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EFFECT OF MICROWAVE IRRADIATION ON REACTIVITY OF METALLURGICAL COKE IN CO_2 ATMOSPHERE

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Influence of microwave irradiation on gasification behavior and crystallite parameters of coke samples was studied in this research. The results indicated that microwave irradiation have significant influence on the carbon structure and the reactivity of coke in CO_2 atmosphere. The thermogravimetric results showed that the temperature of coke at different conversion rates of 10 %, 20 % and 30 % were reduced by 20 °C, 30 °C and 50 °C respectively. Simultaneously, microwave irradiation may lead to variation in lateral size and stacking height of crystallite and subsequently reduce the gasification reaction rate of coke in CO_2 atmosphere.

Key words: blast furnace; metallurgical coke; thermogravimetric analysis; microwave, X-ray diffraction (XRD)

INTRODUCTION

Currently, the long process with blast furnace (BF) and converter is still dominant in Chinese crude steel production [1]. The metallurgical and mechanical properties of sinter and pellets as well as lump coke play a very important role in BF ironmaking process, which determines not only the permeability of stock but also the consumption of carbon-based fuel and consequently the emission of CO_2 [2]. However, with the sharp decrease in price of crude steel in the past years, the cost in crude steel production is attracting more and more attention. Gradually, cutting down the cost in BF process is becoming more and more important and consequently has become the primary task for ironmaking researchers [3].

Many iron and steel enterprises are trying to utilize low grade ores and inferior cokes in order to decrease the cost in ironmaking process. The degradation of sinter and pellet as well as lump coke during reduction in BF has also become more severe due to the inadequate metallurgical property of low grade ores [4]. According to the experimental results of previous investigations [5, 6], the reactivity of pulverized coal (PC) became inferior after long time or high power microwave treatment. Analogously, the reactivity of coke powder (CP) may also be reduced with the utilization of microwave irradiation, by which the carbon solution reaction can be limited and consequently allow coke to utmostly perform its supporting effect in the stock. Thus, the effect of microwave treatment on coke reactivity and carbon structure was studied in this investigation.

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EXPERIMENTAL

Sample

A metallurgical coke which is utilized in actual production is selected the sample of this study, the proximate and ultimate analyses are shown in Table 1. Considering that materials of container may influence the heating behavior of sample in microwave [7, 8], clayey was adopted as a medium.

Table 1 **Proximate analysis and ultimate analyses of CP sample / %**

Sample	Proximate analysis			Ultimate analysis				
	FC_d	V_d	A_d	C_d	H_d	N_d	O_d	S_d
CP	84,88	1,67	13,45	86,12	0,23	0,34	0,28	0,51
PC	70,40	11,23	10,37	75,27	2,70	0,94	3,84	0,73

FC, fixed carbon; V, volatile; A, ash; d, dried;

Thermal behavior of CP sample in microwave environment

Comparison among spectra in Figure 1 indicates that the temperature of CP increased swiftly under high microwave powers, while the thermal effect under low microwave power is not that significant. CP under 396 W and 528 W microwave power was heated to 210 ℃ and 330 ℃ respectively with 120 s irradiation, while the temperature of CP only reached 90 ℃ and 120 ℃ respectively with the same irradiation time under 132 W and 264 W microwave power. It can be inferred that the thermal effect of low microwave power is not that insignificant on CP. Therefore, the utilization of low power microwave on pretreating of metallurgical coke will not lead to sharp increase in coke temperature, namely no obvious variation in the chemical composition of coke.

Besides, the heating rate of CP rose slightly faster than PC at 132 W microwave powers, but PC could be heated to much higher temperatures in comparison to CP with the increase of microwave power to 264 W. With the further increase of microwave power to 396 W, both CP and PC sample seemed to have the similar heating rate. However, the temperature of CP rose much faster than that of PC in 528 W microwave fields in the initial 60 s, the heating rate of CP decreased with the further extension of time to 120 s. The CP and PC sample almost reached the same temperature level after 2 min treatment under 528 W. In order to avoid the thermal effect of microwave on CP during irradiation, lower microwave powers as 132 W and 264 W were selected for the treatment of CP in this study, while irradiation times were set as 40 s and 80 s respectively to control the temperature of samples under 100 °C.

Thermogravimetric analysis

In order to analyze the variation in reactivity of CP sample with CO_2 before and after microwave irradiation, the thermogravimetric behavior of original and treated CP samples were tested with a WCT-2C type thermal analysis device. 17,5 mg sieved CP specimens (under 0,074 mm) was loaded into a corundum crucible and then heated from ambient temperature to 1200 °C in CO_2 atmosphere (flow rate of 60 mL/min) at the heating rate of 20 °C/min, by which the weight loss curve of different CP sample with the rising of temperature was recorded.

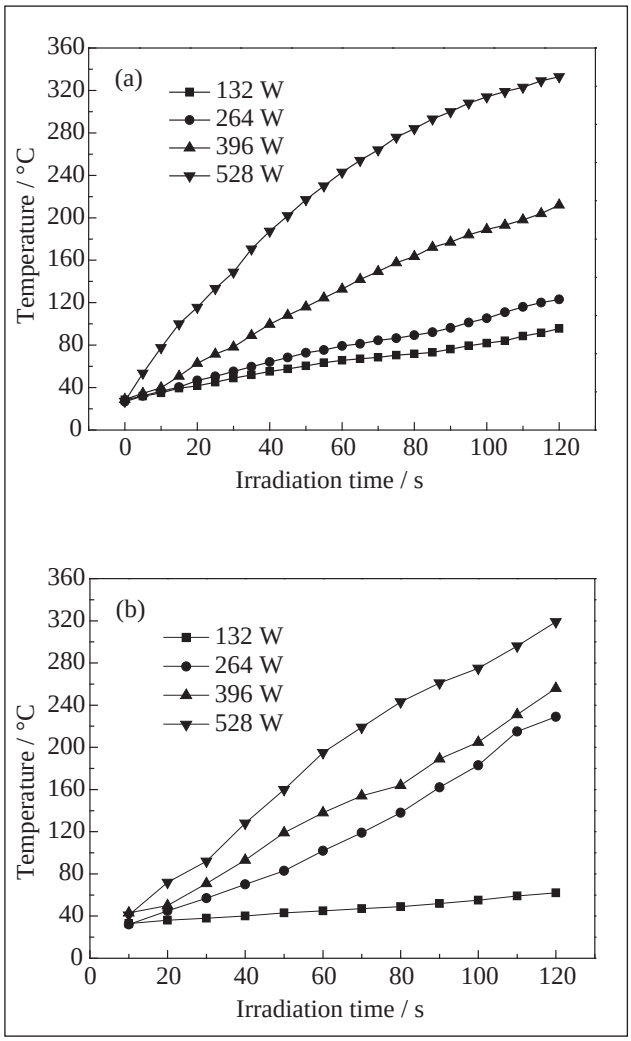

Figure 1 Variation of CP (a) and PC (b) temperature in microwave field

X-ray diffraction (XRD)

X-ray diffraction was utilized to study the transformation of carbon structure of samples. The average lateral size and average stacking height of the crystallite can be calculated by the application of Bragg and Scherrer equations, whose expression can be deduced as follow [9, 10]:

(1) Calculation of 002 and γ band structural parameters

$$d_{002} = \frac{\lambda}{2\sin\theta_{002}} \qquad d_{\gamma} = \frac{\lambda}{2\sin\theta_{\gamma}} \tag{1}$$

$$L_a = \frac{k \cdot \lambda}{\beta_{002} \cdot \cos\theta_{002}} \qquad L_c = \frac{k \cdot \lambda}{\beta_{\gamma} \cdot \cos\theta_{\gamma}} \tag{2}$$

Where λ is the wave length of X ray, whose value is 0,15418Å; d_{002} and d_{γ} respectively represent the crystalline interplanar spacing of 002 and γ band; θ_{002} and β_{002} respectively represent the diffraction angle and peak width at half height of 002 band; θ_{γ} and β_{γ} respectively represent the diffraction angle and peak width at half height of γ band; k is the correction factor, whose value is 1,84 and 0,89 respectively in the calculation of L_a and L_c; L_a and L_c respectively represent the lateral size and stacking height of crystallite.

(2) Calculation of 002 and γ band areas

$$X_{002} = \frac{S_{002}}{S_{002} + S_{\gamma}} \qquad X_{\gamma} = \frac{S_{\gamma}}{S_{002} + S_{\gamma}} \tag{3}$$

Where S_{002} and S_{γ} respectively represent the band areas of 002 and γ band; X_{002} and X_{γ} respectively represent the area proportion of 002 and γ band.

RESULTS AND DISCUSSION

Thermogravimetric analysis

Gasification reaction curves of CP samples are shown in Figure 2. As can be seen that with the extension of irradiation time from 40 s to 80 s under 132 W, the reactivity of CP was gradually decreased. The maximum decrease in reactivity of CP can be achieved under 264 W with 40 s irradiation.

Phase structure analysis

X-ray diffraction profiles of CP samples in Figure 3 showed that the intensity of band in 2θ region between 21 ° and 29 ° was enhanced with the extension of irradiation time from 0 to 80 s under 132 W, while the same trend

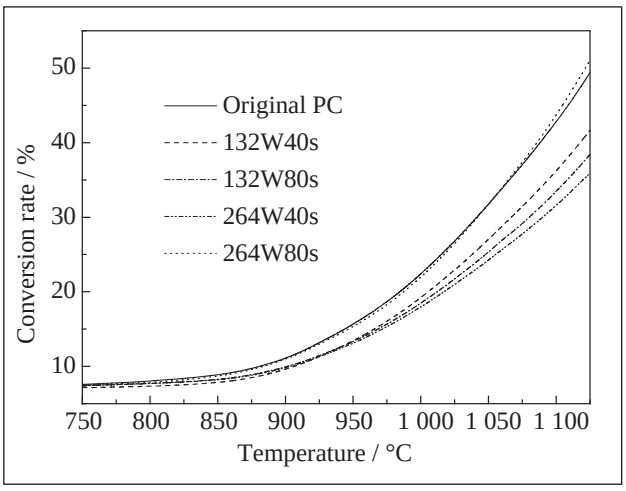

Figure 2 Variation of PC temperature under different microwave powers

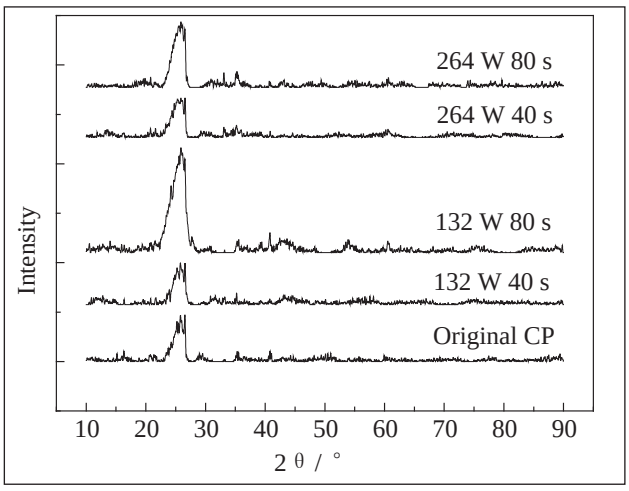

Figure 3 XRD spectra of original and treated CP

Table 2 **Temperature at different conversion rates / °C**

Sample	Temperature at conversion rates / °C			Maximum conversion rate / %
	10 %	20 %	30 %	
OCP	881	984	1041	55,18
132W40s	906	1005	1067	46,67
132W80s	901	1012	1080	42,73
264W40s	903	1017	1090	39,66
264W80s	884	987	1042	57,32

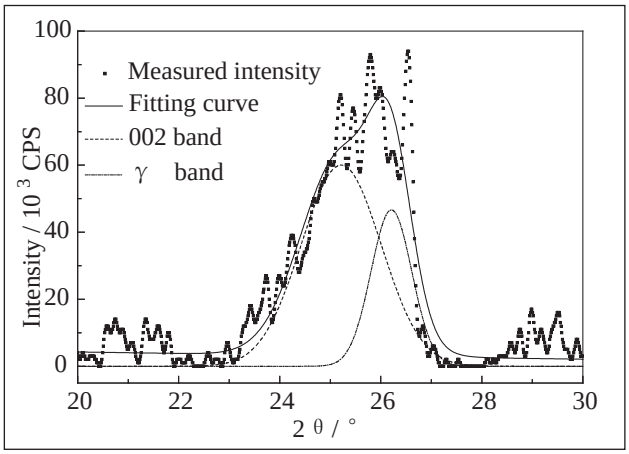

Figure 4 Curve-fitting of two Gaussian peaks for original CP samples

Table 3 **Structural parameters extracted from the fitting curves of XRD spectra**

Sample	d_{002}, Å	d_{γ}, Å	f_a	L_c, Å	L_a, Å
OCP	3,407	3,546	0,715	5,819	11,728
MCP (132W, 40s)	3,421	3,527	0,753	5,879	22,276
MCP (132W, 80s)	3,412	3,562	0,732	5,643	23,312
MCP (264W, 40s)	3,419	3,574	0,741	5,293	24,510
MCP (264W, 80s)	3,402	3,572	0,708	5,455	12,600

was also observed under higher microwave power of 264 W. The temperature of CP samples were below 100 °C during the irradiation process under different microwave powers, which implied the variations occurred in carbon structure of CP was not attributed to the heat effect of microwave. Therefore, it can be presumed according to above results that the reactivity of CP sample may be modified in chemical reaction due to the variation of carbon structure. Above results imply that microwave irradiation treatment may lead to contrary effect on carbon based fuels under different conditions.

The peaks in Figure 4 are the combination of different absorption peaks. Thus, PeakFit was adopted to separate the spectra between 2θ region of 21 ° and 29 ° into different peaks, consequently representative fits of two Gaussian peaks was obtained [9]. The crystallite parameters of different CP samples derived from the calculation based on X-ray diffraction spectra are listed in Table 3.

The crystallite data of CP samples in Table 3 shows that there is no apparent difference in both d_{002} and d_{γ} values among CP samples, which indicated that microwave irradiation will not lead to significant variation to the interlayer spacing of the crystallite structure of CP samples. Besides, the stability of aromaticities of CP samples also revealed that no obvious variation in the chemical bonds between C and H occurred during microwave treatment. However, there are dramatic fluctuations in both L_c and L_a the values, suggesting that the prominent variations in carbon structure of coke have taken place during microwave irradiation process. The value of L_c was slightly increased by the treatment of 40 s under 132 W microwave power and however was decreased with the further extension of irradiation time to 80 s, while the value of L_c was initially decreased by 40 s irradiation and then increased by 80 s treatment under 264 W microwave power. Meanwhile, the value of L_a constantly increased in the initial 80 s under 132 W microwave power, while the increment was significant in the first 40 s and insignificant in the following 40 s. In comparison, the value of L_a increased dramatically in the first 40 s under 264 W microwave power and however decreased to the original level in the following 40 s treatment. Above results showed that treating conditions as irradiation time and microwave power may have a prominent influence on both structural parameters and reactivity of CP. The comparison in data between Figure 2 and Table 3 shows that there is an obvious relationship between the crystallite parameters and

reactivity of CP, which indicated that it is feasible to apply microwave irradiation in reduce the solution of coke in BF.

CONCLUSIONS

Microwave irradiation may lead to significant ordering variation in carbon structure of coke samples while the ordering extents are related to the microwave irradiation conditions.

The ordering of carbon structure may lead to the passivation in reactivity of carbon atoms in coke samples, which means the carbon atoms may become more stable after treatment under certain condition and consequently slow down the gasification reaction of coke in CO_2 atmosphere.

Acknowledgements

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REFERENCES

[1] M. Naito, S. Nomura, K. Kato. Development of production and utilization technology of coke with high strength and high reactivity, Tetsu-To-Hagane 96(2010)5, 201-208.

[2] W. Zuzana, P. Oldrich, S. Ivana, M. Vladimir. Effect of bituminous coal properties on carbon dioxide and methane high pressure sorption, Fuel 139(2015)1, 115-124.

[3] R. Gopalakrishnan, M.J. Fullwood, C.H. Bartholomew. Catalysis of char oxidation by calcium minerals-effects of calcium compound chemistry on intrinsic reactivity of doped spherocarb and zap chars, Energy and Fuels 8(1994)4, 984-989.

[4] A. Babich, D. Senk, H.W. Gudenau. Effect of coke reactivity and nut coke on blast furnace opreration, Ironmaking and Steelmaking 36(2009)3, 222-229.

[5] Q.H. Pang, J.L. Zhang, R. Mao, Z. Jiang, T. Liu. Mechanism of effect of microwave modification on pulverized coal combustion properties, Journal of Iron and Steel Research International 21(2014)3, 38-46.

[6] Q.H. Pang, J.L. Zhang, Y.L. Jin, C.L. Qi, Z.J. He, D.W. Kong. Effect of microwave modification on pulverized coal combustion properties[J]. Metalurgija International 17(2012)2, 5-10.

[7] C. Yan, N. Yoshikawa, S. Taniguchi. Microwave heating behavior of blast furnace slag bearing high titanium, ISIJ International 45(2005)9, 1232-1237.

[8] F. Mushtaq, R. Mat, F.N. Ani. A review on microwave assisted pyrolysis of coal and biomass for fuel production, Renewable & Sustainable Energy Reviews 39(2014)11, 555-574.

[9] O.O. Sonibare, T. Haeger, S.F. Foley. Structural characterization of Nigerian coals by X-ray diffraction, Raman and FT-IR spectroscopy, Energy 35(2010)12, 5347-5353.

[10] O. Francioso, S. Sanchez-Cortes, S. Bonora, M.L. Roldan, G. Certini. Structural characterization of charcoal size-fractions from a burnt pinus pinea forest by FT-IR, Raman and surface-enhanced Raman spectroscopies, Journal of Molecular Structure 994(2011)3, 155-162.

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