. The sampling rod extended 6 m from the tuyere to the furnace core and was divided into 12 sections, each length 0.5 m. After the sampling rod was extended into the inside of the tuyere, the upper cover of the sampling rod was pulled out, and the coke in all parts of the tuyere plane fell into the sampling rod in a natural way. Then the sampling rod was pulled out, and the coke sample taken from the tuyere was segmented into the barrel and cooled by nitrogen. The coke used in this study was MG 2# furnace coke, and the hearth radius of the 2# blast furnace was 5.5 m. Figure 1a,b show the schematic diagram of blast furnace tuyere sampling and the actual diagram of field tuyere sampling.

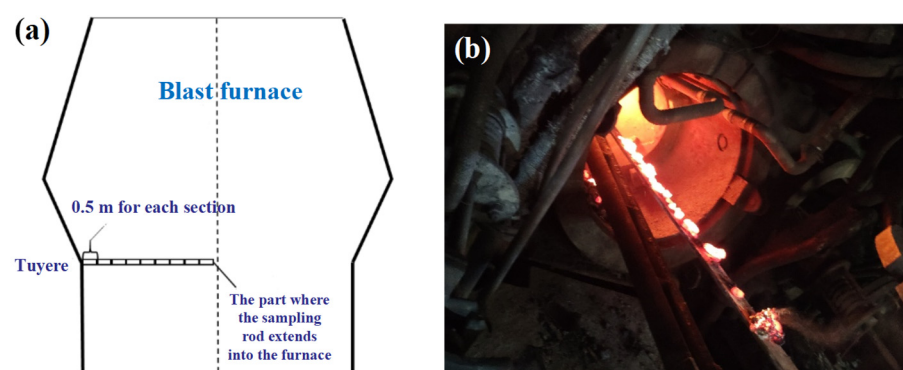


Figure 1. (a) Schematic diagram of sampling at blast furnace; (b) Live tuyere sampling on site.

Under the influence of high-pressure air flow and burden drop, coke was distributed in different forms in the tuyere plane of the blast furnace. The coke taken by the sampling rod at each position of the blast furnace tuyere plane could be divided into four categories. First, the coke was not close to the edge of the furnace shell, which was mainly from the bosh coke that falls here when the blast furnace is off. Further to the direction of the furnace core was the coke that burns violently in the tuyere raceway. The coke in this part had small lumpiness and no edges and corners, and under the action of high temperature, the alkali content in the coke decreased. Then, deep into the furnace core, that is, the melting area, the coke was eroded by slag iron. Finally, it arrived at the furnace core, also known as the dead column area, where the temperature was low, and the coke pulverization was serious. The advantage of the sampling rod was that the coke samples taken included all types of

coke in the tuyere area. Through studying and analyzing the metallurgical properties, the deterioration of coke in the tuyere plane of the blast furnace can be understood in detail, providing a theoretical basis for the smooth operation of the blast furnace.

According to GB/T2001-2013 “coke-determination of proximate analysis” [23] and GB/T1574-2007 “test method for analysis of coal ash” [24], the industrial characteristic indexes and components of coke were measured, respectively, and the results are shown in Tables 1 and 2. Industrial analysis is a key index to analyze the characteristics of coke, and it is also the basis widely used to evaluate the properties of coke [25]. At present, the basic properties of coke are mainly evaluated by measuring the industrial, elemental analysis, and cold and hot strength of coke. Among them, industrial analysis includes the calculation of ash (Ad), volatile matter (Vd), moisture, and fixed carbon (FC_d) content of coke, and according to the results of industrial analysis, can preliminarily judge the nature of coke, such as fixed carbon content can determine the skeleton of coke. Reactivity (CRI) and post-reaction strength (CSR) are indicators reflecting the thermal stress and mechanical force that coke can withstand under high-temperature conditions. The basic property parameters of TC and IC involved in this study are shown in Table 1. By comparing the data in Table 1, it can be seen that the ash content (Ad) of IC was lower than that of TC, indicating that coke fell from the top of the furnace to the tuyere area, and the carbon content in coke gradually reduced through carbon melting reaction, but the ash content was relatively increased. The fixed carbon content (FC_d) of IC was higher than that of TC, indicating that TC’s skeleton function in the blast furnace decreased. The reactivity (CRI) of TC increased, and post-reaction strength (CSR) decreased because after TC participates in the carbon melting reaction in the furnace, the surface pores expand and the reaction area increases, so the reactivity is high.

Table 1. Basic properties of TC and IC (%).

Sample	Ad	Vd	FC _d	CRI	CSR
TC	14.45	0.93	84.62	56.00	30.30
IC	12.70	1.33	85.97	23.10	68.70

Table 2. Ash content and ash composition of IC and TC analyzed by XRF.

Distance Tuyere (m)	Ash Content/Ad (%)	Ash Composition (%)					
		SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
IC	12.70	39.76	34.17	11.30	1.82	0.63	0.85
0–0.5	16.54	23.69	33.71	9.53	4.11	2.31	2.04
1–1.5	13.60	28.30	39.21	11.40	1.83	1.15	0.42
2–2.5	21.26	30.34	30.50	14.96	4.54	2.71	2.74
3–3.5	20.60	27.92	32.18	6.89	5.24	3.86	3.08
4–4.5	20.82	29.63	30.32	6.51	3.36	4.36	4.15
5–5.5	22.11	25.75	28.46	5.52	4.31	4.05	4.79

The ash content of coke directly affects the amount of blast furnace slag, and too high an ash content will affect the reactivity and thermal properties and reduce the strength of coke [26]. For example, the defects of coke structure increase, and the differences of pore wall structure also increase. The Na and K alkali metals in the ash can make CO₂ in the blast furnace adhere to the coke surface and generate carbon and alkali compounds through a catalytic reaction, thus promoting a coke melting loss reaction at high temperature. Table 2 shows the ash content, and the ash composition of IC and TC determined through the X-ray fluorescence (XRF) method. From the variation trend of ash content, the ash content of TC in all radial positions was higher than that of IC, and along the direction of tuyere pointing to the furnace core, the ash content decreased first and then increased. From the furnace to the tuyere, the carbon content in the coke was reduced by the melting loss reaction, and the ash content was relatively increased. In addition, when flux and sinter were inside the

blast furnace, their powder was adsorbed on the coke surface, so it was difficult to separate them when preparing samples, resulting in varying degrees of increase in ash content. At the same time, the SiO₂ content in the ash of TC was lower than that of IC, mainly because the SiO₂ attached to the coke surface reacted with C during the melting loss reaction of TC, and the reduced Si quickly melted into the molten iron, becoming the main source of Si in molten iron.

2.2. Research Methods

The specific surface area and micropore parameters of IC and TC were measured by the accelerated surface area, and a porosimetry system with nitrogen as the adsorbent (BET, ASAP 2460, Micromeritics, Norcross, GA, USA) to compare the pore changes of coke before and after a series of reactions in the blast furnace, and the same method was used to analyze the coke after simulating high-temperature melting loss. The X-ray fluorescence (XRF, AXIOS, PANalytical B.V., Almelo, Netherlands) was used to identify the chemical composition of IC and TC. To intuitively understand the gasification performance of IC and TC, the corresponding thermal gravimetric and differential thermal analysis (TG-DTA) curves were measured with a thermogravimetric analyzer (STA 449C, Netzsch, Selb, Germany) under the constant heating rate of 10 °C/min. The microcrystalline structure of coke was determined by an X-ray diffractometer (XRD, D8 ADVANCE, Bruker, Karlsruhe, Germany). According to the data measured by XRD, the lattice parameters of coke samples were accurately deduced. The average distance $d_{(002)}$ between aromatic layers in the cell was calculated by the Bragg equation, and the microcrystalline size was characterized by stacking height (L_c) and diameter (L_a) of the aromatic lamellar surface (002), which are generally calculated using Scherer equation, as shown in Equations (1)–(3). In addition, the reactivity (CRI) and post-reaction strength (CSR) of coke were calculated from Equations (4) and (5).

$$d_{002} = \frac{\lambda}{2 \sin \theta_{(002)}} \quad (1)$$

$$L_a = \frac{k_1 \lambda}{\beta_{(100)} \cos \theta_{(100)}} \quad (2)$$

$$L_c = \frac{k_2 \lambda}{\beta_{(002)} \cos \theta_{(002)}} \quad (3)$$

$$CRI = \frac{m - m_1}{m} \times 100\% \quad (4)$$

$$CSR = \frac{m_2}{m_1} \times 100\% \quad (5)$$

where λ represents the wavelength of X-ray ($\lambda = 0.15406$ nm). $\theta_{(002)}$ and $\theta_{(100)}$ represent the diffraction angles (°) of the corresponding diffraction peaks (002) and (100). $\beta_{(002)}$ and $\beta_{(100)}$ represent the half-height width (°) of the corresponding planes (002) and (100). The k_1 and k_2 are correction coefficients ($k_1 = 1.84$, $k_2 = 0.94$). The m and m_1 respectively represent the mass (g) of coke before and after the reaction, and m_2 represents the mass (g) of coke with a diameter greater than 10 mm after the drum.

The corresponding spectra of coke before and after high-temperature melting loss reaction were measured by Raman spectrometer (inVia, Renishaw, Wotton-under-Edge, UK), and the peak shape of the spectrum was fitted by origin software to study the change law of the coke phase structure. A Fourier transform infrared spectrometer (FTIR, Nicolet6700, Thermo Fisher, Waltham, MA, USA) was used to measure the structural changes in coke functional groups under different reaction conditions to analyze the internal molecular structure of coke. The micromorphology and element types of coke before and after reaction were observed by a scanning electron microscope with energy disperse spectroscopy (SEM-EDS, JSM-6510LV, JEOL, Akishima, Tokyo, Japan).

3. Results and Discussion

3.1. Graphitization Behavior and Thermal Analysis of IC and TC

The coke used in the blast furnace was made from coking coal into coke with a carbon content of more than 85%. The arrangement structure of carbon atoms changes, forming a structure similar to graphite due to the effect of high temperature. During secondary heating inside the blast furnace, the microcrystalline structure continued to transform on the original basis, deepening the graphitization degree [27]. Among them, is microcrystalline with compact structure, parallel lamellar distribution, and easy stacking called crystalline carbon. On the contrary, the microcrystalline structure was loose and randomly arranged, which is called amorphous carbon. To study the graphitization of coke at different temperatures and the change in its microcrystalline structure, the coke was heated to different temperatures and kept constant for 0.5 h in a high-temperature tubular furnace with N₂ as protective gas to simulate the graphitization of coke in a blast furnace. Figure 2 shows the XRD patterns of coke at different temperatures, from which it can be seen that with an increase in temperature, the (002) peak type corresponding to coke gradually became higher and narrower, indicating that the graphitization degree of IC gradually deepened with an increase in temperature. Three parameters (d_{002} , L_c , L_a) of the coke microcrystalline structure at various temperatures were calculated by using the Bragg equation and Scheler formula, and the results are shown in Table 3.

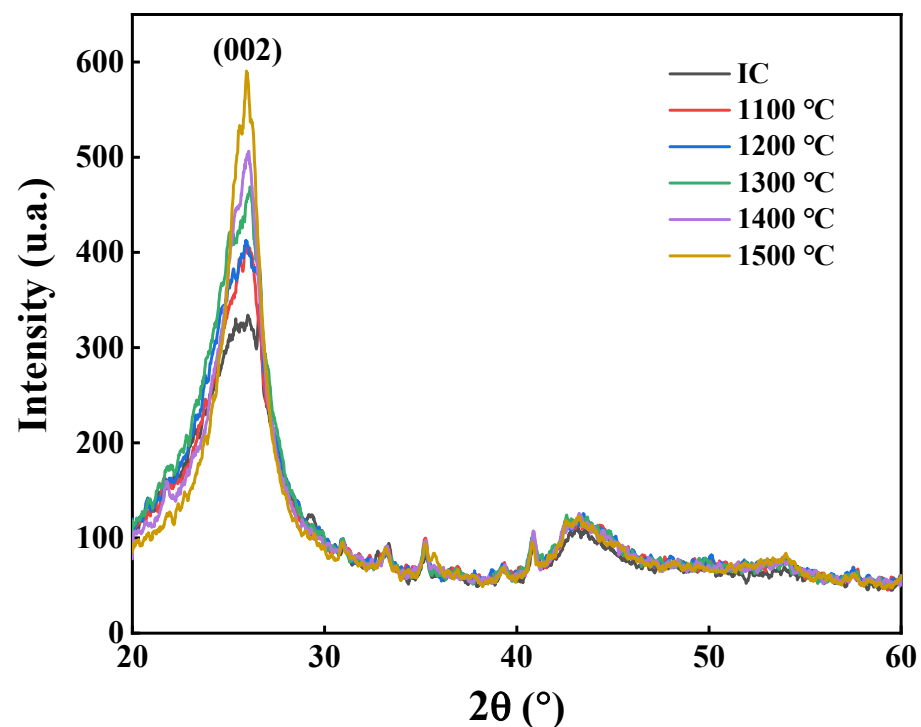


Figure 2. XRD patterns of coke at different temperatures.

Table 3. Microcrystalline parameters of coke at different temperatures.

T (°C)	$2\theta_{002}$ (°)	$2\theta_{100}$ (°)	β_{002} (°)	β_{100} (°)	d_{002} (nm)	L_c (nm)	L_a (nm)
IC	26.02	43.16	0.921	0.699	0.3422	9.24	24.98
1100	25.98	44.62	0.809	0.684	0.3427	10.53	25.67
1200	26.16	44.49	0.789	0.681	0.3419	10.79	25.77
1300	26.04	44.35	0.677	0.653	0.3403	12.58	26.86
1400	26.30	44.31	0.654	0.652	0.3386	13.03	26.90
1500	26.32	44.26	0.642	0.644	0.3384	13.27	27.23

The variation trend of microcrystalline parameters d_{002} , L_c , and L_a at different temperatures is shown in Figure 3a. It can be seen that the average distance between microcrystalline layers (d_{002}) gradually decreased with an increase in temperature, while the microcrystalline stacking height (L_c) and the microcrystalline average diameter (L_a) in the carbon structure both presented an upward trend. The microcrystalline parameters tended to graphitization standard parameters, indicating that the microcrystalline lamellar structure in the coke tended to be ordered under the condition of gradually increasing temperature. The graphitization degree of IC was low due to the low coking temperature, but the graphitization degree can be further deepened under secondary heating. Graphitization of coke is the most basic structural transformation of blast furnace coke, so clarifying the graphitization mechanism and correctly regulating the quality of IC are necessary measures to ensure the smooth operation of a blast furnace.

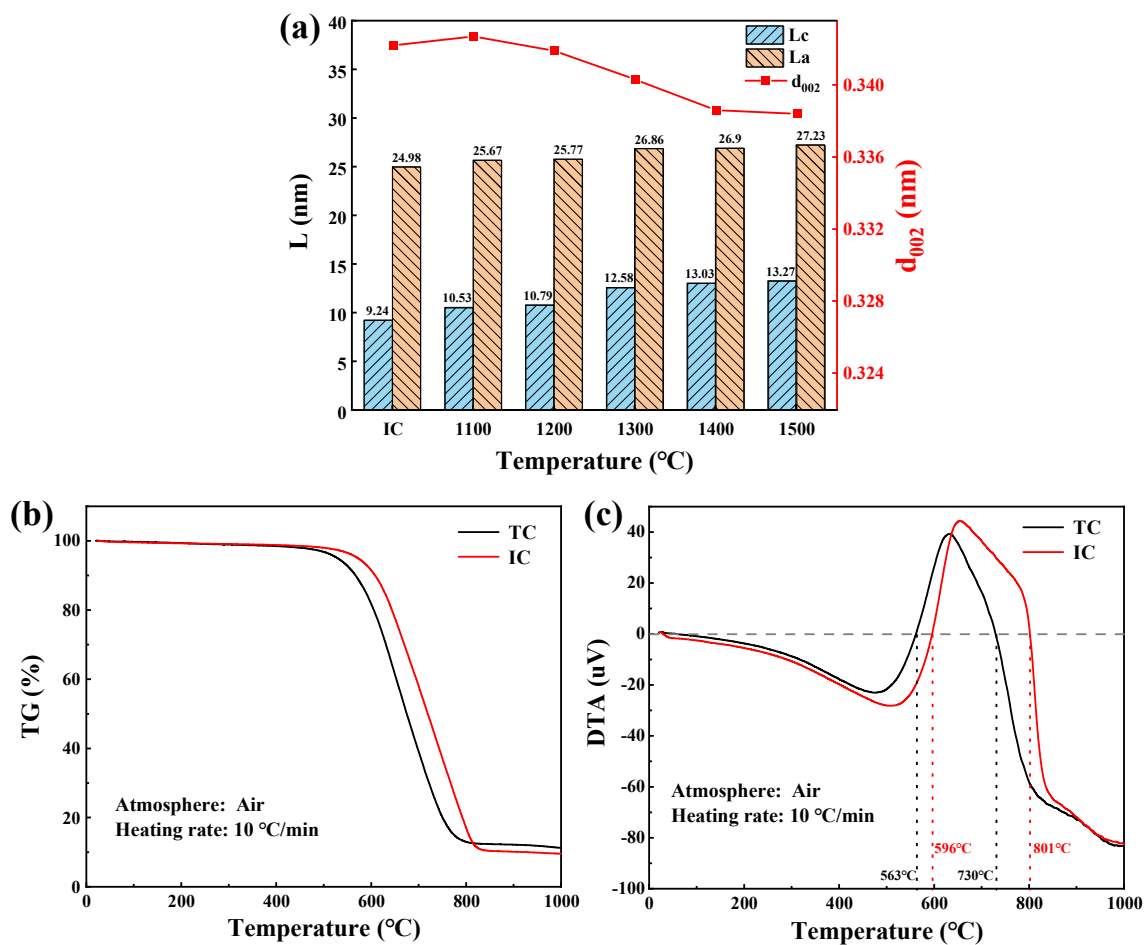


Figure 3. (a) Variation trends of coke microcrystal parameters at different temperatures. (b,c) TG-DTA curves of TC and IC.

In addition, Figure 3b,c also show the TG and DTA curves of IC and TC. It can be seen from Figure 3b that the TG curve of IC shifted to the right compared with the whole TC, and the larger the offset, the greater the temperature difference between the TC and IC when the weight loss was the same. Again, the final residual mass ratio of TC was higher than that of IC, which may be related to the high ash content in TC. It can be seen from Figure 3c that the curves corresponding to TC and IC were concave before 563 °C and 596 °C, indicating that both were in an endothermic state at this time. However, after 563 °C and 596 °C, the curves of the two samples changed from concave to convex, indicating that after the temperature point of TC and IC, respectively, the heat released by their own combustion was greater than the heat required for their combustion, and they had entered a complete

combustion state. The complete combustion end temperatures of TC and IC were 730 °C and 801 °C, respectively. The temperature difference of complete combustion for TC was 167 °C, while the temperature difference of IC was 205 °C. Although the temperature point of TC entering the complete combustion was lower than that of IC, the temperature span of complete combustion for IC was longer than that of TC, which is related to the lower gasification reactivity from IC.

3.2. XRD Analysis of IC and TC

Generally, there are only two peaks in the XRD spectra of coke: (002) peak and (100) peak. The higher and narrower the peak type of (002), the higher the lamellar orientation in the coke microcrystalline structure, and the more ordered the crystal structure [27]. The XRD spectra of IC and TC are shown in Figure 4. Compared with the IC spectra, the (002) peak in TC spectra was higher and narrower, indicating that the microcrystalline structure of TC was more orderly under high temperature after secondary heating inside the blast furnace. It also showed that the coking temperature of coke before entering the blast furnace was lower than the reaction temperature in the tuyere area of the blast furnace, resulting in the graphitization degree not being high. It was established that the temperature variation trend of different radial points on the tuyere plane of a blast furnace can be determined by comparing the peak intensity of (002) peak in the XRD spectrum of TC and the variation trend of microcrystalline parameters.

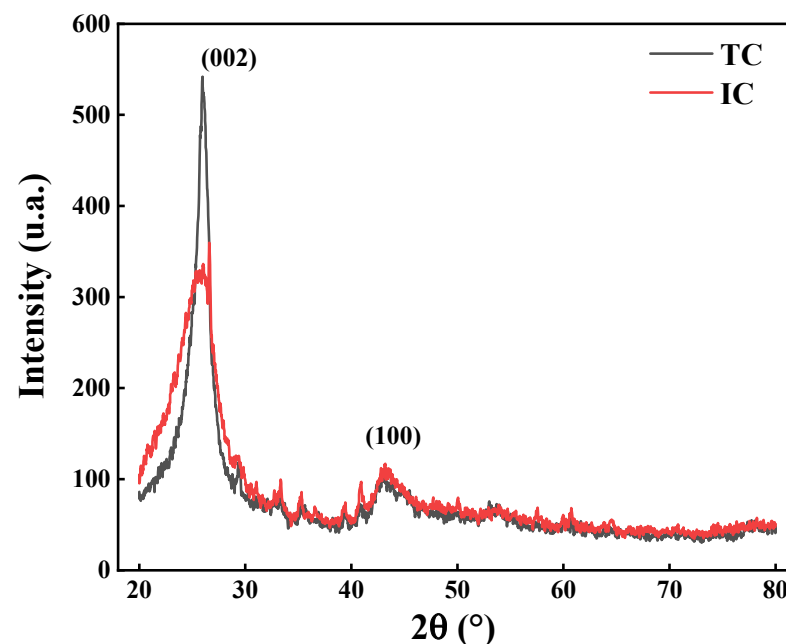


Figure 4. XRD patterns of IC and TC.

Figure 5 shows the XRD patterns of TC at each position. It can be seen from the patterns that the peak (002) in the corresponding pattern of TC was the highest and narrowest at 1–1.5 m away from the tuyere, indicating that the graphitization degree of TC was the highest here. From the tuyere to the furnace core direction, the peak height of (002) in the XRD pattern of TC increased first and then decreased, and the peak height of (002) began to decrease in the region of 2–2.5 m. It can be inferred that the changing trend of temperature in the radial direction of the tuyere plane was also increased first and then decreased.

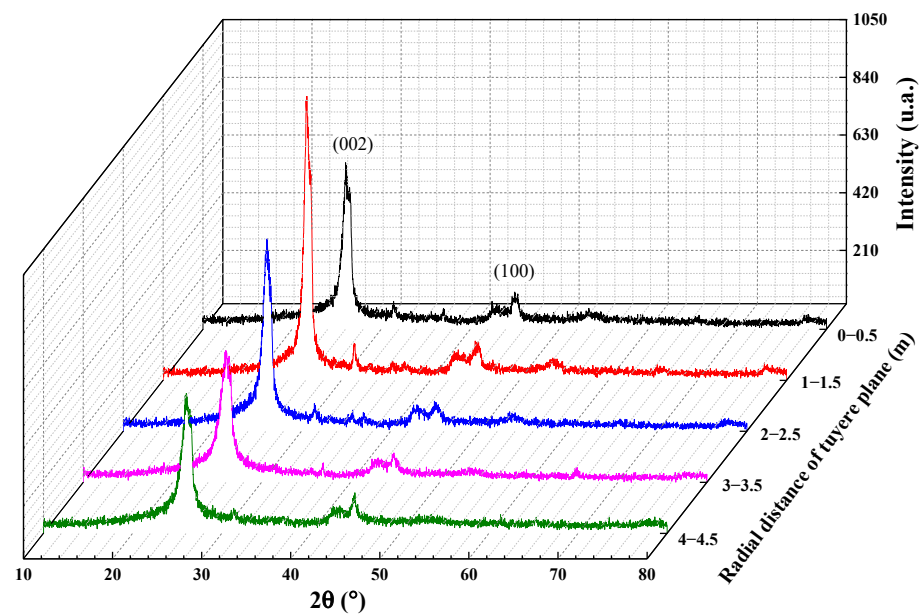


Figure 5. XRD patterns of TC.

The microscopic parameters of TC calculated by the Scherer and Bragg equations are shown in Table 4. Compared with the IC, the (002) peak position of TC shifted to the right, and the lamellar spacing d_{002} decreased to a certain extent. The smaller the lamellar spacing d_{002} , the higher the graphitization degree of coke. As can be seen from Figure 6, the Lc increased first and then decreased, and reached the maximum value at 1–1.5 m away from the tuyere, but Lc also decreased accordingly as the temperature at the furnace core decreased. The d_{002} of TC reached a valley value in the range of 2 to 2.5 m, and La reached a peak value in the range of 1 to 1.5 m. Both the graphitization parameters and the peak pattern in the spectrum of TC showed that the temperature was the highest in the area about 1–2 m away from the tuyere, indicating that the area where coke was located is the tuyere raceway zone. The coke in the tuyere raceway zone burns intensely and emits significant heat, which increases the temperature and leads to a deeper graphitization degree of coke. By comparing the graphitization and microcrystalline structure evolution of IC and TC and related to the transformation of macro performance of coke in the blast furnace, the degradation mechanism of coke was deeply analyzed. The XRD patterns and microcrystalline parameters of coke at different positions in the tuyere plane were compared to clarify the deterioration differences and temperature distribution at various radial positions of the tuyere plane, providing data support for the operation of the blast furnace.

Table 4. Microcrystalline parameters of coke in different radial directions of the tuyere plane.

Sample	$2\theta_{002}$ (°)	$2\theta_{100}$ (°)	β_{002} (°)	β_{100} (°)	d_{002} (nm)	Lc (nm)	La (nm)
IC	26.02	43.161	0.921	0.699	0.3422	9.246	24.987
0–0.5	26.04	45.181	0.826	0.817	0.3421	10.309	21.531
1–1.5	26.10	45.458	0.728	0.668	0.3411	11.699	26.361
2–2.5	26.16	45.121	0.788	0.697	0.3404	10.810	25.233
3–3.5	26.04	45.001	0.839	0.672	0.3419	10.150	26.160
4–4.5	26.02	44.940	0.884	0.677	0.3422	9.633	25.961

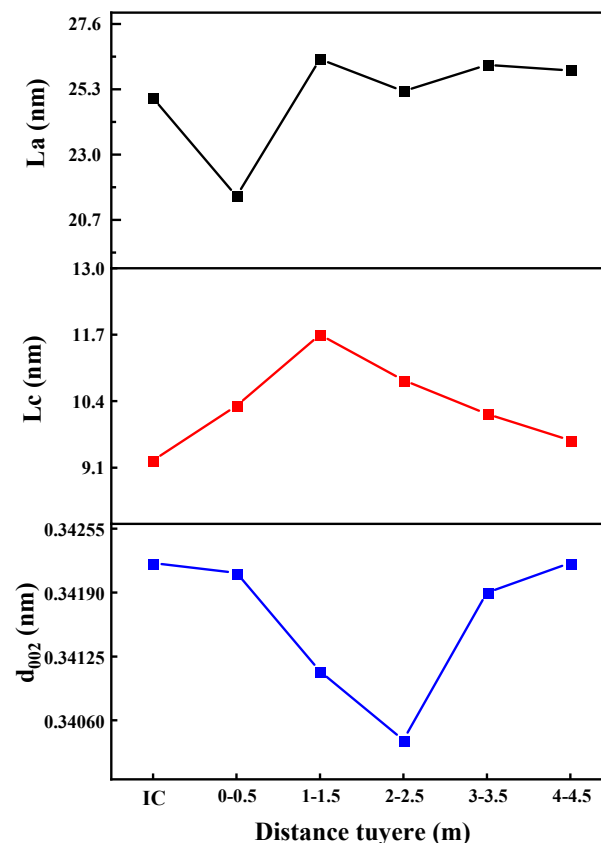


Figure 6. Variation trend of microcrystalline parameters of different radial coke.

3.3. Micropore Structure and Distribution of IC and TC

At present, the research on coke pores focuses on the formation process, structure, and distribution of various pores, so as to study the influence of pores on coke reactivity and post-reaction strength. The content of micropores in coke was less, but the specific surface area of micropores cannot be ignored. When the gasification reaction of coke takes place in the blast furnace, the pores not only provide the reaction place, but also are the diffusion channels for the gasification reaction to gradually trend towards the inside of coke. When the volume fraction of CO₂ is small, the closed pores in coke will open and promote the growth of fine microscopic pores and small pores, thus increasing the specific surface area of coke [28]. In order to study the change of micropores in coke from entering the furnace to the tuyere, the samples were degassed at 300 °C in vacuum for 3 h, and then adsorption and desorption experiments were carried out. Nitrogen was used as an adsorbent to measure specific surface area and micropore parameters of IC and TC, and the results are shown in Table 5.

Table 5. Micropore parameters of different radial cokes.

Distance Tuyere (m)	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
IC	9.022	0.01156	17.289
0–0.5	14.233	0.02461	11.135
1–1.5	15.794	0.02457	10.389
2–2.5	15.496	0.02643	10.794
3–3.5	14.954	0.02382	11.830
4–4.5	14.536	0.02055	11.660
5–5.5	14.845	0.02149	11.540

According to the data in Table 5, there was an obvious gap between the micropore parameters of the IC and TC. The specific surface area and pore volume of TC were all higher than that of IC, while the average pore size was lower than that of IC. It showed that from the furnace to the tuyere, a certain amount of fine pores were generated in the inner part of TC after the coke gasification, erosion, carburization, and other reactions, resulting in an increase of the specific surface area and a decrease in the average pore size. In the direction of the tuyere to the furnace core, the average pore size of TC decreased first and then increased, while the specific surface area and pore volume increased first and then decreased, which was consistent with the changing trend of the radial temperature in the tuyere plane, indicating that there is a certain relationship between the specific surface area of coke and temperature. In conclusion, the temperature in the area 1–2 m away from the tuyere in the radial direction was the highest, and the edge of the tuyere raceway was about 2 m. The coke reacted violently under the high-temperature condition in this area; the coke surface dissolved and the particle size decreased. At the same time, a large number of volatiles in the coke separated and volatilized due to the effect of high temperature, which generated micropores in the process, resulting in an increase in specific surface area and a decrease in average pore size.

The adsorption and desorption curves of IC and TC are shown in Figure 7. It can be seen that when the relative pressure was in the region of low and medium pressure (0–0.8), the adsorption curves of the samples rose slowly. The curves were flat and began to coincide with the desorption curves in the region of low pressure, which indicated that there were micropores in the test coke samples. However, in the high-pressure region (0.8–1.0), the curves rose rapidly, and the adsorption amount increased greatly. The adsorption curves did not show a saturated state until the end, indicating that there were also a certain number of macroporous structures and cracks in the samples. Moreover, the adsorption capacity of IC was only $15.6 \text{ cm}^3/\text{g}$, but the adsorption capacity of TC at each position increased compared with that of IC. The adsorption capacity of TC was about $30 \text{ cm}^3/\text{g}$, except for TC in the area 2–2.5 m away from the tuyere, which was only $22 \text{ cm}^3/\text{g}$; the higher the adsorption capacity of TC, the more the pore structure content in TC, which further proves that the number and volume of pores in the IC increased after a series of reactions, thereby causing the increase in adsorption capacity. This is consistent with an increase in specific surface area and pore volume of TC in Table 5.

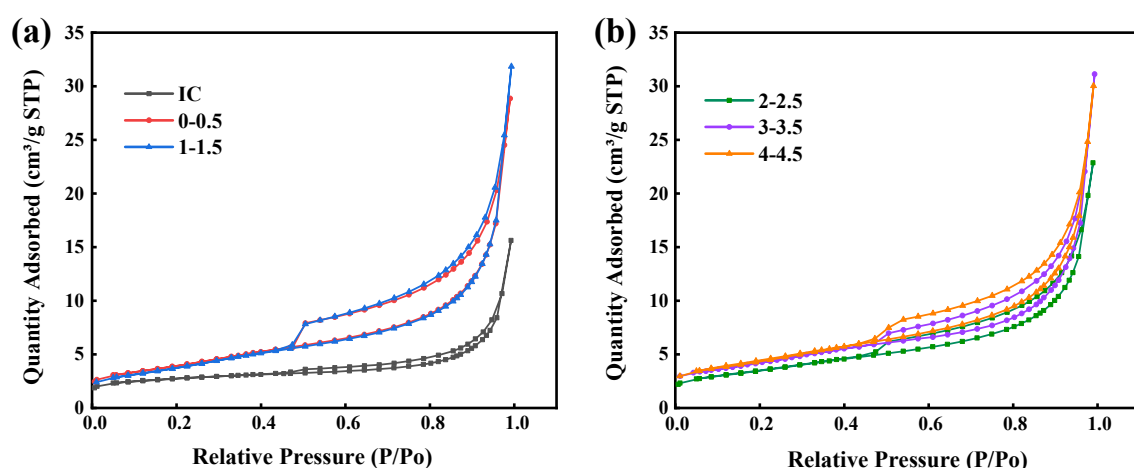


Figure 7. The radial coke adsorption and desorption curves of IC and TC. (a) IC, TC: 0–0.5 and 1–1.5; (b) TC: 2–2.5, 3–3.5 and 4–4.5.

By comparing six types of characteristic adsorption and desorption curve models, it was determined that the adsorption and desorption isotherms of IC and TC are of type IV [29]. Due to capillary condensation, the desorption curve deviated from the adsorption curve, forming a “hysteresis loop”. This phenomenon means that in the adsorption process,

there is only single-layer adsorption on the pore surface at the initial stage, but multi-layer adsorption and capillary condensation occur in the coke pores with a gradual increase in pressure, which is caused by the presence of mesopores and macropores. As can be seen from Figure 7, the downward trend of desorption curves at the upper part of the “hysteresis loop” was the same as that of adsorption curves, and there was no adsorption saturation in the high-pressure region. However, it suddenly dropped near the low pressure of 0.5. It closed with adsorption curves, which is consistent with the H4 type “hysteresis loop” phenomenon, indicating that there is a slit pore structure inside coke [30]. The “hysteresis loop” width of TC was obviously larger than that of IC, indicating that there are more micropores and slits in TC, and the pore structure is more developed.

As the pore size distribution curve of the desorption branch had a false peak at 3.8 nm, adsorption branch data was selected to draw the pore size distribution diagram of IC and TC, as shown in Figure 8. The embedded dot line diagram in the upper right corner of the figure is an enlarged view of the abscissa in the range of 0 to 10 nm in the original figure. It can be seen from Figure 8 that there were obvious peak patterns in the aperture distribution diagrams of the IC and TC, and the higher the peak patterns, the larger the proportion of the corresponding pore volume in the total pore volume. The narrower the peak patterns, the more uniform the pore size distribution. The peak patterns of all coke samples were basically concentrated between 2 and 4 nm. It can be seen from Figure 8a that the peak value of the pore size distribution curve of IC was $0.0011 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{nm}^{-1}$, while that of TC was twice or more than that of IC. That is, the peak value of TC increased significantly between 2–4 nm, and the peak value shifted to the right, indicating that from IC to TC, not only a large number of pores with sizes between 2–4 nm were generated, but also the pore sizes of the original micropores in the IC were expanded so that the average pore sizes increased. This was the same with the analysis result of adsorption and desorption curves. Compared with IC, the pore size distribution curves of TC were all located above the corresponding pore size distribution curves of IC, which indicates that the number of pores in other ranges also increased except for the large increase in the number of transition pores between 2 and 4 nm in the radial TC.

Based on the analysis of micropore parameters, adsorption and desorption, and pore size distribution curve, it can be seen that the coke was subjected to high temperature during the falling process. The melting loss of coke itself, and the decomposition and volatilization of inorganic compounds such as internal volatiles led to the expansion of the original pore size in the coke and the formation of a large number of micropores, which is consistent with the previous research results [31]. Moreover, the temperature difference between the surface and the center of the coke as the coke was heated unevenly inside and outside, and the surface coke expanded, resulting in cracks. The above phenomena are the reasons for coke deterioration.

3.4. Micro Morphology Analysis of IC and TC

SEM was used to observe the microstructure and pore structure of IC and TC to further clarify the change of pore structure and morphology from coke entering the furnace to tuyere. As can be seen from Figure 9a, in addition to large pores visible to the naked eye, there were also a certain number of small pores on the coke surface. Such pores were evenly distributed, with thick hole walls and shallow hole grooves. The microscopic morphology of TC after the melting loss reaction changed compared with that of IC. By comparing the microscopic morphology of IC and TC in Figure 9, it was found that the pores were obviously connected on the surface of TC, the pore wall was thinner, and the surface layer was damaged.

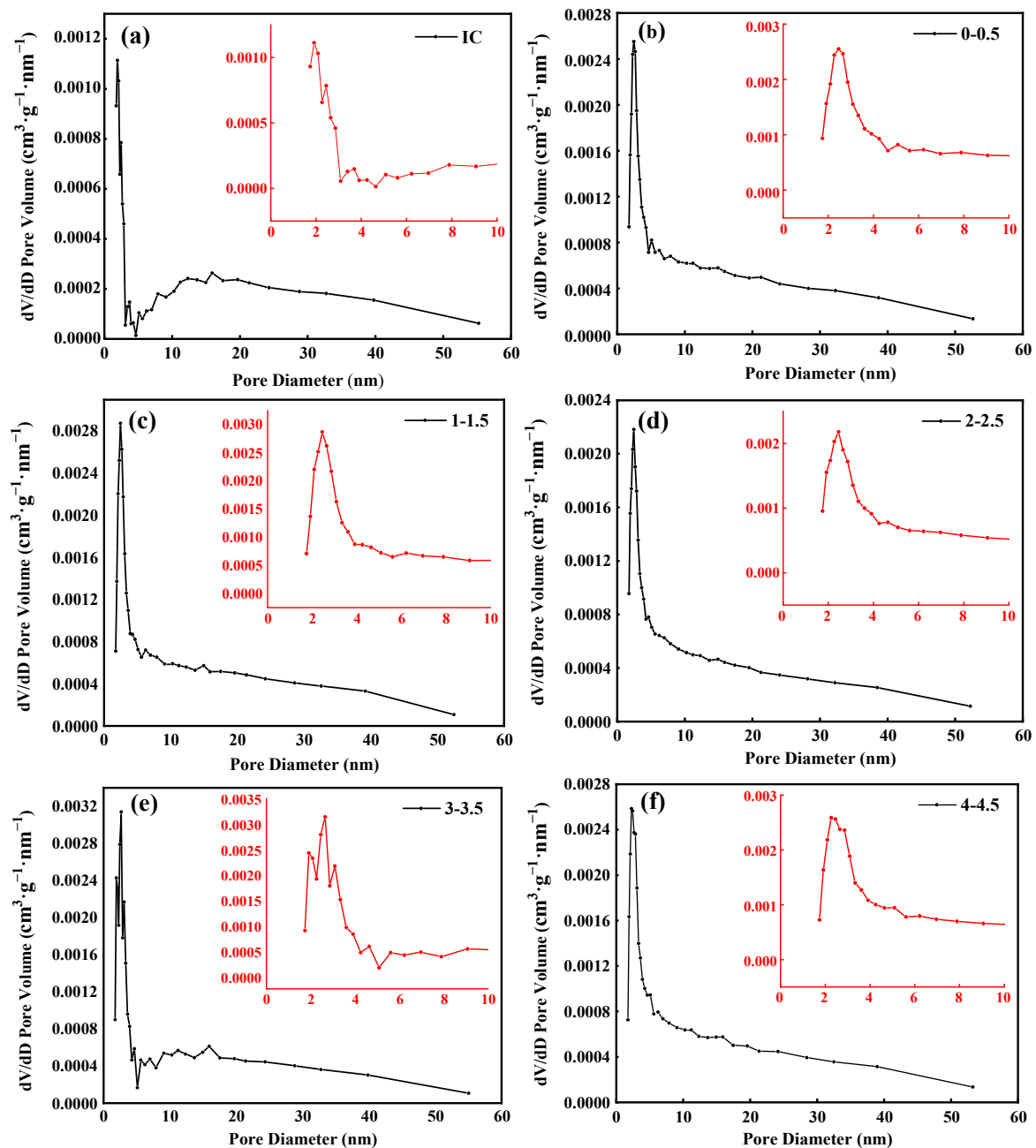


Figure 8. Pore size distribution of IC and TC. (a) IC; (b) 0–0.5; (c) 1–1.5; (d) 2–2.5; (e) 3–3.5; (f) 4–4.5.

It can be seen from Figure 9b that the pore structure on the surface of TC at the distance of 0–0.5 m from the tuyere was complex. The pore size distribution was uneven, mainly because the TC here bore the impact wear caused by the blast and the extrusion caused by the downward pressure of the furnace charge, as well as the carbon melting reaction under high-temperature conditions, which made the coke here suffer complicated conditions and had many types of pore structure. When the distance from the tuyere was 1–1.5 m, the pore structure on the surface of TC was compact, and most of them were small pores. This phenomenon is due to the rapid volatilization of ash and inorganic matter in the coke caused by the high temperature here, so that the number of small pores increased, and the pore structure was compact. However, the temperature dropped slightly when leaning toward the furnace core, but the melting reaction was still intense. The original micropores began to expand, the pores began to connect with each other, and large pores appeared on the surface. The deterioration of the coke matrix began to appear. It can be seen from

Figure 9e,f that the matrix on the TC surface near the furnace core area was significantly damaged. The main reason is that the pores on the coke surface expanded and fused, the pore structure began to collapse, the pores connected with each other, and cracks appeared on the pore wall during the melting loss and erosion process of the coke, resulting in the reduction in the strength of the coke surface and spalling. At the same time, the surface pores also extended to the interior of the coke and gradually penetrated into the coke inside to decompose the coke.

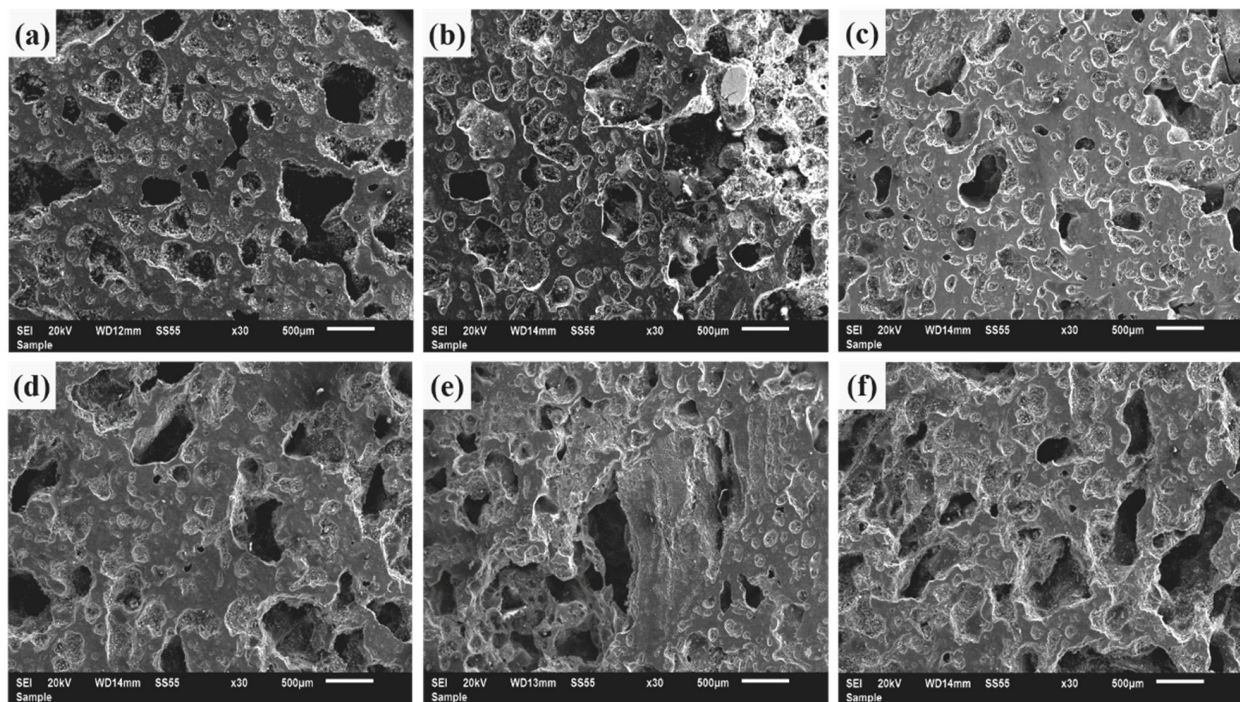


Figure 9. Micro morphology of IC and TC in different radial directions of the tuyere plane. (a) IC; (b) TC: 0–0.5 m; (c) TC: 1–1.5 m; (d) TC: 2–2.5 m; (e) TC: 3–3.5 m; (f) TC: 4–4.5 m.

3.5. Raman Analysis of IC and TC

Raman spectroscopy has been widely used to characterize the physical and chemical structures of materials such as coal coke due to its high detection efficiency and wide crystal structure. The standard graphite crystal structure has an obvious peak near 1575 cm^{-1} of the Raman spectrum, which is called the G peak. For the incomplete graphite crystal structure, there will also be a peak near 1350 cm^{-1} of the Raman spectrum, which is called the D peak. Among them, the G peak is usually used to characterize the graphite structure inside the coke, and the D peak is used to characterize the disordered carbon structure, that is, the disorder degree of coke. The higher the D peak, the more unstable carbon atoms in the samples, and the higher the disorder degree. When the temperature is too high, a peak appears near 2600 cm^{-1} , which is generally called the 2D peak. Such peak shifts to a higher wave number, and its pattern becomes narrower with the increase in carbon structure order. When the disorder of carbon structure increases, the 2D peak even disappears. At present, the integral ratio of D peak to G peak is commonly used to characterize the degree of coke ordering [32]. Figure 10 shows the Raman spectrum of IC and TC.

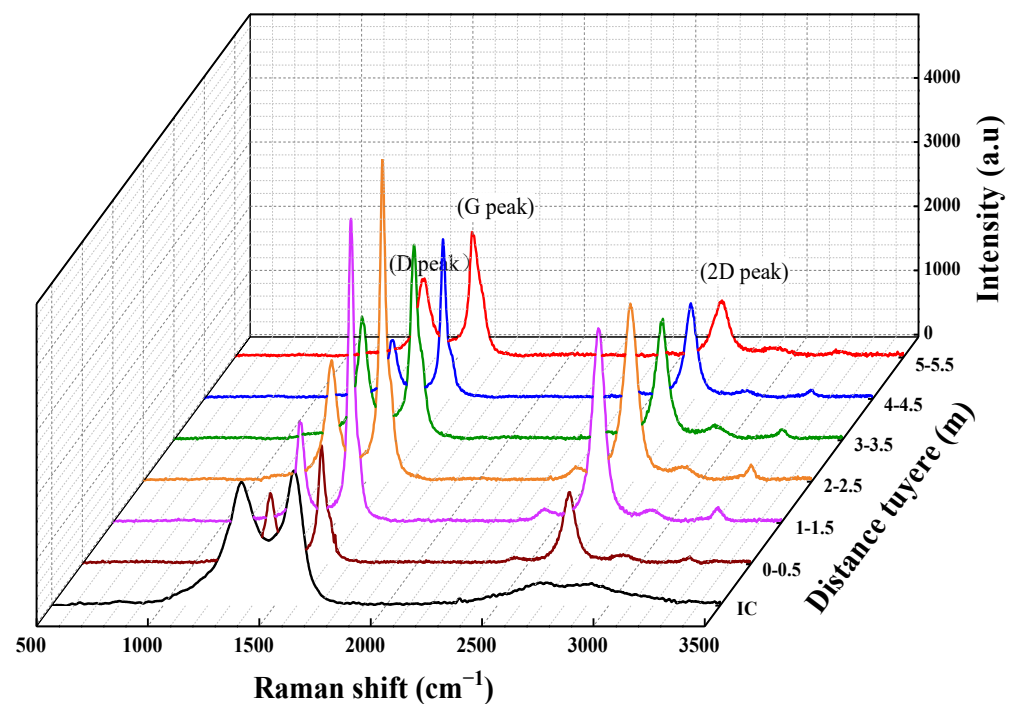


Figure 10. Raman spectrum of IC and TC.

As can be seen from Figure 10, the peak height and peak width of IC and TC changed, indicating that the internal disordered structure and graphite structure of the coke from the furnace to the tuyere changed. In addition, it can be seen from the figure that the intensity of the G peak and D peak corresponding to IC was not significantly different, indicating that the graphitization degree of the microcrystalline structure in IC was not high, and the number of disordered carbon atoms also existed. However, the G and D peaks of TC were obviously higher than those of IC, indicating that in addition to the increasing graphitization degree of TC microcrystalline structure, the number of unstable carbon atoms also increased. The G peak of the TC was higher than its corresponding D peak, indicating that the microcrystalline structure in the TC was mainly a graphitized structure. In the direction of the tuyere to the furnace core, the 2D peak and the G peak had the same variation trend, with the peak heights rising first and then decreasing, which further proves that the ordering degree of TC near the furnace wall and the furnace core was lower than that near the tuyere raceway. This was the same as the XRD analysis results: the TC microcrystalline structure order increased first and then decreased in the radial direction.

The peak patterns in the Raman spectrum of IC and TC were composed of multiple characteristic peak spectra. Therefore, in order to accurately reflect the microstructural changes of IC and TC, it was necessary to perform peak fitting on their spectra. According to relevant literature, the original D and G peaks can be fitted within $1000\text{--}2000\text{ cm}^{-1}$ and divided into five characteristic peaks whose peak positions are around 1200, 1350, 1500, 1580, and 1620 cm^{-1} , respectively [33]. The corresponding meanings of each peak are shown in Table 6.

Table 6. Meaning of characteristic peaks of Raman spectrum.

Characteristic Peak	Peak Position (cm ⁻¹)	Characterization of the Carbon Structure
D ₄	1200	sp ³ disordered carbons/sp ² -sp ³ mixed carbons
D ₁	1350	C-C bond vibrations between aromatic rings and aromatic compounds with ≥6 rings
D ₃	1500	Amorphous sp ² disordered carbon atoms such as organic molecules and functional groups
G	1580	Regular arrangement of sp ² disordered carbon atoms stretching vibration
D ₂	1620	Monolayer graphite lattice vibration

The peak fitting diagram of IC and TC (TC was taken as an example at a distance of 5–5.5 m from the tuyere) is shown in Figure 11, where the black line represents the original spectrum data obtained in the experimental process, and the red line represents the cumulative fitting peak data. The degree of peak fitting can be judged by comparing the coincidence degree of the two. By visually comparing the peak fitting diagram, it is obvious that the I_{D1}/I_G value of IC was significantly greater than that of TC, indicating that IC had higher activity and a lower graphitization degree. The important parameters such as integral area and half height width (FWHM) of each peak were obtained by peak fitting. Significant work has been done on how to use parameters to characterize carbon materials both at home and abroad. Cuesta et al. [34] found through Raman spectrum analysis of various carbon materials that the smaller the FWHM of peak D and the smaller the ratio of D peak area to the sum of D and G peak area, the higher the order degree of carbon material structure. In the early stage, a large number of domestic scholars carried out studies on it, but the focus basically included the fields of carbon fiber, nanocomposite materials, and so on, and was seldom applied to the structural composition analysis of coke. Studies showed [35] that the ratio of characteristic peak integral area can be used to reflect the structural order degree of carbonaceous materials such as coke, and the specific meanings are shown in Table 7.

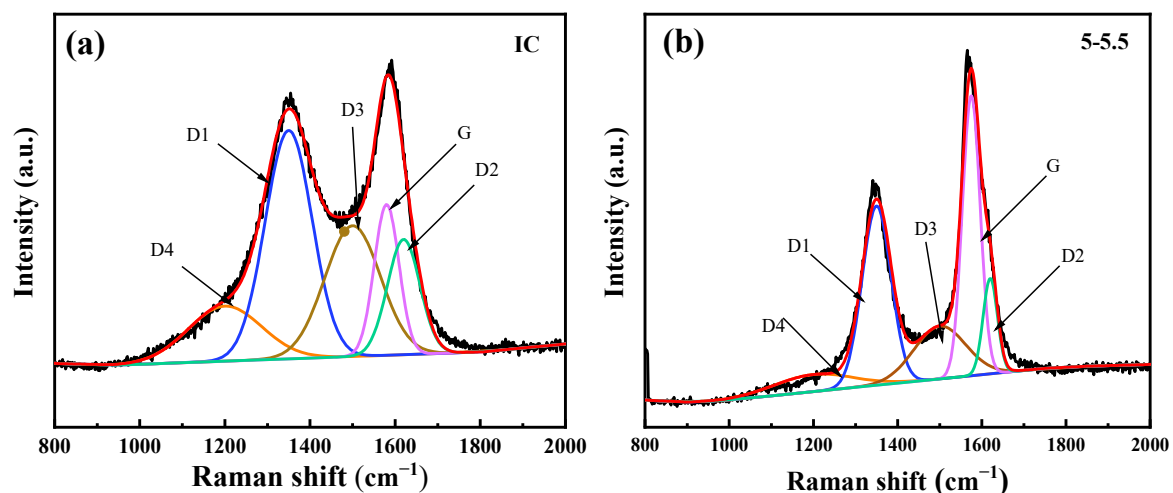
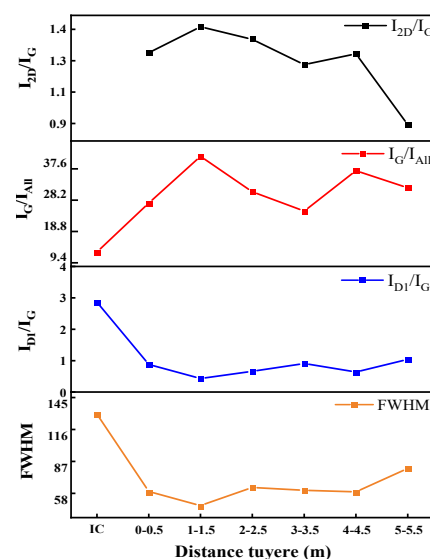
**Figure 11.** Fitting spectrum of IC and TC. (a) IC; (b) TC (5–5.5 m).

Table 7. Meaning of peak area ratio of characteristic peaks.

Peak Area Ratio	Meaning Represented
I_{D4}/I_G	The relative content of unstable structures
I_{D1}/I_G	Degree of graphitization, an indicator of structural order
I_{D3}/I_G	The relative content of amorphous structures
I_G/I_{All}	The relative content of graphite structure
I_{D2}/I_G	The relative content of irregular structures

In addition to the fitting peak area ratio, the FWHM of fitting peak D_1 can also be used to demonstrate the amount of disordered structure in coke samples. The narrower or smaller FWHM indicates a reduction in disordered structure in coke samples. After the 2D peak is fitted separately by the same method, the integral area I_{2D} of its peak can be obtained. The value of I_{2D}/I_G corresponds to the order degree of coke, and the larger the I_{2D}/I_G , the higher the order degree. In this study, the peak area ratio I_{D1}/I_G , I_G/I_{All} , I_{2D}/I_G , and D_1 peak FWHM obtained after fitting was used to characterize the microstructure of IC and TC, and the variation trend is shown in Figure 12. It can be seen that I_{2D}/I_G increased first and then decreased from the tuyere to the furnace core, and the peak value was 1–1.5 m away from the tuyere, indicating that the crystal order degree inside the TC was the highest here. The variation trend of I_{2D}/I_G was the same as that of I_G/I_{All} , indicating that in the radial direction, the ordered structure of TC in this part was not only the highest but also its relative content reached the maximum. The ratio of I_{D1}/I_G decreased greatly from IC to TC, and the smaller I_{D1}/I_G , the higher the graphitization degree and structure order degree. Although the I_{D1}/I_G value of TC at each position in the radial direction changed little, it still showed a trend of decreasing first and then increasing, which was contrary to the changing trend of I_G/I_{All} and conformed to the result of higher graphitization degree of TC. The changing trend of FWHM showed that the disordered structure in TC decreased, but a slight rise occurred in the furnace core, indicating that the content of disordered coke structure in the furnace core increased relatively. From the variation characteristics of the above parameters, compared with the IC, the internal graphite structure of TC increased, and the crystal structure became larger. In the radial direction, the number of amorphous structures in coke further decreased with an increase in temperature, the ordering continued to increase, and the graphite structure also continued to grow. However, the closer it was to the furnace core, the greater the temperature decrease, while the amorphous structure content stagnated and the graphitization decreased.

**Figure 12.** Characteristic peak area ratio and FWHM of IC and TC.

3.6. FTIR Analysis of IC and TC

Like other spectra, infrared spectroscopy can judge the chemical structure of molecules by peak position, shape, and intensity. Absorption peaks appeared in the spectrum, indicating that the test sample absorbed light of various wavelengths. Thus the functional groups and their relative contents in the sample could be inferred from the peak pattern characteristics. Therefore, in order to analyze the molecular structure and evolution law of coke at different positions of blast furnace, infrared spectroscopy was also a useful method. As can be seen from Figure 13, both IC and TC appeared as obvious wide-strength peaks in the region of 3200 to 3700 cm^{-1} , which was caused by the stretching vibration of -OH associated with the H bond, especially phenol-OH. However, the peak intensity of IC was significantly higher than that of TC, indicating that the content of the -OH bond decreased under high temperatures. Furthermore, the spectral lines on both sides of the peak pattern were not symmetrical, which was caused by the presence of a large number of H bonds in the coke samples [36]. The characteristic peaks at 1631 cm^{-1} were caused by the stretching vibration of carbonyl C=O, and the peak pattern weakened from the furnace inlet to tuyere, indicating that the C=O structure decreases during this process. Near the 1055 cm^{-1} obvious wide strong peaks also appeared, which mainly corresponded to the relative content of C-O, while the C-O peak of TC at 0–2.5 m distance from tuyere was weak because the C-O bond on the coke surface broke and peeled off at high temperature during graphitization. The C atoms connected with each other to form a dense layer, which made the graphitization higher than the IC. The out-of-plane vibration of aromatic C-H near 875 cm^{-1} caused the peak to appear only in the spectrum of IC, indicating that the bond effect gradually disappears with an increase in temperature. However, from the type of functional groups, there was no significant change in the functional groups from IC to TC.

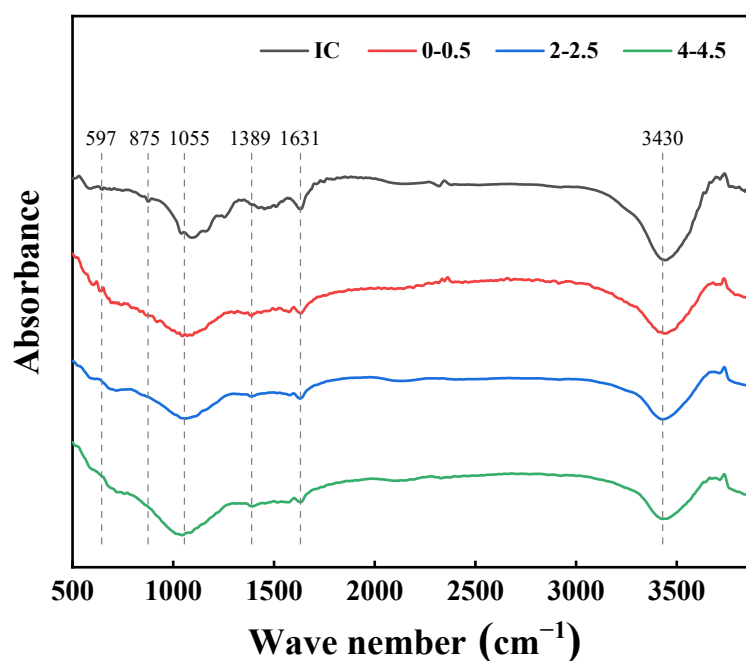


Figure 13. Infrared spectra of IC and TC.

4. Conclusions

In this study, XRD, BET, SEM, Raman spectroscopy, and FTIR were used to study the evolution of the graphitization degree, pore size distribution, micromorphology, and structure of IC and TC. Compared with IC, the microcrystalline structure of TC was more orderly, and its order degree first increased and then decreased in the radial direction, with the highest value in the range of 1 to 2 m. Furthermore, the porosity of TC was significantly higher than that of IC, and the pore wall was also thinner. The pore size

of original micropores in the TC was enlarged, and simultaneously a large number of micropores and cracks were also generated, resulting in the specific surface area and pore volume of TC being higher than that of IC. The micropore diameter of TC was mainly distributed between 2 and 4 nm, and the micropore distribution of the coke at 1–1.5 m away from the tuyere was the most uniform. In addition, the graphite structure inside the TC increased, and the crystal structure became larger. In the radial direction, the number of amorphous structures in coke decreased, the ordering increased, and the graphite structure continued to grow with an increase in temperature. However, along the furnace core direction, a decrease in temperature led to the stagnation of amorphous structure content and a decrease in graphitization degree. Through FTIR analysis, it was found that the coke was mainly composed of -OH and C-O bonds, while the types of functional groups did not change.

Author Contributions: The manuscript was written through contributions of all authors. Y.Z. and J.Y. performed the Resources, Writing—Review & Editing, Supervision, Data Curation. H.W. performed the SEM, EDS, and LSCM measurements; L.Y. performed the surface cleaning and sample polishing; S.C. performed samples prepared and image processing. All authors have read and agreed to the published version of the manuscript.

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