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THE THERMAL DECOMPOSITION MECHANISM OF SMALL PARTICLE LIMESTONE UNDER HIGH CO_2 PARTIAL PRESSURE

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Converter blown limestone powder steelmaking process has the advantages of energy saving and high efficiency to meet the needs of low carbon metallurgy. Based on a thermogravimetric-differential thermal analyzer, the effect of high CO_2 partial pressure on the pyrolysis behavior of limestone at steelmaking temperatures was investigated at 20 °C/min, 30 °C/min, and 40 °C/min, the kinetic parameters of limestone pyrolysis were calculated by the improved double extrapolation method.

Keywords: small particle limestone; decomposition mechanism; high CO_2 partial pressure; low carbon

INTRODUCTION

The iron and steel industry has played an important leading and driving role in the process of industrialization and economic development. However, the rapid expansion of the iron and steel industry has brought about many problems such as high pollution and high energy consumption. With the strategy of “carbon peaking and carbon neutrality“, the converter process, as an important part of long-process steelmaking, is also in urgent need of low-carbon and energy-saving development [1-2]. H. Li[3] proposed limestone instead of lime slag steelmaking, to avoid high pollution and high energy consumption of lime production and transportation links, in the environment of the converter to achieve the production and efficient use of high-activity lime, to meet the smelting needs of the basis of the dephosphorization rate to achieve an increase [4-5] At present, the particle size of limestone for metallurgical use is generally between 10-40 mm, and the larger limestone blocks are not easy to calcine decomposition, and there is the problem of low CO_2 utilization rate. Ghiasi [6] found that the effect of temperature on the equilibrium partial pressure is greater than the effect of particle size on the equilibrium partial pressure, which can be achieved by increasing the temperature to allow the reaction to continue in the presence of a higher CO_2 gas pressure; Scaltsoyiannes [7]studied that temperature is the main factor affecting the calcination of limestone and that the increase in particle size and CO_2 concentration inhibits the decomposition of limestone. X. Chen [8] found that CO_2 inhibited the decomposition of limestone powder, but the reaction time was rather shortened with increasing temperature. C. Li [9-10] proposed the use of converter-blown limestone powder slag steelmaking, the study found that the average particle size of 0.44mm of small particles of limestone dephosphorization effect is better.

The decomposition characteristics of limestone are currently the subject of several studies; however, the small particle limestone powder is blown into the melt pool, the high emperature and small particle size will promote the accelerated decomposition of converter limestone, CO_2 accelerates the escape, CO_2 partial pressure increases, and the undecomposed small particle size limestone powder will be wrapped by the surrounding environment of high CO_2 partial pressure, for which the decomposition mechanism has not been reported. Using the improved double extrapolation method, the author studied the thermal decomposition mechanism of small-grained limestone under high CO_2 partial pressure, intending to provide a theoretical basis for the further application of converter-blowing small-grained limestone slagging for steelmaking.

EXPERIMENTAL MATERIALS AND METHODS

Experimental materials

The material used in the test was limestone for steelmaking in a steel plant in Shijiazhuang, and the chemical composition of the sample was determined by X-ray Fluorescence (XRF), as shown in Table 1. The CaO mass fraction of the limestone used in the test reaches

Table 1 **Limestone composition**

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	K_2O
54,38	0,96	0,17	0,234	0,258	0,08
Others	Loss				
0,066	43,875				

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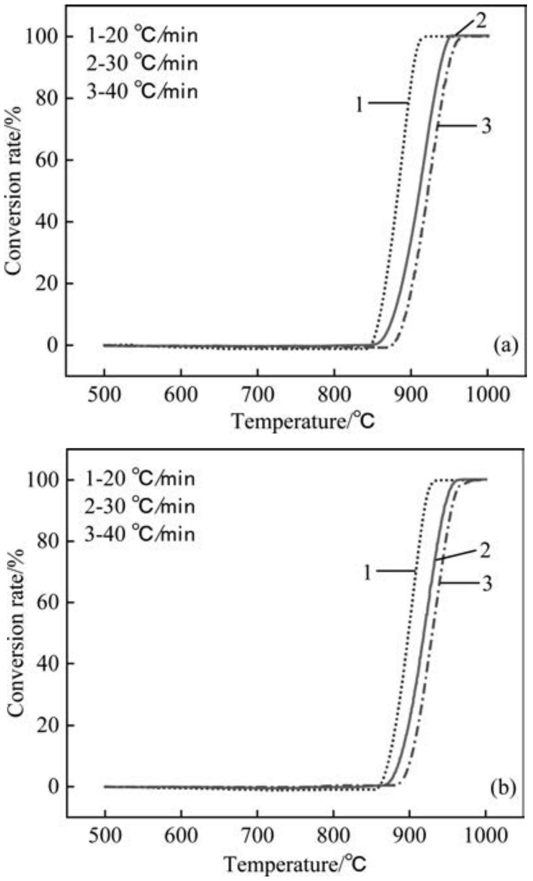


(a) - Conversion curve at 75 % CO_2 partial pressure;
(b) - Conversion curve at 100 % CO_2 partial pressure

Figure 1 Effect of different CO_2 partial pressures on limestone decomposition

54,38 %, with less impurity content, which belongs to high-quality limestone.

Experimental methods

The conversion rate α of the limestone samples was calculated from equation (1).

$$\alpha = \frac{w_0 - w_t}{w_0 - w_x} \times 100\% \tag{1}$$

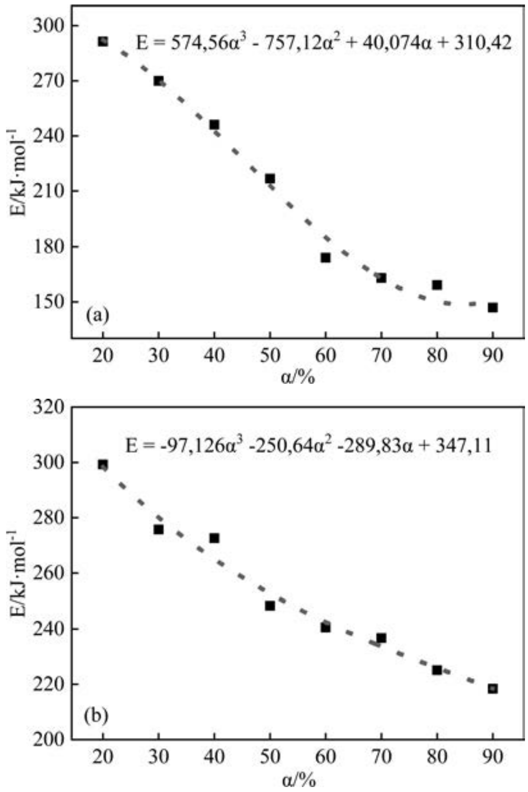
Where: α is the conversion rate of the limestone, W_0 is the original weight of the lime-stone sample, W_t is the weight of the limestone sample at a point t of the reaction, and W_x is the mass of the sample at the complete decomposition.

Based on the Arrhenius formulation, the reaction rate constant k is related to the thermodynamic temperature T as follows:

$$k = Ae^{-E/RT} \tag{2}$$

Where: E is the activation energy, A is the finger forward factor, and R is the gas reaction constant, 8,3145 J/mol·K.

The apparent activation energy E corresponding to a fixed conversion rate α and the apparent activation energy E corresponding to a fixed heating rate β were obtained by fitting using the Starink differential equation $\ln(\beta/T^{1,8}) = C_s - 1,0037E/RT$ and Coats-Redfern equation $\ln(G(\alpha)/T^2) = \ln(AR/(\beta E)) - E/(RT)$, respectively. Equations (3) and (4) are used to obtain the value of $E_{\alpha\to 0}$ without any interference of side reactions and the system in the original state and to obtain the value of kinetic parameter $E_{\beta\to 0}$ for the sample in the thermal equilibrium state. Comparing the results obtained from the two extrapolations, if they are equal or similar, the corresponding G(α) mechanism function equation is considered the most probable mechanism function in the thermal decomposition process of limestone.



(a) - E to α fitting curve at 75 % CO_2 partial pressure;
(b) - E to α fitting curve at 100 % CO_2 partial pressure

Figure 2 E to α curves at different partial pressures

$$E = a_1 + b_1\alpha + c_1\alpha^2 + d_1\alpha^3 \tag{3}$$

$$E = a_2 + b_2\beta + c_2\beta^2 + d_2\beta^3 \tag{4}$$

Where: a_1, b_1, c_1, d_1 and a_2, b_2, c_2, d_2 are the parameters, α is the conversion rate of the limestone, β is the rate of heating.

ANALYSIS OF EXPERIMENT RESULTS

Thermal decomposition properties of small particle limestone

The thermal analysis experiments were carried out using carbon dioxide partial pressures of 75 % or 100 % at three heating rates, and the variation curves of the thermal decomposition conversion of 0.44 mm limestone particles with temperature are shown in Figure 1.

Under the same atmosphere, with the increase of heating rate, the decomposition temperature of small limestone particles produces a certain lag phenomenon,

Table 2 **Fitting results obtained by the Coats-Redfern integration method**

CO_2/%	n	E/(kJ·mol^{-1})	R^2	E/(kJ·mol^{-1})	R^2	E/(kJ·mol^{-1})	R^2
		20 °C/min		30 °C/min		40 °C/min	
75 %	1	630,91	0,9939	539,03	0,9935	387,81	0,9933
	2/3	414,18	0,9937	352,83	0,9932	251,91	0,9929
	1/2	305,82	0,9935	259,72	0,9930	183,97	0,9925
100 %	1	680,89	0,9984	630,31	0,9944	552,21	0,9980
	2/3	447,42	0,9987	413,62	0,9942	361,47	0,9979
	1/2	330,68	0,9983	305,27	0,9941	266,09	0,9978

Table 3 **E and mechanism functions for limestone decomposition**

CO_2/%	$E_{\beta\to0}$/(kJ·mol^{-1})	R^2	G(α)	n
75	309,03	0,9989	$[-\ln(1-\alpha)]^{1/2}$	1/2
100	340,20	0,9976	$[-\ln(1-\alpha)]^{1/2}$	1/2

which is mainly due to the acceleration of the heating rate will increase the heat transfer temperature difference between the limestone and the crucible, which will lead to thermal hysteresis, resulting in the decomposition of the reaction temperature increases. In the same heating rate, with the change of atmosphere, limestone thermal decomposition temperature will produce a certain lag phenomenon. This is mainly due to the increase in the partial pressure of CO_2 in the reaction atmosphere so that the decomposition of limestone lags, but in the high concentration of CO_2 environment, with the increase in temperature, limestone can still complete the decomposition, this is mainly because of the decomposition of CO_2 produced by the temperature of the gas is much higher than the temperature of the carrier gas, so it can be separated from the solid to escape, continue to complete the decomposition.

Kinetic study of thermal decomposition of small-grained limestone

According to the conversion rate, the temperature corresponding to each conversion rate under different heating rates is obtained, the conversion rate is fixed, the corresponding activation energy E under different conversion rates is obtained, and the fitted result for $E_{\alpha\to0}$ is shown in Figure 2 below.

The Coats-Redfern integral method was fitted to obtain the apparent activation energy E at a fixed rate of temperature increase β., the values of $E_{\beta\to0}$ were obtained for 75% CO_2 and 100% CO_2 partial pressures, respectively, which were in thermal equilibrium. Combined with the mechanism function [11] $G(\alpha)=[-\ln(1-\alpha)]^{n}$, n is in 1/2~1 to calculate $\ln[G(\alpha)/T^2]$ corresponding to T. The results of the Coats-Redfern method are shown in Table 2 below. The corresponding E and mechanism functions for limestone decomposition are shown in Table 3.

Compare the value of $E_{\beta\to0}$ with the value of $E_{\alpha\to0}$, The models for the thermal decomposition of limestone at high CO_2 partial pressures are all stochastic nucleation and subsequent growth models with a functional equation of mechanism $G(\alpha)=[-\ln(1-\alpha)]^{1/2}$ and a reaction level of 1/2.

CONCLUSION

With the increase of heating rate, small particles of limestone decomposition temperature increases, limestone decomposition produces a certain hysteresis, the reaction moves to the high-temperature region, but the reaction can be fully reacted within 1 000 °C.

75 % CO_2 and 100 % CO_2 partial pressure limestone decomposition apparent activation energy of 310,42 KJ/mol and 347,11 KJ/mol, respectively, CO_2 partial pressure increases, the apparent activation energy of thermal decomposition of limestone increases, the decomposition of the reaction is more difficult.

The improved double extrapolation method was used to calculate the kinetic parameters of the decomposition of limestone small particles under high CO_2 partial pressure, and it was concluded that the model of the thermal decomposition reaction of limestone under high CO_2 partial pressure is the model of random nucleation and subsequent growth. The functional equation of the mechanism is $G(\alpha)=[-\ln(1-\alpha)]^{n}$ and the number of reaction stages is 1/2. Limestone decomposition initially occurs in certain localities, after which, as the reaction proceeds, these neighbouring decomposition products will aggregate to form a new physical phase, CaO, and then the interfacial reactions of the surrounding $CaCO_3$ molecules will continue until the entire solid phase is completely decomposed.

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Note: The responsible translator for English language is Y. ZHANG - North China University of Science and Technology, China