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**Research Article** 

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# Effect of particle size on reduction behavior in iron ore-coal composite pellets

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## ABSTRACT

The reduction of iron ore-coal composite pellets was carried out in the temperature range of  $500 \sim 1200^{\circ}C$  by thermogravimetry. This study aims to investigate the effect of particle size of iron ore on reduction behavior. Three samples of different particle size were selected:  $25 \sim 48 \mu m$ ,  $75 \sim 106 \mu m$  and  $150 \sim 180 \mu m$ . The reaction kinetic parameters were estimated based on the thermogravimetric data. The characterization of the heated residues was identified by X-ray diffraction and Scanning electron microscope. The experimental results indicated that the selected iron ore with particle size  $25 \sim 48 \mu m$  was appropriate for the reduction of iron ore-coal composite pellets in the experimental conditions, and particle size  $75 \sim 106 \mu m$  and  $150 \sim 180 \mu m$  were insufficient to complete the reduction. With the increase of particle size, the activation energy increased from 53.04 k J/mol to 131.72 k J/mol. Particle size  $25 \sim 48 \mu m$  had the faster reduction which may be ascribed to more developed surface.

**Keywords:** Kinetics analysis, Direction reduction, Reduction characteristics, Particle size, Iron ore-coal composite pellets.

### INTRODUCTION

Iron and steel making are two of the largest energy intensive industries with the highest growth rate in energy consumption of all energy utilisation sectors. Traditional iron making techniques reduce iron ores to metallic iron in blast furnaces [1]. In some countries, the traditional blast furnace has been partially replaced by direct reduced iron [2]. A principal advantage of the direct reduction relies on the fact that DRI does not require high temperature burden preparations such as coke making and sintering [3,4]. Both coke making and sintering, being at the front end of the conventional blast furnace iron making technology, are considered as costly for the new process construction and are consistently causing environmental concerns. It is therefore necessary to have an insight into the reduction characteristics and fundamental mechanisms for these complex reactions [5,6]. The reduction of iron oxide is a gas-solid reaction, which has been extensively studied in the process conditions test, energy saving and reducing consumption [7-11]. The knowledge about the reduction characteristics and fundamental mechanisms is investigated from several aspects. Rao [12] investigated the reduction kinetics of a mixture of hematite and carbon powders in the temperature range of  $850 \sim 1087^{\circ}$ C, and the isothermal weight loss of the samples was determined as a function of time. Precipitated iron oxide samples were characterized using temperature-programmed reduction in H<sub>2</sub> [13]. The reductive degree and rate of Bama ilmenite concentrate by graphite under argon atmosphere were measured by using thermogravimetric analysis system at the temperatures from 850 to 1400°C [14]. Pineau et al. [15,16] discussed the reduction of Fe<sub>2</sub>O<sub>3</sub> by H<sub>2</sub> in the temperature range of  $220 \sim 680^{\circ}$ C and the reduction of Fe<sub>3</sub>O<sub>4</sub> by H<sub>2</sub> in the temperature range of  $210 \sim 950^{\circ}$ C. Ding et al. [17] applied thermogravimetry to estimate the kinetics of isothermal reduction of the carbon bearing pellets in the temperature range of  $1000 \sim 1400^{\circ}$ C. The reduction roasting of chromite overburden with  $CO/CO_2/N_2$  gas mixture in the temperature range of 700 $\sim$ 750°C has been studied [18]. The reduction kinetics of Fe<sub>2</sub>O<sub>3</sub>

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to FeO in the presence of syngas constituents was investigated based on the thermogravimetric data [19]. Luo et al. [20] presented a novel iron making technology using biomass and iron oxide. The effects of briquettes composition, reduction temperature, reaction time and reducing gas composition on the quality of metallic iron were discussed. Weiss et al. [21]investigated the reduction kinetics of iron ore fines under fluidised bed conditions with hydrogen-rich gas mixtures in the temperature range of  $400 \sim 700$  °C, and the influence of both temperature and reducing gas composition on the reaction rate was considered. Halder et al. [9,22,23] examined the rates and shrinkage of Iron-Oxide-Carbon Composites. The fundamental reactions occurring during the heat treatment of cold bonded pellets (CBP) comprised of iron and steelmaking by-products have been studied [24]. However, the effect of particle size on reduction behavior has been studied little.

Due to the importance of iron making in the current and future technologies, the reduction of iron ore-coal composite pellets is probably one of the most studying topics. The objective of the present investigation is to study the reduction characteristics of iron ore-coal composite pellets. For this purpose the thermogravimetry methods are applied to estimate the reduction kinetics of iron ore with different particle sizes and the heated residues are identified by X-ray diffraction.

#### **EXPERIMENTAL SECTION**

#### 2.1. Materials

The iron ore from Qian`an, Hebei used in the study contained 64.5% Fetotal, 10.57% FeO, 6.35% SiO<sub>2</sub>, 0.25% CaO, 1.02% Al<sub>2</sub>O<sub>3</sub>, 0.09% MgO and 0.03% S. The particle size distribution were  $25 \sim 48 \mu m$ ,  $75 \sim 106 \mu m$  and  $150 \sim 180 \mu m$ , and the average size were  $38 \mu m$ ,  $90 \mu m$ ,  $163 \mu m$ , respectively. The reductant selected for this analysis was bituminous coal supplied from Datong. The main constituents of this bituminous coal were 13.01% ash, 12.51% volatile matter and 74.8% fixed carbon. The particle size of coal ranged from 74 to  $147 \mu m$ , and the average size was  $109 \mu m$ . The coal was devolatilized at  $600^{\circ}$ C for an hour in nitrogen before mixed. There was no any further weight loss when the material was treated at  $900^{\circ}$ C, which indicated that most of the volatile matter was removed.

#### 2.2. Experimental

The sample was mixed to obtain mole ratio of fixed carbon  $C_{Fix}$  against oxygen  $O_{TFe}$  in iron ore particles of 1.0, enabling a complete reduction reaction. The iron ore/carbon mixtures were homogenized by mixing in a laboratory size rotating bowl mixer for 10 minutes. Pellets were made of 1% bentonite binder and iron ore/carbon mixtures in a disc pelletizer(diameter 1000 mm, rim height 300 mm, angle of inclination 45° and rotating 24 rpm) and drying at 110°C for 2 hours to remove moisture before the reduction process. The diameter of pellets in 12~15mm were selected. The kinetics of reduction was investigated by means of the continuous thermogravimetry measurement technique. The thermogravimetric analyzer apparatus was made of a vertical furnace, a quartz glass tube reactor, an electronic balance and a temperature controller. The experiments were carried out in nitrogen atmosphere under the continuous flow of N<sub>2</sub> at 0.51/min. The furnace was heated to the desired temperature. Then the sample was placed in heating zone. All experiments were performed at a linear heating rate of 10°C /min and the experiments were completed when the temperature reached to 1200°C.

The samples dropped off oxygen and carbon along with the reduction. The mass loss of the samples was measured continuously and the mass loss value was then converted into conversion degree using the following formula [25,26]:

$$\alpha = \frac{(W_0 - W_T) \times 16}{oxygen(mass) \times 28} \tag{1}$$

Where  $W_0$  is the initial mass of samples after removal of moisture,  $W_T$  is the mass of samples at temperature T.

The Oxygen (mass) was calculated for the total mass of oxygen presented in every individual mixture in form of  $Fe_2O_3$ ,  $Fe_3O_4$  and FeO.



Fig.1. Reduction process conversion degree versus time in temperature range of 500~1200°C

The conversion degree  $\alpha$  for all temperatures in the range of 500 $\sim$ 1200°C is shown in Fig.1. As the temperature increased, the reduction conversion degree increased for all mixtures. The reduction of samples with particle size of 163µm occurred at approximately 830°C, while the reduction of samples with particle size of 38µm and 90µm began at 600°C and 680°C, respectively. It was found that the change of particle size caused the change of initial reaction temperature and reduction rate. The reduction rate of samples with the average particle size of 38µm was significantly higher than the others. It may be attributed to the differences in specific surface area.



#### **RESULTS AND DISCUSSION**

Fig.2. X-ray diffraction analysis of ore sample and the heated residues (a)iron ore at 20°C, (b) iron ore(150~180μm) at 1200°C, (c) iron ore(75~106μm) at 1200°C, (d) iron ore(25~48μm) at 1200°C.

#### **3.1. XRD characterization of the samples**

In order to reveal the degree of reduction reaction, the heated residues were further researched by X-ray diffraction analysis and compared with the unreacted sample. The X-ray diffractograms of the samples were obtained at a incidence angle of  $10^{\circ} \sim 100^{\circ}$  with a Cu-K $\alpha$  line of 0.15406nm. The phase composition of ore sample and the heated residues are shown in Fig.2. It indicates that the main phases of the iron ore were hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) at 20°C. However, both magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) were detected in the residues. For the iron ore with particle size of 163µm, the reduction by the X-ray diffraction analysis showed the presence of predominantly wustite (FeO) and small amounts of metallic iron. The appearance of wustite (FeO) and metallic iron illustrated that the

reduction process has been improved. Evidently, the selected iron ore with particle size of 163 $\mu$ m was insufficient to complete the reduction. With further decrease of the iron ore particle size to 90 $\mu$ m, the X-ray diffractograms indicated that the intensities of the peak characteristics for metallic iron phases increased highly, whereas the intensities of the peak characteristics for wustite (FeO) was greatly decreased. Based on the principle of phase reduction, the presence of metal iron indicated a high reduction degree. When the iron ore particle size decreased to 38 $\mu$ m, almost the whole reduction of the iron ore achieved at 1200°C. The X-ray diffraction analysis of this mixture showed that metallic iron phase occupied an important position in the residue. This indicated that the iron ore particle size of 38 $\mu$ m was sufficient to complete the reduction.

#### 3.2. Scanning electron microscope (SEM) analysis

In order to reveal morphology characteristics of reduction reaction, the heated residues were crushed and made into samples. Fig.3. shows the scanning electron microscope (SEM) images for both the fresh and the used samples. The microscopic structure of reduced samples obtained from the non-isothermal experiment conducted at 163 $\mu$ m did not reveal any significant alteration due to the slow rate of reduction. In the 90 $\mu$ m sample prepared at 1200°C, it was evident that ore particles were porous system and the structure became relatively loose. The ore particle size in 38 $\mu$ m sample exhibited a developed porous system and some bright area appeared which was confirmed to be metallic iron through the energy spectrum analysis.



Fig.3. Scanning electron microscope analysis of samples (a)iron ore at 20 □, (b) iron ore(150~180µm) at 1200°C, (c) iron ore(75~106µm) at 1200°C, (d) iron ore(25~48µm) at 1200°C.

#### 3.3. Kinetic analysis

Knowledge of the kinetic behavior is essential to understand and predict the reduction processes. In order to estimate the reaction process, the activation energies and pre-exponential factors were tested based on the conversion degree. The common equation is usually expressed as a function of Arrhenius parameters with reaction model under non-isothermal conditions:

$$\beta \frac{d\alpha}{dT} = A e^{-E/RT} f(\alpha)$$
<sup>(2)</sup>

Where T is the temperature,  $\alpha$  is the fraction reacted till temperature T,  $\beta$  is the heating rate, A is the pre-exponential or frequency fact, E is the activation energy, R is the gas constant and f( $\alpha$ ) is the reaction model function. The patterns  $d\alpha/dT$  versus T can be calculated by integration as follow:

$$\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\beta} \int_{T_{0}}^{T} \exp\left(-\frac{E}{RT}\right) dT$$
(3)

Where  $T_0$  is the initial temperature of reduction reaction, the activation energy has been defined as the energy barrier, and the pre-exponential factor describes the frequency of occurrence of the reaction situation. The initial temperature of reduction reaction was considered low, and the reaction rate was negligible. Integration can be calculated between  $0 \sim \alpha$  and  $0 \sim T$ , the equation is expressed as:

$$\int_{0}^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\beta} \int_{0}^{T} \exp\left(-\frac{E}{RT}\right) dT$$
(4)

The right-hand side of the equation has no exact integral. A simplified mathematical form of the reaction kinetics by Coats-Redfern can be described as:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$
(5)

At a fixed conversion degree, the temperature is moderate and the value of E is great,  $\ln[AR/\beta E(1-2RT/E)]$  can be considered as constant. Plotting the left-hand side versus 1/T leads to a temperature-programmed Arrhenius plot, in which the slope is equal to -E/R and  $\ln[AR/\beta E(1-2RT/E)]$  may be calculated from the intercept with vertical axis of the plot of  $\ln[G(\alpha)]$  against 1/T.

The reduction of iron oxide is a gas-solid reaction, and the reduction process may be controlled by the following link: (1) carbon gasification reaction; (2) three-dimensional diffusion; (3) interfacial reaction. The models deduced from the sphere shrink model or the formation and growth of nuclei mode were listed in table 1.

Table 1. Models selection for gas-solid reaction

No.	Kinetics process controlling	Equation G(α)
1	First order formation and growth (carbon gasification)	$-\ln(1-\alpha)$
2	Three-dimensional diffusion	$\left[1-(1-\alpha)^{1/3}\right]^2$
3	Three-dimensional interfacial reaction	$1 - (1 - \alpha)^{1/3}$

Applying the regression method, the values of conversion  $\alpha$  were calculated. The root mean square deviation (RMSD) was employed for comparison of the calculated results and experimental data. The following equation was applied [19]:

$$RMSD = \sqrt{\frac{\sum (\alpha_{calc} - \alpha_{exp})^2}{n-1}}$$
(6)

Where  $\alpha_{calc}$  is the calculated result,  $\alpha_{exp}$  is the experimental data, and n is the number of experimental data points. The calculated results are detailed in table 2.

Model	Particle size (µm)	Temperature range T(°C)	Correlation coefficient R	RMS
	•			D
First order formation and growth (carbon gasification)	$150 \sim 180$	830~1200	0.991	0.0085
	75~106	680~1200	0.992	0.0268
	$25 \sim 48$	$600 \sim 1200$	0.984	0.0367
Three-dimensional diffusion	$150 \sim 180$	830~1200	0.992	0.0061
	75~106	680~1200	0.995	0.0235
	$25{\sim}48$	600~1200	0.994	0.0257
Three-dimensional interfacial reaction	$150 \sim 180$	830~1200	0.993	0.0056
	75~106	680~1200	0.995	0.0218
	$25{\sim}48$	$600 \sim 1200$	0.995	0.0235

Table 2. the calculated results of reduction process

Upon comparing RMSD values, it can be concluded that the three-dimensional interfacial reaction model is best suited to the experimental data. The plot of  $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$  against 1/T are presented in Fig.3, which exhibit linear plots

well. The calculated activation energies and pre-exponential factors for the three particle size ranges of iron ore reduction are detailed in Table 3.



Fig.3. The relation between  $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$  and 1/T for reduction composed of different mixtures

Table 3. Kinetic parameters of detected particle size ranges of iron ore reduction

Particle size (µm)	$150 \sim 180$	$75 \sim 106$	$25 \sim \!$
Activation energy E(kJ/mol)	131.72	71.07	53.04
Frequency factor A(s <sup>-1</sup> )	13.57	7.79E-0	2.17 E-02
		2	

The reduction rate increased obviously as the temperature raised and the particle size decreased. The reaction activation energy increased from 53.04 kJ/mol to 131.72 kJ/mol when the particle size of iron ore increased from  $38 \mu \text{m}$  to  $163 \mu \text{m}$ . The increase of activation energy means the decrease of reacting moles which lead to the decrease of adsorption rate. Also increasing activation energy means that the mass diffusion and chemical reaction become more difficult.

The reduction of iron ore-coal composite pellets in the temperature range of  $500 \sim 1200^{\circ}$ C was studied using thermogravimetry method. Three kinds of iron ore with different particle sizes ( $25 \sim 48 \mu$ m,  $75 \sim 106 \mu$ m, and  $150 \sim 180 \mu$ m) were investigated. The following conclusions are drawn:

(1) X-ray diffraction analysis and thermogravimetric experiments show that, the particle size of  $38\mu m$  is appropriate for the reduction of iron ore-coal composite pellets in the experimental conditions. When the coal was mixed with iron ore in the particle size of  $163\mu m$ , it was reduced to predominantly wustite (FeO), with small amounts of metallic iron presenting in the residue. For iron ore with the particle size of  $90\mu m$ , the residue was mainly composed of wustite (FeO) and metallic iron. As to the iron ore with the particle size of  $38\mu m$ , the residue was predominantly composed of metallic iron.

(2) The three-dimensional interfacial reaction model enabled a satisfactory fit to the experimental data. The kinetics of the reduction of iron ore-coal composite pellets indicated that there were considerable variation of kinetics parameters E and A with the change of particle size. The reaction activation energy increased from 53.04kJ/mol to 131.72kJ/mol when the particle size of iron ore increased from  $38\mu$ m to  $163\mu$ m. The initial reaction temperature increased from  $600^{\circ}$ C to  $830^{\circ}$ C. The kinetic parameters reflected the faster reduction of iron ore with the particle size of  $38\mu$ m compared to the other two, which may ascribe to more developed surface.

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