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Mechanism of effective iron extraction from rare earth-bearing iron ores by low-temperature suspension reduction method

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Abstract: Bayan Obo iron ore is a rare complex deposit in the world. An isothermal kinetic study of the mineral phase transformation process of hematite in suspension to magnetite in Bayan Obo iron ore was carried out. It was calculated that in the reduction process of the H₂ atmosphere, E_{α} was 99.87 kJ/mol and lnA was 13.07 min⁻¹. In the reduction process of CO atmosphere, E_{α} was 37.06 kJ/mol and lnA was 3.40 min-1. The reduction paths of Bayan Obo hematite under different reducing atmospheres are not the same: (1) H₂: hematite-magnetite-iron; (2) CO: hematite-magnetite-wüstite-iron. Under a CO atmosphere, the magnetic properties of the wüstite produced by the over-reduction of hematite were too weak, which seriously jeopardizes the magnetism of the reduced products. The pore structure was enlarged during the reduction of hematite, which greatly reduced the internal diffusion resistance of the reaction and accelerated the reaction rate.

Keywords: suspension magnetization roasting, hematite, kinetic, phase transformation, microstructure evolution

1. Introduction

Bayan Obo ore deposit is a rare complex deposit in the world (Cheng et al., 2024; Ning et al., 2024; Liu et al., 2020), with the following remarkable features: (1) The composition of elements and minerals in the ore are complex. 71 kinds of elements and 172 kinds of minerals have been found in Bayan Obo ore, among which 26 kinds of elements can be comprehensively utilized. (2) The ore grade is low. Its total iron grade is about 30%, rare earth content is about 6%. (3) The crystallization size of each useful mineral in the ore is fine. (4) The mineral composition in the ore is highly variable, and the ore structure and tectonics are complex. Magnetization roasting technology is one of the effective methods for processing complex and difficult iron ore resources (Zhou et al., 2024, Ding et al., 2025; Yu et al., 2020). Microwave roasting technology, characterized by selective heating, and fluidization roasting technology, noted for their high heat transfer efficiency, had demonstrated benefits over vertical furnace roasting and rotary kiln roasting in the effective development of complex iron ore deposits (Samouhos et al., 2013; Rath et al., 2016).

With the awakening of environmental protection consciousness in various countries, low-carbon development has become the main theme of development in today's world. For the efficient utilization of iron ore resources, green, low-carbon and clean technology and theoretical research have become an important future development direction in the field of iron ore resource processing. For the reduction behavior, mechanism and kinetics of hematite, researchers have also carried out extensive research under various experimental conditions. Du et al. (2022) systematically investigated the relationship between the particle size of iron ore and the behavior of the hydrogen reduction reaction by using a fluidized bed in the temperature range of 600-800 °C. The results showed that the increase of reduction temperature can significantly enhance the reduction rate of iron ore; the increase of particle size can increase the number of fluidization and the temperature of loss of flow. Mao et al. (2022) studied the

reduction kinetics of hematite using thermogravimetric reduction in the temperature range of 650-1100 °C. They found that with the increase of the H₂ content from 20% to 100%, the control step of the reaction was gradually changed from the combined control of gas diffusion and interfacial reaction to the control of a single interfacial reaction. Lu et al. (2022) investigated the reduction mechanism of hematite reduced by H₂-CO mixture in the temperature range of 750-900 °C with the help of a miniature rotary electric furnace reactor. They found that the reduction process of this hematite was controlled by the combined control of diffusion and interfacial reaction; the pore space and the cracks of the particles widened with the increase of reaction time. Zuo et al. (2015) also obtained a similar conclusion that the higher the H₂ content, the greater the increase of reaction rate with the increase of temperature. Chernavsky and Pankina (2022) investigated the effect of magnetic field on the H₂ reduction process of hematite, and found that the increase of the magnetic field intensity significantly accelerated the rate of the reduction within the range of 300-500 °C.

Many researchers tried to establish a generalized kinetic model for hematite reduction, but the reduction process of hematite is elusive, containing multi-step reactions with multiple processes such as $Fe_2O_3 \rightarrow Fe_3O_4$, $Fe_3O_4 \rightarrow FeO$, $Fe_2O_3 \rightarrow FeO$, $FeO \rightarrow Fe$, and $Fe_3O_4 \rightarrow Fe$, etc. The apparent activation energies of the reduction reactions are affected by the range of the reduction temperatures, the reduction atmospheres, the hematite particle size and shape, sample impurities and test methods (Qu et al., 2019; Lyu et al., 2022; Hammam et al., 2021; Heidari et al., 2021). The values of apparent activation energy for the reaction kinetics of the magnetization roasting process ($Fe_2O_3 \rightarrow Fe_3O_4$) of hematite derived from the study varied in a wide range from 14.16 to 120 kJ mol-1 (Manchili et al., 2020; He et al., 2021; Hou et al., 2012; Tang et al., 2022; Zhao et al., 2020; Zhou et al., 2023; Gaob et al., 2020; Yuan et al., 2022; Yu et al., 2019; Chen et al., 2014; Dilmac 2021; Ponomar et al., 2019; Zhu et al., 2023; Wang et al., 2017). Currently, the research work on the suspension magnetization roasting of iron ore focused on the carbon-based reduction process, and there was a lack of systematic basic research on the aspect of the hydrogen-based mineral phase transformation process. In the reduction process, due to the difference in the reduction behavior of H₂ and CO gases, the use of H₂ instead of CO as a reductant would change the degree and rate of the reaction between the reductant and iron ore in the reactor, which will have a great influence on the reduction process and the control mechanism. Therefore, this study focused on the reduction kinetics as well as the differences in reduction behavior during the transformation of complex polymetallic iron ores in suspension state mineral phase. This study is the first to explicitly compare the applicability of three-dimensional diffusion model of H₂ and CO under suspension roasting compared to existing studies, and the first to reveal the negative effect of weakly magnetic wüstite in CO reduction products.

2. Materials and methods

2.1. Materials

The Bayan Obo hematite ore samples were obtained from the mining site in Inner Mongolia, China. The samples were first hand-sorted to select hematite-rich clasts. It was finely crushed to less than 1 mm by a high-pressure roller mill. Then the process of grinding-weak magnetic separation-strong magnetic separation-heavy separation was carried out to get the purified Bayan Obo hematite. The content of - 0.074 mm grain size in the Bayan Obo hematite is 89.38%.

The chemical composition, iron physical phase and XRD analyses of Bayan Obo hematite were carried out, and the results were shown in Table 1, Table 2 and Fig. 1. From the results, it can be seen that the TFe content of hematite raw material is 63.14% and FeO content is 0.12%. The main impurities

	TFe	FeO	REO	CaO	MgO
Content	63.14	0.12	1.20	3.70	0.22
	Р	SiO2	Na	LOI*	Al_2O_3
Content	0.32	0.27	0.20	0.51	0.20

Table 1. Chemical composition analysis of hematite sample (mass%)

* LOI: loss on ignition at 1000 °C

Iron	Fe in	Fe in	Fe in	Fe in	Fe in	Total
Phase	Magnetite	Siderite	Hematite/Limonite	Pyrite	Silicate	Total
Content	4.31	0.07	57.95	0.59	0.22	63.14
Percentage	6.83	0.11	91.78	0.93	0.35	100.00

Table 2. Iron phase analysis of hematite sample (mass%)



Fig. 1. XRD patterns of Bayan Obo hematite

CaO and REO content is 3.70% and 1.20%, other impurities Al₂O₃, MgO, SiO₂, Na content is less, the content of harmful element P is 0.32%, and the raw material loss on ignition (LOI) is 0.51%. The iron in the raw material is mainly endowed in hematite iron ore, and its iron distribution rate is as high as 91.78%. Combined with the XRD analysis results, it can be seen that the main mineral in the raw material is hematite, in addition to a small amount of moganite (SiO2), fluorite and rare earth. In summary, the purity of this hematite raw material is high, with the typical characteristics of bainite iron ore, which can meet the test requirements.

H₂ (99.99%), CO (99.99%) and N₂ (99.99%) from Shenyang, Liaoning Province, China were utilized for reducing and fluidizing purposes in the roasting process.

2.2. Methods and equipment

2.2.1. Experimental apparatus and procedure

The suspension reduction was carried out in a self-designed fluidized calcination system, and the system was shown in Fig. 2. The system mainly consists of a gas mixing device, a suspension roasting device and a temperature control device (accuracy $\pm 1^{\circ}$ C). In each experiment, a 10 g sample was positioned on a porous quartz plate within a quartz furnace tube, and 480 mL/min of N₂ was introduced to maintain the sample in an optimal fluidized condition. When the furnace temperature reached a predetermined temperature, the quartz furnace tube was placed into the suspension roasting device to preheat for 10 min (so that the temperature of the sample was consistent with the furnace temperature). A gas mixture of 120 mL/min CO (or H₂) and 480 mL/min N₂ was introduced to start the hematite mineral phase transformation. When the transformation was completed, the tube was taken out and the reduction products were cooled down under nitrogen to obtain the reduction products. The tail gas was discharged to the tail gas treatment unit through the outlet at the top of the furnace tube.

2.2.2. Data analysis

By analyzing the FeO and TFe content of the reduction products, the conversion degree and reaction rate of hematite to magnetite can be determined. Equation (1) and (2) represents the chemical reaction of hematite with CO/H_2 and the formation of magnetite.

$$3Fe_2O_3 + CO(g) = 2Fe_3O_4 + CO_2(g)$$
(1)

$$3Fe_2O_3 + H_2(g) = 2Fe_3O_4 + H_2O(g)$$
(2)



Fig. 2. Schematic diagram of the mineral phase conversion system in suspended state

The reaction progress of hematite during reduction roasting is expressed as the conversion of Fe_2O_3 to Fe_3O_4 . The reaction fraction at any reduction time during the reaction process can be calculated according to the equation (3).

$$\alpha = \frac{f}{f_m} \frac{\omega(FeO)}{\omega(TFe)} \cdot \frac{1}{f_m} \cdot 100\%$$
(3)

where *a* is the degree of hematite to magnetite transformation (%); *f* is the reduction product magnetic rate (%); f_m is the theoretical magnetic rate, i.e., when all the hematite in the iron ore is reduced to magnetite (*a* = 100.00%) reduction product magnetic rate, f_m is 42.86%; ω (FeO) is the mass fraction of FeO in the reduced product (%); ω (TFe) is the mass fraction of all iron in the reduced product (%).

From the chemical composition analysis and iron phase analysis, it can be seen that the hematite sample contains a small amount of magnetite (ω (FeO) = 0.12%, ω (TFe) = 63.14%). So, the magnetic rate at reduction time *t* of 0 s can be expressed as:

$$f_0 = \frac{\omega(FeO)}{\omega(FFe)} \cdot 100\% = \frac{0.49}{66.00} \cdot 100\% = 0.74\%$$
(4)

The reaction fraction of the reduced product at time t can be expressed as:

$$\alpha_t = \frac{f_t - f_0}{f_m - f_0} = \frac{f_t - 0.74}{42.86 - 0.74} = \frac{1}{42.12} \cdot \left(\frac{\omega(FeO)_{(t)}}{\omega(TFe)_{(t)}} - 0.74\right)$$
(5)

2.2.3. Kinetic analysis

The experiments were conducted isothermally by heating the material to a specific temperature in the range of 425-525 °C. The kinetic equation for a homogeneous or inhomogeneous chemical reaction under isothermal conditions can be expressed as equation (6).

$$v = \frac{d\alpha}{dt} = k(T)f(\alpha) \tag{6}$$

where v is the reaction rate (min⁻¹); f(a) is the differential form of the reaction mechanism function; t is the reaction time (min); k(T) is the reaction rate constant; T is the thermodynamic temperature (°C). By arranging the integrals of the equation (6), the equation (7) can be obtained.

$$F(\alpha) \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = \int_0^t k(T) dt = k(T)t$$
(7)

where F(a) is the integral form of the reaction mechanism function f(a).

From equation (7), F(a) has a linear correlation with the reduction time t. The f(a) associated with the F(a) exhibiting the strongest linear correlation (R^2) is the ideal mechanism function, while the response rate constant k is the slope of the regression equation linked to this optimal mechanism function. The function model of gas-solid reaction is shown in Table 3. The reaction rate constant can be characterized by the Arrhenius equation, as shown in equation (8).

model	symbol	formula of <i>f</i> (<i>a</i>)	formula of <i>F</i> (<i>a</i>)
nucleation and nuclei growth	A1	1- а	$-\ln(1-a)$
	A2	$2(1-a)[-\ln(1-a)]^{1/2}$	$[-\ln(1-a)]^{1/2}$
	A3	$3(1-a)[-\ln(1-a)]^{2/3}$	$[-\ln(1-a)]^{1/3}$
	A4	$4(1-a)[-\ln(1-a)]^{3/4}$	$[-\ln(1-a)]^{1/4}$
phase boundary	R1	1	а
	R2	$2(1-a)^{1/2}$	$1 - (1 - a)^{1/2}$
	R3	$3(1-a)^{2/3}$	$1 - (1 - a)^{1/3}$
	R4	$4(1-a)^{3/4}$	$1 - (1 - a)^{1/4}$
diffusion	D1	1/2a ⁻¹	a ²
	D2	$[-\ln(1-a)]^{-1}$	$a + (1 - a)\ln(1 - a)$
	D3	$(1-a)^{1/2}[1-(1-a)^{1/2}]^{-1}$	$[1 - (1 - a)^{1/2}]^2$
	D4	$3/2(1+a)^{2/3}[(1+a)^{1/3}-1]^{-1}$	$[(1 + a)^{1/3} - 1]^2$
	D5	$3/2(1-a)^{4/3}[(1-a)^{-1/3}-1]^{-1}$	$[(1-a)^{-1/3}-1]^2$
	D6	$3/2(1-a)^{2/3}[1-(1-a)^{1/3}]^{-1}$	$[1 - (1 - a)^{1/3}]^2$
	D7	$6(1-a)^{2/3}[1-(1-a)^{1/3}]^{1/2}$	$[1 - (1 - a)^{1/3}]^{1/2}$
	D8	$3/2[(1-a)]^{-1/3}-1]^{-1}$	$1 - 2/3a - (1 - a)^{2/3}$
power-law model	P4	4 <i>a</i> ^{3/4}	a ^{1/4}
	P3	3a ^{2/3}	a ^{1/3}
	P2	$2a^{1/2}$	a ^{1/2}
	P1	1	а
chemical reaction order-based	F1	$(1-a)^2$	$(1-a)^{-1}-1$
	F2	$2(1-a)^{3/2}$	$(1-a)^{-1/2}$
	F3	$1/2(1-a)^3$	$(1-a)^{-2}$

Table 3. Differential and integral expressions of common reaction mechanism functions

$$k(T) = Ae^{\left(-\frac{E_a}{RT}\right)} \tag{8}$$

In equation (8), *A* is the preexponential factor (min⁻¹); E_a is the apparent activation energy of the reaction(J mol⁻¹.°C⁻¹); *R* is the ideal gas constant (8.314). Taking logarithms on both sides of equation (8) simultaneously gives equation (9).

$$lnk(T) = lnA - \frac{E_a}{R} \cdot \frac{1}{T}$$
(9)

2.2.4. Characterization methods

In this study, the DIFF function of Mathematics mathematical operations module of OriginPro 2021 software was used to obtain the reaction rate by first-order derivation of the reaction fraction versus reaction time curve. The total iron (TFe) and FeO contents in the study were determined by chemical elemental analysis, while the contents of other elements were determined by inductively coupled plasma (ICP) emission spectroscopy. XRD (Smartlab, Japan) was used to analyze the physical phase, and the working parameters were: Cu target radiation, $\lambda = 0.1541$ nm, scanning range of 5~90°, 40 kV, 40 mA, a scanning speed of 8 °/min, working temperature 25 °C. The XRD data were analyzed using X'Pert HighScore Plus software. A Vibrating Sample Magnetometer (JDAW-2000D, China) was used to analyze the magnetic properties. The samples were analyzed by nitrogen adsorption-desorption using a specific surface area and porosity analyzer (BET, model ASAP2460, USA). An Apreo 2C scanning electron microscope manufactured by Thermo Fisher USA was used to analyze the micro-morphology and micro-zone composition of the samples.

3. Results and discussion

3.1. Conversion degree

The fluctuation of reaction fraction with roasting duration in the reduction of hematite by H_2 or CO was assessed at reduction temperatures of 425 °C, 450 °C, 475 °C, 500 °C, and 525 °C, respectively. As can be seen from Fig. 3, under H_2 or CO atmosphere, both reduction temperature and reduction time had significant effects on the reaction fraction. Under the condition of the same reaction time, the reaction fraction increased with the increase of reduction temperature, and the longer the reaction time, the more obvious the trend of increasing reaction fraction. Under the condition that H_2 was the reducing agent and the reduction time was 10 minutes, when the reduction temperature is increased from 450 °C to 500 °C, the reaction fraction increased from 0.46 to 0.94, and the value added was 0.48. Fig. 3(b) showed a similar trend in the reaction fraction curves for the CO reduction products compared to the H_2 reduction. The reaction fractions of the H_2 reduction products were consistently lower than those of the CO reduction products under identical reaction circumstances.



Fig. 3 Variation of reaction fractions with roasting time under different reducing atmospheres. (a): H₂, (b): CO

3.2. Determination of the kinetic model

The R^2 of the commonly used kinetic mechanism functions for different conditions were calculated according to the methodology described in Section 2.2.3, as shown in Fig. 4. Fig. 4 showed that the R^2 of various mechanism functions varies widely. Among them, the correlation coefficient of D8 model was higher than the other models. Therefore, the best generalized mechanistic function for the isothermal kinetics of mineral phase transformation under a single gas component (H₂ or CO) of Bayan Obo hematite was the three-dimensional diffusion model D8:

$$f(\alpha) = \frac{3}{2} \left[(1 - \alpha)^{-1/3} - 1 \right]^{-1}$$
(10)

$$f(\alpha) = 1 - \frac{2}{2}\alpha - (1 - \alpha)^{2/3}$$
(11)

The values of the reaction rate constant k (slope of the fitted line) for various reduction temperatures were derived by fitting the F(a) to the t at various reduction temperatures. Fig. 5 presented the outcomes of the linear regression analysis of the D8 model F(a) in relation to the t. The corresponding values of the reaction rate constant k and the linear correlation coefficients, as well as the calculated $\ln k$ and 1/T are shown in Table 4.

Table 4. Reaction rate constants of kinetic mechanism function

			H_2					СО		
T (°C)	425	450	475	500	525	425	450	475	500	525
k(T) (min ⁻¹)	0.0098	0.0344	0.0568	0.0900	0.0970	0.0424	0.0745	0.0896	0.0965	0.1056
R^2	0.9780	0.9968	0.9972	0.9949	0.9944	0.9783	0.9800	0.9951	0.9982	0.9985

From Fig. 5 (a) and Table 4, the average value of R^2 between the D8 model F(a) and the roasting time t at different reduction temperatures under the H₂ reduction system reached 0.9901. It indicated that the fitting results had a high degree of confidence. From Fig. 5 (b) and Table 4, the average value of the R^2 between the D8 model F(a) and the roasting time t at different reduction temperatures under the CO reduction system reached 0.9921. It indicated that the fitting results had high confidence. In kinetic models for the reduction of hematite by H₂ or CO, k(T) had a positive correlation with the reduction temperature. In either H₂ or CO reduction systems, increasing the reduction temperature helped to increase the reaction rate of the mineral phase transformation process. The reaction rate constants k at different temperatures from Table 4 were brought into Eq. (9). The linear regression was fitted to lnk and 1/T. The results were shown in Fig. 6. From the fitting results, it can be seen that: under the H₂ reduction system, the D8 model mechanism function refers to a preexponential factor lnA of 13.07 min⁻¹ and an apparent activation energy of 99.87 kJ/mol; under the CO reduction system, the D8 model mechanism function refers to a preexponential factor lnA of 3.40 min⁻¹ and an apparent activation energy E_a of 37.06 kJ/mol.



Fig. 4 Correlation coefficients calculated using common reaction mechanism functions. (a): H₂, (b): CO



Fig. 5 Linear fitting between function F(a) of D8 model and t at different temperatures. (a): H₂, (b): CO



Fig. 6 Linear fitting of $\ln k$ (*T*) and 1/T. (a): H₂, (b): CO

3.3. Phase transition

The XRD patterns of Bayan Obo hematite reduction products under different reduction conditions were shown in Fig. 7. Under different reduction conditions, the composition of the product's physical phase showed a similar pattern of change, and the XRD pattern of the reduced product showed a total of five diffraction peaks of hematite, magnetite, wüstite, iron and fluorite phases. Fig. 7(a) showed that the relative intensity of the hematite diffraction peak decreased continuously while magnetite diffraction peaks enhanced continuously when the reduction temperature was increased from 425 °C to 525 °C under the condition of H_2 as the reducing agent and 9 min reduction time. When the reduction temperature was increased to 550 °C, hematite diffraction peaks disappeared in the reduced product. Simultaneously, faint diffraction peaks of iron and wüstite emerged, signifying the full transformation of hematite into magnetite., and some of the magnetite was further over-reduced to wüstite and iron. Figure 4(c) showed that the relative intensity of hematite diffraction peaks decreased while magnetite diffraction peaks increased when the reduction temperature increased from 425 °C to 500 °C under the condition of CO as the reducing agent and 9 min reduction time. When the reduction temperature was increased to 525 °C, a wüstite diffraction peak appeared, indicating that hematite had been completely converted to magnetite, and some of the magnetite was further over-reduced to wüstite. As the temperature increased, the CO reduction products were more likely to be over-reduced at lower temperatures, and the CO over-reduced products were only weakly magnetic wüstite. The H₂ reduction products required higher temperatures for over-reduction, and the over-reduced products were wüstite and iron.

As can be seen in Fig. 4(b), with H_2 as the reducing agent and the reduction temperature of 500 °C, with the extension of the reduction time, the intensity of hematite diffraction peaks was obviously weakened, and magnetite diffraction peaks enhanced, indicating that the hematite in the samples was reduced to magnetite. When the reduction time reached 11 min, diffraction peaks of iron appeared,



Fig. 7. XRD patterns of reduction products, (a) H₂ reduction products at different reduction temperatures, (b)H₂ reduction products at different reduction time, (c) CO reduction products at different reduction temperatures, (d)CO reduction products at different reduction time

indicating that the magnetite began to be over-reduced to iron. Fig. 4(d) illustrated the use of CO as the reducing agent at a reduction temperature of 500 °C. With the extension of the reduction time, the intensity of hematite diffraction peaks decreased significantly, and magnetite diffraction peaks enhanced, indicating that the hematite in the samples was reduced to magnetite. When the reduction time reached 11 min, diffraction peaks of iron and wüstite appeared simultaneously, indicating that magnetite began to be over-reduced to iron and wüstite. The main products of the reaction of hematite with reducing gases are magnetite, wüstite and iron, and different reduction products are produced under different reduction conditions. With the extension of the reduction time, the CO over-reduced product had weakly magnetic wüstite and iron, while the H_2 over-reduced product had only iron. Therefore, the reduction paths of Bayan Obo hematite under different reducing atmospheres are not the same: (1) H_2 : hematite- iron; (2) CO: hematite- magnetite- wüstite- iron.

3.4. Magnetic transition

Previous studies showed that the suspension roasting led to the conversion of hematite to magnetite. Since magnetite is ferromagnetic and hematite is only weakly magnetic, suspension roasting significantly changed the magnetic properties of the samples. The magnetic difference is a key indicator to realize the separation of iron from other elements in the ore. The H_2/CO reduction products at different reduction temperatures and reduction time were analyzed by Vibrating Sample Magnetometer (VSM), and the results were shown in Fig. 6. From Fig. 6 (a), (b), (d) and (e), it can be seen that at different reduction temperatures and reduction time, the magnetization intensity of the reduced products showed a trend of rapid increase followed by gradual flattening with the increase of the external magnetic field strength. The magnetization intensity of the reduced products all tended to be saturated

at the external magnetic field strength of 12000 Oe. Figure 5(c) and (f) showed that in the temperature range of 425~600 °C and the reduction time of 1~15 min, with the increase of the reduction temperature and reduction time, the saturation magnetization intensity curves of H₂ and CO reduction products showed a gradual growth trend. When the reduction temperature was lower than 500 °C or the reduction time is lower than 5 min, the saturation magnetization intensity of H₂ reduction products was lower than that of CO reduction products. When the reduction temperature was higher than 500 °C or the reduction time was more than 5 min, the saturation magnetization intensity of H₂ reduction products was lower than that of CO reduction products. The above results indicated that increasing the temperature or prolonging the reaction time was conducive to promoting the conversion of weakly magnetic hematite into magnetite. Combined with the results of XRD analysis in section 3.3, it can be seen that with the increase of reduction temperature and reduction time, the phenomenon of overreduction occurred in both H₂ or CO reduction processes. Under CO atmosphere, the magnetic properties of the wüstite produced by the over-reduction of hematite were too weak, which seriously jeopardizes the magnetism of the reduced products. This problem was not found in the case of the H₂ reduction processes.



Fig. 8. VSM analysis of the different samples, (a) H₂ reduction products at different reduction temperatures, (b)
 CO reduction products at different reduction temperatures, (c) Saturation magnetization at different reduction temperatures, (d) H₂ reduction products at different reduction time, (e) CO reduction products at different reduction time, (f) Saturation magnetization at different reduction time

3.5. Microstructure evolution

The microscopic morphology of the surface of H₂/CO-reduced particles was obviously different, and the H₂/CO-reduced products with different reduction time at a reduction temperature of 500 °C were comparatively analyzed. As shown in Fig. 5, when the reduction time was 1 min, the surface morphology of the particles (Fig. 5(a), (b)) did not change significantly. When the reduction time was 3 min, cracks ($<5 \mu$ m) started to appear on the surface of the H₂-reduced particles (Fig. 5(b)). With the further extension of the reaction time, the surface of the particles gradually became rough, and the number and size of cracks increased significantly. As shown in Fig. 5(c) and (d), the structure of the particles was obviously damaged. Similarly, the roughness of the surface of the CO-reduced particles (Figs. e-h) also increased with the reaction time, but the size of the microcracks (5-30 µm) was salient larger than that of H₂-reduced particles. The disruption of the structure of CO-reduced particles was higher compared to H₂-reduced particles. This was because the evolution process of hematite particle structure and morphology was essentially a mineral phase transformation process of hematite in

reduction. Therefore, the rate-limiting step of the reaction was the gas diffusion rate in the pores during the whole reduction process of Bayan Obo hematite, which verified the correctness of the kinetic analysis. Combined with the results of kinetic analysis, it can be seen that the reduction efficiency of CO is higher than that of H₂, which leads to more drastic changes in the structure and morphology of CO-reduced particles.



Fig. 9. SEM images of products at different reduction time, (a) H₂-1min, (b) H₂-3min, (c) H₂-7min, (d) H₂-9min, (e) CO-1min, (f) CO-3min, (g) CO-7min, (h) CO-9min

3.6. Pore characteristics

The mineral phase transformation process of hematite involves a series of physical and chemical changes that are closely related to the internal pore structure of the particles. The pore structure characteristics of H_2 or CO reduced products under different reduction time were analyzed. As can be seen from Fig. 7, the N_2 adsorption-desorption isotherms of the H_2/CO reduced products under different reduction time were similar in character, and all of them are type III isotherms. According to the International Union of Pure and Applied Chemistry (IUPAC) hysteresis loop classification, it can be judged that the hysteresis loops of the reduced products were all of type H3, which indicated that the pore structures of the reduced products were slit structures with parallel walls, cracks and wedges, and the shapes and sizes of these pore channels were non-uniform. As the reduction period was extended, the N_2 terminating adsorption and the hysteresis ring area of the samples progressively increased, signifying an enlargement of the pore size, which peaked at 7 to 9 minutes. The pore structure characteristics of the samples are shown in Table 5. The pore structure parameters of the samples were only 0.5539 m²/g and 0.001634 cm³/g was dense. As the reduction duration was extended, the BET surface area and total pore volume of the H₂/CO reduced products progressively rose. With identical



Fig. 10 N₂ adsorption-desorption isotherm of products under different reduction time. (a) - (d): H₂, 1, 3, 7, 9 min; (e) - (h): CO: 1, 3, 7, 9 min

	Reduction time	BET surface area	total pore volume	BJH average pore diameter
	(min)	(m ² ·g ⁻¹)	(cm ³ ·g ⁻¹)	(nm)
	0	0.5539	0.001634	10.9048
	1	1.2359	0.001555	10.7253
	3	1.4431	0.004239	10.7897
H ₂	7	2.1552	0.006304	10.9481
	9	2.2091	0.006172	10.2498
СО	1	0.9628	0.002564	10.9048
	3	1.8553	0.008412	10.4147
	7	2.2794	0.017239	16.4432
	9	2.5571	0.018216	27.4558

Table 5. Pore structure parameters of products at different reduction time

reduction durations, the BET surface area and total pore volume of the H_2 reduction products were inferior to those of the CO reduction products. The Barret-Joyner-Halenda (BJH) average pore diameter of the H_2 reduction products did not change much, but the BJH average pore diameter of the CO reduction products increased with the extension of the reduction time. The results of pore parameters indicated that the pore structure was enlarged during the reduction of hematite by CO, which greatly reduced the internal diffusion resistance of the reaction and accelerated the reaction rate.

4. Conclusions

In this study, the kinetics of mineral phase transformation at low temperatures in the suspension state of Bayan Obo complex polymetallic iron ore were systematically investigated. The mechanism function for the isothermal kinetics of mineral phase transformation under different reduction systems (H₂ or CO) of Bayan Obo hematite is the three-dimensional diffusion model D8. The apparent activation energy *Ea* was 37.06 kJ mol⁻¹ with a preexponential factor ln*A* of 3.4 min⁻¹ for the H₂ reduction system and 99.87 kJ mol⁻¹ with a preexponential factor ln*A* of 13.07 min⁻¹ for the CO reduction system. Phase transition studies showed that an increase in reduction temperature and reduction time contributed to the phase transition of hematite. H₂-reduced products would only over-reduce to iron, while CO-reduced particles, and the particles changed from a dense massive structure to a loose massive structure with many pores. The porous structure was essential for mass transfer and ensured that H₂/CO passed quickly through the product layer to the reaction interface. The rate-limiting step of the reaction was the gas diffusion rate in the pores. The results provided a feasible and effective method for the separation of complex polymetallic iron ores after low-temperature reduction.

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