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# KINETICS OF DIRECT REDUCTION OF CHROME IRON ORE

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## Abstract

The kinetics of direct reduction of artificial chrome iron ore was studied by isothermal and non-isothermal methods. In the initial, middle and final periods, the reaction is controlled by nucleation and growth, a phase boundary reaction, and diffusion, respectively. In the main reaction region, the kinetic equation is $1-(1-\alpha)^{1/3}=kt$ and the apparent activation energy is 270 kJ $\mathrm{mol}^{-1}$ . The kinetic mechanisms found with the isothermal and non-isothermal methods do not differ, and the activation energy values are approximately the same. However, the non-isothermal method can demonstrate the kinetic process completely.

**Keywords:** chrome iron ore, kinetics, TG

## Introduction

Chromium is one of the most general alloy elements. Study of the direct reduction of chrome iron ore powder for the utilization of chrome iron ore is important as concerns metallurgical technology. The kinetics of direct reduction of chrome iron ore has been studied extensively, but opinions differ. McKewan [1] and Rankin [2] suggested that the mechanism of direct reduction is a phase boundary reaction, Galway [3] considered that the reaction is controlled by nucleation and growth, and Sandelin [4] reported that both a phase boundary reaction and diffusion control the process. The present paper investigates the direct reduction kinetics of chrome iron ore and compares isothermal and non-isothermal kinetic methods. The findings provide a basis for industrial experiments.

## Experimental and methods

### *Isothermal method*

Chrome iron ore powder, graphite and polyacrylonitrile were mixed with water and pelleted to ř8.0×8.5 mm cylinders, which were dried at 150°C for 5 h. These samples were tested via thermogravimetric curves (PE Co., TG7) in an argon flow of 40 ml $\mathrm{min}^{-1}$ at a constant temperature of 1063, 1099, 1125, 1153 or 1185°C. The temperature was corrected with fine copper and nickel wire. The reduction rate $\alpha$ or the fraction reacted at time $t$ was calculated via the following equation:

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$$\alpha = \frac{w_0 - w_t}{Bw_0} \tag{1}$$

where $w_0$ and $w_t$ are the masses of the sample initially and at time $t$, respectively, and $B$ is the highest rate of theoretical mass loss, i.e. the rate of mass loss for complete reduction of the chrome iron oxide. For artificial ore, $B$=0.3753.

According to the law of mass action, the basic kinetic equation can be given by

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{2}$$

or

$$g(\alpha) = \int \frac{\mathrm{d}\alpha}{f(\alpha)} = kt \tag{3}$$

where $k$ is the rate constant of the reaction, and $f(\alpha)$ and $g(\alpha)$ are mathematical functions depending on the reaction mechanism. There are 41 mechanism functions representing chemical reaction, diffusion, nucleation and nuclei growth [5]. The data on $t$ and $\alpha$ from the TG curves at constant temperature were regressed linearly by computer on the basis of Eq. (2) or (3). The function $g(\alpha)$ giving the best linearity is considered the actual kinetic mechanism function. The rate equation of the reduction reaction and the kinetic parameters $k$ and $E$ can be obtained.

### *Non-isothermal method*

The TG and DTG curves were measured in the range 800–1250°C at a heating rate of 10°C $\mathrm{min}^{-1}$ and an argon flow rate of 40 ml $\mathrm{min}^{-1}$. On the basis of these curves, the reaction fraction $\alpha$ and $\mathrm{d}\alpha/\mathrm{d}t$ at time $t$ can be calculated. The kinetic equations for the differential and integral methods are as follows [6, 7]:

$$\ln\left[\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \tag{4}$$

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\Phi E}\right) - \frac{E}{RT} \tag{5}$$

where $\Phi$ is the heating rate, $E$ is the activation energy of reaction, $A$ is the pre-exponential factor, $T$ is the absolute temperature and $R$ is the gas constant.

From Eqs (4) and (5), the kinetic analyses were completed by the linear least-square method based on the 41 mechanism functions. When the values of $E$ and $A$ from the two methods are approximately the same and the linear correlation coefficient is the highest, $f(\alpha)$ and/or $g(\alpha)$ are/is taken as the probable mechanism function of the reaction.

## Results and discussion

### *Isothermal kinetics*

For the artificial chrome iron ore, the curve of reduction rate with time (Fig. 1) demonstrates that the reaction velocities are increased by the elevation of temperature.

The rate constants $k$ were $6.7\cdot10^{-3}$, $1.23\cdot10^{-2}$, $2.02\cdot10^{-2}$, $3.02\cdot10^{-2}$ and $5.30\cdot10^{-2}$ min$^{-1}$ at temperatures of 1063, 1099, 1125, 1153 and 1185°C, respectively. The activation energy is 270 kJ mol$^{-1}$, which is consistent with the data range 230–355 kJ mol$^{-1}$ given in the literature [8].

The rate equation of the reduction reaction is best described as $1-(1-\alpha)^{1/3}=kt$, which represents a phase boundary reaction (Fig. 2). At 1063°C in the final period, the reaction is controlled by three-dimensional diffusion and has a rate constant of

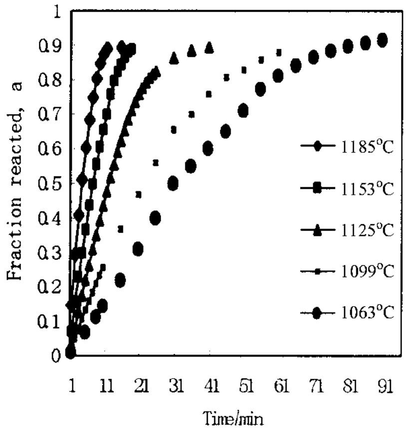

**Fig. 1** Fraction reacted as a function of time at various temperatures

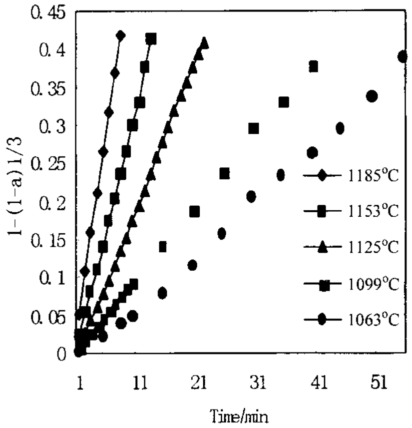

**Fig. 2** Relationship between $1-(1-\alpha)^{1/3}$ and time

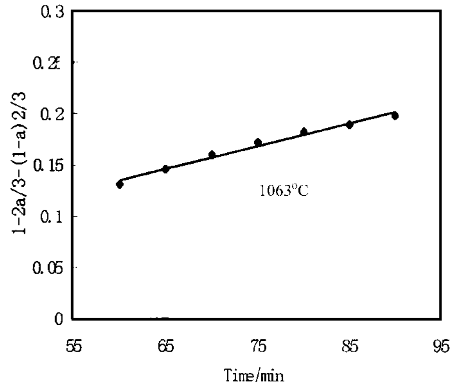

**Fig. 3** Relationship between $1-2\alpha/3-(1-\alpha)^{2/3}$ and time

$1.78\cdot10^{-3}$ min$^{-1}$. The kinetic equation is $1-2\alpha/3-(1-\alpha)^{2/3}=kt$ (Fig. 3). However at temperatures of 1099–1185°C, the diffusion-controlled step was not obvious.

### *Non-isothermal kinetics*

The direct reduction of artificial chrome iron ore occurred between 1010 and 1205°C at a heating rate of 10°C min$^{-1}$. The results of the experiments kinetics of direct reduction are listed in Table 1.

**Table 1** Non-isothermal kinetics of direct reduction

| $\alpha$ | Differential method | | Integral method | |
|---|---|---|---|---|
| | $f(\alpha)$ | $E$/kJ mol$^{-1}$ | $g(\alpha)$ | $E$/kJ mol$^{-1}$ |
| <0.1 | $5/2(1-\alpha)[-\ln(1-\alpha)]^{3/5}$ | 359 | $[-\ln(1-\alpha)]^{2/5}$ | 364 |
| 0.1–0.75 | $3(1-\alpha)^{2/3}$ | 273 | $1-(1-\alpha)^{1/3}$ | 277 |
| >0.75 | $3/2[(1-\alpha)^{-1/3}-1]^{-1}$ | 485 | $1-2\alpha/3-(1-\alpha)^{2/3}$ | 492 |

The data in this Table demonstrate that the kinetic mechanisms found with the differential method and the integral method do not differ, and the activation energies are nearly equal. The direct reduction process involves three steps. In the initial period ($\alpha$<0.1), the kinetic equation is $[-\ln(1-\alpha)]^{2/5}=kt$, which corresponds to the Avrami equation and indicates that this reaction is controlled by nucleation and nuclear growth. The transformation index $n$ is 2.5, which indicates that the nucleation rate does not change with time and the reaction is a three-dimensional nuclear growth process controlled by diffusion. The activation energy is about 362 kJ mol$^{-1}$.

In the middle period ($\alpha$=0.1–0.75), the kinetic equation is $1-(-\alpha)^{1/3}=kt$. The reaction mechanism is a phase boundary reaction, i.e. controlled by the chemical reaction. The activation energy is about 275 kJ mol$^{-1}$, which is consistent with the activation energy determined by the isothermal kinetic method.

In the final period ($\alpha>0.75$), the kinetic equation is $1-2\alpha/3-(1-\alpha)^{2/3}=kt$, which corresponds to a three-dimensional diffusion mechanism and the activation energy is 488 kJ mol$^{-1}$.

### *The kinetic mechanism of direct reduction of artificial chrome iron ore*

The kinetic process of direct reduction of chrome iron ore involves three steps. In the initial period, the reaction is limited by nucleation and growth and is slow. After new phases form, the reaction is controlled by a phase boundary reaction, the activation energy of which is the smallest and the reaction velocity is the highest. In the final period, the product layer thickens and the reaction is controlled by the diffusion of reductive agents in the product layer. The reaction velocity becomes low.

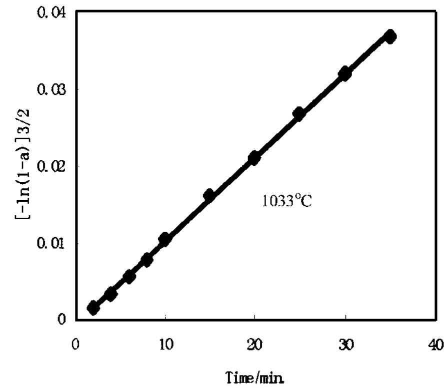

**Fig. 4** Relationship between $[-\ln(1-\alpha)]^{3/2}$ and time

In the middle period, i.e. the main reaction region, the kinetic mechanisms found from the isothermal and non-isothermal methods do not differ, and the values of the activation energy are approximately the same. However, the step of nucleation and nuclear growth at the beginning of the reaction is not obvious with the isothermal method, because the measurement should be carried out from ambient up to a temperature higher than 1000°C, and then new phases have formed. Only at a lower temperature, such as 1033°C is the step of nucleation and growth obvious with the isothermal method in the initial period (Fig. 4). Therefore, the non-isothermal method can completely demonstrate the kinetic mechanism for the direct reduction of artificial chrome iron ore.

## Conclusions

The kinetic results obtained with the isothermal and non-isothermal methods are the same in the main reaction region. The kinetic mechanism and kinetic parameters can be obtained completely by the non-isothermal method.

The kinetics of direct reduction of chrome iron ore involves three steps. In the initial, middle and final periods, the reaction is controlled by nucleation and growth, a phase boundary reaction, and diffusion, respectively. In the main reaction region, the direct reduction is controlled by a phase boundary reaction. The kinetic equation is $1-(1-\alpha)^{1/3}=kt$, and the apparent activation energy is about 270 kJ $\mathrm{mol}^{-1}$.

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