**Article**

Kinetic Analysis of Isothermal and Non-Isothermal Reduction of Iron Ore Fines in Hydrogen Atmosphere

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**Abstract:** Direct reduction of iron ore with H\(_2\) has become an alternative technology for iron production that reduces pollutant emissions. The reduction kinetics of iron ore fines in an H\(_2\) atmosphere under isothermal and non-isothermal conditions were studied by thermogravimetric analysis. X-ray diffraction and scanning electron microscopy were used to measure the mineral composition and analyse the morphology of the reduced fines, respectively. In the isothermal reduction experiment, it was found that the final reduction time was shorter, the higher the temperature, and the metallic iron particles formed a dense matrix structure. It is likely that the initial stages reduction process is the result of a combination of gaseous diffusion and interfacial chemical reaction mechanisms, and that the later stages a combination of interfacial chemical reaction and solid diffusion is the rate control mechanism. In the non-isothermal experiment, the heating rate had a significant effect on the reaction rate. The results show that the non-isothermal reduction proceeded through three stages: mixing control model, two-dimensional diffusion, and three-dimensional diffusion.

**Keywords:** hydrogen gas; isothermal reduction; non-isothermal reduction; activation energy; kinetics mechanism

1. Introduction

Energy generation activities dominated by the large-scale utilization of fossil fuels cause the rapid rise of CO\(_2\) and greenhouse gas concentration in the atmosphere, which are the main reasons for climate change [1,2]. With the aggravation of global warming, the zero emission of CO\(_2\) as a target is becoming increasingly urgent. The iron and steel industry is the largest source of CO\(_2\) and the Chinese government and industry are becoming increasingly concerned. In 2020, China’s iron and steel industry accounted for more than 60% of the world’s total steel carbon emissions, accounting for about 15% of the country’s total carbon emissions [3]. Therefore, decreasing CO\(_2\) emissions by the iron and steel industry is particularly important if China is to achieve its carbon neutrality goals. To reduce CO\(_2\) emissions, new reducing agents need to be found to replace the carbon used in the iron reduction process. As a reducing agent, H\(_2\) does not cause pollution and is an ideal substitute for carbon [4,5]. In recent years, an increasing number of studies have focused on the reduction of iron ore with H\(_2\) or H\(_2\)-rich gases to reduce carbon emissions. H\(_2\) is considered to be the most promising clean energy source in the 21st century owing to its diverse sources, high calorific value, good thermal conductivity, and wide range of applications. It has high potential as a replacement for carbon as a reducing agent in the iron and steel industry [6–8].

Mousa et al. [9] studied and compared the effect of H\(_2\)-rich gas on reduction of pellets in terms of its activation energy and rate-determining steps. Ding et al. [10,11] explored fluxed sintering reduction with CO and H\(_2\) gas using thermodynamic and kinetic model functions. It was concluded that H\(_2\) increases the reduction rate and decreases the activation energy. Bahador et al. [12] analysed magnetite concentrate particle reduction with H\(_2\)
gas in the temperature range of 700–900 °C, and an activation energy of approximately 29.48 kJ mol\(^{-1}\) was obtained. Bai et al. [13,14] found that the reduction rate constant increased with an increase in temperature, as well as efficient reduction gas content through kinetic analysis of pellet reduction using H\(_2\)–N\(_2\) under isothermal and non-isothermal conditions. Lin et al. [15] and Tiernan et al. [16] used the temperature-programmed reduction method to study the kinetics of H\(_2\) reduction of iron oxide. They found that Fe\(_2\)O\(_3\) was reduced to Fe in two steps: Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\) and then Fe\(_3\)O\(_4\) to Fe. The first step is described by the random formation and growth of nuclei, while the second step is matched to a two-dimensional nucleation according to the Avrami–Erofeev model. Chen et al. [17,18] studied the reduction behavior of hematite and magnetite in the suspension ironmaking process using a drop tube furnace reactor. Assuming that the reduction process is a one-step reaction from Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) to Fe, the nucleation growth model was used to calculate the kinetic parameters. Previous research has focused on the reduction of sinters and pellets rather than iron ore fines. New ironmaking technologies that use iron ore fines directly as raw materials (FINEX, HIsarna and flash ironmaking processes) are receiving increasing attention owing to their advantages in terms of environmental protection, energy conservation, and consumption reduction. Therefore, studying the kinetics of iron ore fines is extremely important. However, there is little literature on the simultaneous study of the isothermal and non-isothermal reduction behavior of iron ore fines.

The purpose of this study is to compare the isothermal and non-isothermal reduction processes of iron ore fines in an H\(_2\) atmosphere. The activation energy, rate-controlling steps, and model functions were deduced using thermogravimetric techniques. The current study can help further the understanding of reduction behavior of iron ore fines in an H\(_2\) atmosphere and provide an accurate kinetic model for the optimization of the ironmaking process.

2. Materials and Methods

2.1. Preparation of Sample

The iron oxide particles used in the investigation were provided by a commercial iron and steel plant. The iron oxide particles were crushed into iron ore fines with a particle size < 100 μm. The chemical composition of the iron ore fines is shown in Table 1, which indicates that the main phase in the sample was Fe\(_2\)O\(_3\). The iron ore fines were examined by x-ray diffraction (XRD) analysis, as shown in Figure 1. Scanning electron microscopy (SEM) was used to analyse the morphology of the iron ore fines, as shown in Figure 2.

| Chemical Composition (wt%)          |
|------------------------------------|
| TFe      | Fe\(_2\)O\(_3\) | FeO  | CaO  | SiO\(_2\) | MgO  | Al\(_2\)O\(_3\) |
|----------|----------------|------|------|-----------|------|-----------------|
|          | 62.04          | 87.36| 1.06 | 1.18      | 5.60 | 1.53            | 1.29 |

Table 1. Chemical composition of the iron ore fines (wt%).

![Figure 1. X-ray diffraction of iron ore fines sample.](image-url)
In these experiments, the furnace was flushed with N\textsubscript{2} (60 mL·min\textsuperscript{-1}) for 40 min before the heating procedure was performed. In the isothermal experiments, the furnace was heated to the target temperature at a heating rate of 20 °C·min\textsuperscript{-1}, during which N\textsubscript{2} was introduced into the furnace at a flow rate of 20 mL·min\textsuperscript{-1}. Then, the ore fines were reduced for 60 min in a mixture of 30% H\textsubscript{2}-70% N\textsubscript{2} at a flow rate of 20 mL·min\textsuperscript{-1} at temperatures of 800 °C, 850 °C, 900 °C, 950 °C, 1000 °C, 1050 °C, and 1100 °C. In the non-isothermal experiments, the sample was heated to 1000 °C at different heating rates of 5, 10, 15, and 20 °C·min\textsuperscript{-1}. During the process, a mixture of 30% H\textsubscript{2}-70% N\textsubscript{2} had been introduced into the furnace since the sample started to heat. The weight loss owing to the removal of oxygen from the iron ore fines was continuously recorded by computer for each heating rate. At the end of the experiment, the reduction gas was replaced with N\textsubscript{2}, and the furnace was cooled to 25 °C. Subsequently, the samples were packed in a resin and analyzed using SEM.

2.3. Thermal Analysis Kinetics

The reduction degree is defined as the ratio of the weight loss at a fixed time to the theoretical weight loss from iron ore fines, and can be expressed as:

\[
\alpha = \frac{m_0 - m_1}{m_0 - m_1} \tag{1}
\]

where \(\alpha\) is the reduction degree (%); \(m_0\) is the initial sample mass (mg); \(m_1\) is the sample mass at a particular time \(t\) (mg); and \(m_1\) is the sample mass after reaction at the end (mg).

The kinetics equation based on the Arrhenius rule [19] can be expressed as follows:

\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{2}
\]

where \(d\alpha/dt\) is the reduction rate min\textsuperscript{-1}, when the reduction time corresponds to \(t\); \(A\) is the pre-exponential factor, min\textsuperscript{-1}; \(E\) is the apparent activation energy, kJ·mol\textsuperscript{-1}; \(R\) is the gas constant, 8.314 J/(mol·K); and \(f(\alpha)\) is a model function that reveals the reaction kinetics mechanism. A detailed flowchart of the kinetic analysis under isothermal and non-isothermal conditions in this study is shown in Figure 3.
2.3.1. Isothermal Condition

The model-free method [20] was used to obtain the relationship between the reduction rate and temperature at the same reduction degree. Therefore, the activation energy can be calculated as follows:

\[ E = -R \frac{d \left( \frac{\ln \left( \frac{da}{dt} \right)}{T} \right)}{d \left( \frac{1}{T} \right)} \] (3)

The apparent activation energy was calculated from the slope of the plots of \( \ln(da/dt) \) against \( 1/T \). \( G(\alpha) \), which is the integral function of \( f(\alpha) \), described as follows:

\[ G(\alpha) = \int_0^\alpha \frac{da}{f(\alpha)} = \int_0^T A \exp \left( -\frac{E}{RT} \right) dt = k(T)t \] (4)

Model function \( G(\alpha) \) was obtained to describe the relationship of the reduction degree with time. The relationship between \( G(\alpha) \) and \( n \) for normal solid reactions and its reaction mechanism is shown in Table 2 [21].

Table 2. Model function \( G(\alpha) \) for normal solid-state reactions.

| Function | Mechanism | \( G(\alpha) \) | \( da/dt \) | \( n \) |
|----------|-----------|----------------|-------------|-------|
| \( D_1(\alpha) \) | One-dimensional diffusion | \( \alpha^2 \) | \( 0.5k\alpha^{-1} \) | 0.62 |
| \( D_2(\alpha) \) | Two-dimensional diffusion | \( (1 - \alpha)\ln(1 - \alpha) + \alpha \) | \( k[-\ln(1 - \alpha)]^{-1} \) | 0.57 |
| \( D_3(\alpha) \) | Three-dimensional diffusion, Jander equation | \( \left[ 1 - (1 - \alpha)^{1/3} \right]^2 \) | \( 1.5k\left[ 1 - (1 - \alpha)^{1/3} \right]^{-1} (1 - \alpha)^{2/3} \) | 0.54 |
| \( D_4(\alpha) \) | Three-dimensional diffusion, Ginstling-Brounstein equation | \( (1 - 2/3\alpha) - (1 - \alpha)^{2/3} \) | \( 1.5k\left[ (1 - \alpha)^{1/3} - 1 \right]^{-1} \) | 0.57 |
| \( F_1(\alpha) \) | (instantaneous nucleation and unidimensional growth) | \( -\ln(1 - \alpha) \) | \( k(1 - \alpha) \) | 1 |
| \( R_2(\alpha) \) | Phase boundary controlled reaction (bidimensional shape) | \( 1 - (1 - \alpha)^{1/2} \) | \( 2k(1 - \alpha)^{1/2} \) | 1.11 |
| \( R_3(\alpha) \) | Phase boundary controlled reaction (tridimensional shape) | \( 1 - (1 - \alpha)^{1/3} \) | \( 3k(1 - \alpha)^{2/3} \) | 1.07 |
| \( A_2(\alpha) \) | Random instant nucleation and two-dimensional growth of nuclei (A-E equation) | \( [-\ln(1 - \alpha)]^{1/2} \) | \( 2k[-\ln(1 - \alpha)]^{1/2}(1 - \alpha) \) | 2 |
| \( A_3(\alpha) \) | Random instant nucleation and three-dimensional growth of nuclei (A-E equation) | \( [-\ln(1 - \alpha)]^{1/3} \) | \( 3k[-\ln(1 - \alpha)]^{2/3}(1 - \alpha) \) | 3 |
The model functions describing the degree of reaction as a function of time and elucidating the reaction mechanism are solved mainly by two methods, namely ln-ln [22] and sharp [23] analysis. These two methods are indirectly and widely used to explore known model functions for polymeric materials but are also applicable to other types of reactants. The ln-ln analysis is based on the Avrami–Erofeev model [24,25]:

\[
\alpha = \frac{\ln[-\ln(1 - \alpha)]}{\ln t} \quad \text{for normal solid-state reactions.}
\]  

(5)

The sharp analysis defines a non-dimensional parameter \( y(\alpha) \) to be the target model function, described as:

\[
y(\alpha) = \frac{G(\alpha)}{G(0.5)} = \frac{k(T)t}{k(T)_{0.5}} = \frac{t}{t_{0.5}}
\]  

(6)

where \( G(0.5) \) refers to a fixed \( G(\alpha) \) with \( \alpha = 0.5 \), and \( t_{0.5} \) is the time corresponding to \( \alpha = 0.5 \).

The model function of the normal solid-state reactions draws the standard curve under a series of \( \alpha \) values, and the experimental data are drawn on a standard curve. If the experimental data point coincides with the standard curve of the model function, the model function is obtained.

2.3.2. Non-Isothermal Condition

To calculate the activation energy values for the reduction with \( \text{H}_2 \) at different heating rates, the Kissinger–Akahira–Sunose (KAS) [26] iso-conversion rate solution method was used:

\[
\ln \frac{\beta}{T^2} = \ln \left[ \frac{AR}{E \cdot m(\alpha)} \right] - \frac{E}{RT}
\]  

(7)

where \( \beta \) is the heating rate. The principle of the iso-conversion method under non-isothermal conditions, is that when \( \alpha \) is a fixed value, \( m(\alpha) \) is constant. According to Equation (7), the plot of \( \ln(\beta/T^2) \) vs. \( 1/T \) gives the activation energy from the slope and intercept of the curve under different reaction conditions.

The model function under a non-isothermal condition usually adopts the Malek method [27]. The idea of the Malek method is to match the experimental data and the standard curve by defining the function \( y(\alpha) \).

\[
y(\alpha) = \left( \frac{T}{T_{0.5}} \right)^2 \left( \frac{\frac{da}{dt}}{\frac{da}{dt}} \right)_{0.5} = \frac{f(\alpha)F(\alpha)}{f(0.5)F(0.5)}
\]  

(8)

The differential expression \( f(\alpha) \) and integral \( F(\alpha) \) of the model function are substituted into the above equation, and a series of curves drawn by \( y(\alpha) \) corresponding to the \( \alpha \) value are obtained. The mechanism can be used to describe the simplification process when the corresponding curve is consistent with the experimental data. The standard curves \( F(\alpha) \) and \( f(\alpha) \) functions are shown in Table 3 [28].

| No. | Function | Mechanism | \( F(\alpha) \) | \( f(\alpha) \) |
|-----|----------|-----------|-----------------|----------------|
| 1   | Parabolic law | One-dimensional diffusion | \( t^2 \) | 0.5 \( t^{-1} \) |
| 2   | Valensi equation | Two-dimensional diffusion | \((1 - \alpha)\ln(1 - \alpha) + \alpha \) | \([-\ln(1 - \alpha)]^{-1} \) |
| 3   | Jander equation (2D, \( n = 1/2 \)) | Two-dimensional diffusion | \([1 - (1 - \alpha)^{1/2}]^{1/2} \) | \([4(1 - \alpha)^{1/2}1 - (1 - \alpha)^{1/2}]^{1/2} \) |
| 4   | Jander equation (2D, \( n = 2 \)) | Two-dimensional diffusion | \([1 - (1 - \alpha)^{1/2}]^{2} \) | \([1 - (1 - \alpha)^{1/2}]^{-1} \) |
| 5   | Jander equation (3D, \( n = 1/2 \)) | Three-dimensional diffusion | \([1 - (1 - \alpha)^{1/3}]^{1/2} \) | \([6(1 - \alpha)^{2/3}1 - (1 - \alpha)^{1/3}]^{1/2} \) |
| 6   | Jander equation (3D, \( n = 2 \)) | Three-dimensional diffusion | \([1 - (1 - \alpha)^{1/3}]^{2} \) | \([2(1 - \alpha)^{2/3}1 - (1 - \alpha)^{1/3}]^{-1} \) |
### Table 3. Cont.

| No.  | Function                   | Mechanism                        | \( F(a) \)                                              | \( f(a) \)                                               |
|------|----------------------------|----------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| 7    | Ginstling–Brounstein       | Three-dimensional diffusion      | \( 1 - \frac{3}{2}a - (1 - a)^{2/3} \)                   | \( \frac{3}{2}(1 - a)^{1/3} - 1 \)                       |
| 8    | Antagonistic Jander        | Three-dimensional diffusion      | \( \left[ (1 + a)^{3/2} - 1 \right]^2 \)                 | \( \frac{2}{3}(1 + a)^{2/3} - (1 + a)^{2} - 1 \)         |
| 9    | Prout–Tompkins equation    | Three-dimensional diffusion      | \( \alpha \)                                             |                                                         |
| 10   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(1/4)                                          | 4(1 - a)(-ln(1 - a))^(3/4)                                |
| 11   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(1/3)                                          | 3(1 - a)(-ln(1 - a))^(2/3)                                |
| 12   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(2/5)                                          | \( \frac{5}{4}(1 - a)(-ln(1 - a))^{3/5} \)               |
| 13   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(1/2)                                          | 2(1 - a)(-ln(1 - a))^(1/2)                                |
| 14   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(2/3)                                          | \( \frac{2}{3}(1 - a)(-ln(1 - a))^{1/3} \)               |
| 15   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(3/4)                                          | \( \frac{4}{3}(1 - a)(-ln(1 - a))^{1/4} \)               |
| 16   | Mampel single law         | Random nucleation and subsequent | -1 n(1 - a)                                               | 1 - a                                                   |
| 17   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(3/2)                                          | \( \frac{3}{2}(1 - a)(-ln(1 - a))^{-1/2} \)             |
| 18   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(2)                                            | \( \frac{1}{2}(1 - a)(-ln(1 - a))^{-1} \)               |
| 19   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(3)                                            | \( \frac{1}{2}(1 - a)(-ln(1 - a))^{-2} \)               |
| 20   | Avrami–Erofeev equation   | Random nucleation and subsequent | -1n(1 - a)^(4)                                            | \( \frac{1}{2}(1 - a)(-ln(1 - a))^{-3} \)               |
| 21   | Prout–Tompkins equation    | Three-dimensional diffusion      | ln \[ \frac{\alpha}{1 - \alpha} \]                     | \( \alpha(1 - a) \)                                       |
| 22   | Mampel power law           | Phase boundary reaction          | a                                                         |                                                         |
| 23   | Mampel power law           | Phase boundary reaction          | a                                                         |                                                         |
| 24   | Mampel power law           | Phase boundary reaction          | a                                                         |                                                         |
| 25   | Mampel power law           | Phase boundary reaction          | a                                                         |                                                         |
| 26   | Mampel power law           | Phase boundary reaction          | a                                                         |                                                         |
| 27   | Mampel power law           | Phase boundary reaction          | a                                                         |                                                         |
| 28   | Order of reaction          | Phase boundary reaction          | a                                                         |                                                         |
| 29   | Spherical contraction      | Phase boundary reaction          | a                                                         |                                                         |
| 30   | Cylindrical contraction (3D)| Phase boundary reaction          | a                                                         |                                                         |
| 31   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 32   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 33   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 34   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 35   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 36   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 37   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 38   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 39   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 40   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
| 41   | Cylindrical contraction (2D) | Spherical contraction (symmetrical sphere) | a                                                         |                                                         |
3. Results and Discussion

3.1. The Calculation of Kinetic Parameter with Isothermal Reduction

3.1.1. Reduction Degree and Rate

Figure 4 shows the reduction curves of iron ore fines with H$_2$ gas at different temperatures. It shows that after any specific reduction time an increase in temperature resulted in an increase in the reduction degree. During the early stages of the reaction, the rate of oxygen removal was very high and the degree of reduction increased significantly. In the later stages, the removal rate of oxygen was very low, showing an obvious decrease in the rate until the end of the reduction process, giving a plateau-type curve in the final reduction stage. On the other hand, iron existed in the form of α-Fe when the temperature was <912 °C, and the form of γ-Fe when the temperature was >912 °C. In γ-Fe, the diffusion rate of H$_2$ and reduction product (H$_2$O) were slower than those in α-Fe. Secondly, the dense iron layer was formed by reduction increases as temperature increased, and it became dense due to continuous crystals. The dense iron layer hindered the diffusion of the reducing gas, so that the unreduced iron oxide was not easily reduced by direct contact with the reducing gas [29,30]. However, the H$_2$ reduction reaction of iron oxide is endothermic and has a high reduction potential at high temperature. Therefore, a higher reduction temperature may reduce the effects of kinetic limitations. The reduction curve comprises three consecutive stages: induction, acceleration, and descent.

![Figure 4](image_url)

**Figure 4.** Reduction degree ($\alpha$) of sample in H$_2$ atmosphere at 800–1100 °C.

The reduction rates $\frac{dx}{dt}$ (min$^{-1}$) of iron ore fines at 800–1100 °C were calculated from the reduction degree vs. time curve (Figure 5a), and the relationship between the initial (0–30%) and final (80–90%) reduction rate (Figure 5b). It has been shown that the reduction of iron ore fines is a complex multi-step reaction, which is the result of multiple couplings of chemical and structural changes. The theoretical reduction degree of the Fe$_2$O$_3$ (Fe$_2$O$_3$ → Fe$_3$O$_4$) and Fe$_3$O$_4$ (Fe$_3$O$_4$ → FeO) is fixed at 0.11 and 0.33, respectively. The reduction rate in the initial and final stages gradually increased with increasing temperature, which is consistent with the basic principles of chemical kinetics and diffusion [31].
The relationship between the activation energy and rate-controlling steps is presented in Table 4 [32]. The activation energy and rate-controlling steps with different degrees of reduction are shown in Figure 7. The activation energy of iron ore fines fluctuated in the range from 27 to 93 kJ·mol\(^{-1}\) as the degree of reduction increased.
The sharp analysis results strongly agreed with the ln-ln analysis results. This was the same rate-determining step as for CO [34]. In the later stages, the rate-controlling step was the rate-determining step. However, CO was controlled by an interfacial chemical reaction, which was the rate-controlling mechanism. The value of $n$ is directly related to the Avrami–Erofeev exponent $n$ of the samples at 800–1100 °C and indicates that the reduction process was most likely controlled by a combined effect of both gaseous diffusion and interfacial chemical reaction mechanisms. This was the same rate-determining step as for CO [34]. In the later stages, the $E$ value obtained was 79.15 kJ·mol$^{-1}$, which revealed that the interfacial chemical reaction and solid diffusion mechanism was the rate-determining step. However, CO was controlled by an interfacial chemical reaction, which was the rate-controlling mechanism.

### 3.1.3. Model Function Results

According to the ln-ln analysis, the value of $n$ is directly related to $G(\alpha)$. The Avrami–Erofeev exponent $n$ of the samples at 800–1100 °C is shown in Table 5. Table 5 shows the relationship between $ln(−ln(1−\alpha))$ and $ln\hat{t}$ for the samples, which reveals that the range of $n$ was 1.02–1.23 at a reduction temperature of 800–1100 °C and indicates that the reduction of the sample was expressed by the function $F_1$ (instantaneous nucleation and unidimensional growth) toward $R_2$ (bidimensional shape).

**Table 4.** Relationship between activation energy and reduction mechanism.

| $E$, kJ·mol$^{-1}$ | Rate-Controlling Step                   |
|-------------------|-----------------------------------------|
| 8–16              | Gaseous diffusion                       |
| 29–42             | Combination of gaseous diffusion and interfacial chemical reaction |
| 60–67             | Interfacial chemical reaction           |
| >90               | Solid diffusion                         |

**Figure 7.** (a) $\ln(\frac{\alpha}{\partial t})$ against $1/T$ of sample, and (b) activation energy with the increasing of reduction degree.

Under isothermal conditions, the iron ore fines were completely reduced by H$_2$ in a shorter time than that taken by using CO [33]. The $E$ value in the initial stages was 28.96 kJ·mol$^{-1}$, which indicates that the reduction process was most likely controlled by a combined effect of both gaseous diffusion and interfacial chemical reaction mechanisms. This was the same rate-determining step as for CO [34]. In the later stages, the $E$ value obtained was 79.15 kJ·mol$^{-1}$, which revealed that the interfacial chemical reaction and solid diffusion mechanism was the rate-determining step. However, CO was controlled by an interfacial chemical reaction, which was the rate-controlling mechanism.

### Table 5. Avrami–Erofeev exponent $n$ at 800–1100 °C for samples.

| Temperature/°C | 800  | 850  | 900  | 950  | 1000 | 1050 | 1100 |
|----------------|------|------|------|------|------|------|------|
| $n$            | 1.02 | 1.03 | 1.01 | 1.13 | 1.12 | 1.18 | 1.23 |
| Function       | $F_1\rightarrow R_2$ |

Based on the sharp analysis, the standard curves and experimental data of the iron ore fines are shown in Figure 8. The $y(\alpha)$ values for the iron ore fine reductions lay on the curve based on Function $F_1$ and then gradually tended to lie on the curve based on function $R_2$. The sharp analysis results strongly agreed with the ln-ln analysis results.
3.2. The Calculation of Kinetic Parameter with Non-Isothermal Reduction

3.2.1. Reduction Degree and Rate

Figure 9 shows the values of $\alpha$ and $da/dt$ versus time at different heating rates. The curve shape is similar for all degrees of reduction. It can be seen from the experimental results that the reduction reactions proceeded at $\geq 350 \, ^\circ C$, and the rates increased with increasing temperature. As can be seen from the figure, the heating rate had a significant influence on the reduction reaction rate. However, with an increase in heating rate, the starting and ending temperatures reflected a slight delay in the reduction process. It can be seen from the $da/dt$ curve that the reaction rate changed significantly during the entire reaction process. This is because the process of $H_2$ reduction of iron ore fines is more sensitive to an increase in the heating rate.

The morphological changes in the sample after reduction were observed by SEM, as shown in Figure 10. The size of the metallic iron particles was relatively large when the sample was reduced at a low heating rate of $5 \, ^\circ C \cdot min^{-1}$. With an increase in the heating rate, the grains gathered and formed a dense iron layer, with many metallic iron particles uniformly distributed. In addition, it was found that product organization existed in the pores. On the one hand, the structural changes reduced the porosity and
hindered the diffusion of atmospheric water vapor as a macromolecule, and it changed the diffusion path.

![Image](image_url)

**Figure 10.** Microstructure after non-isothermal reduction with H$_2$ up to 1000 °C: (a) 5 °C·min$^{-1}$, (b) 10 °C·min$^{-1}$, (c) 15 °C·min$^{-1}$, (d) 20 °C·min$^{-1}$.

### 3.2.2. Apparent Activation Energy and Rate-Controlling Steps

The activation energies with different reduction degrees are listed in Table 6. Evidently, the activation energy of iron ore fines did not change significantly with an increase in the degree of reduction. The average activation energy was 26 kJ·mol$^{-1}$, and the reduction reaction was controlled by gaseous diffusion.

#### Table 6. Apparent activation energy of iron ore fines in different reduction degrees.

| α     | Slope | Activation energy (kJ·mol$^{-1}$) | Average activation energy (kJ·mol$^{-1}$) |
|-------|-------|----------------------------------|------------------------------------------|
| 0.1   | 2944  | 24                               | 26                                        |
| 0.2   | 3251  | 27                               | 27                                        |
| 0.3   | 3210  | 27                               | 27                                        |
| 0.4   | 3137  | 26                               | 26                                        |
| 0.5   | 3126  | 26                               | 26                                        |
| 0.6   | 3060  | 26                               | 26                                        |
| 0.7   | 3100  | 26                               | 26                                        |
| 0.8   | 3186  | 26                               | 26                                        |
| 0.9   | 3662  | 30                               | 27                                        |
| 1     | 3367  | 26                               | 26                                        |

In the non-isothermal reduction experiment, for CO as reducing agent, a high activation energy was obtained in the initial stage that decreased with an increase in reduction [34]. The average activation energy for H$_2$, in comparison, was lower during the entire stage. This was due to the special characteristics of H$_2$; its smaller molecular size leads to lower density and viscosity, better diffusivity and permeability, better chemical reaction and heat exchange between the gas and the burden, and thus, lower activation energy. Therefore, H$_2$ is a more effective reducing agent in terms of kinetics.

### 3.2.3. Model Function Results

The Malek [27] method is a kinetic analysis based on multi-heating rate methods, which can be used to determine the reaction mechanisms. The relation curve between $y(\alpha)$ and $\alpha$ is drawn according to the experimental data for the four heating rates, as shown in Figure 11. It can be seen from the figure that the data points under different heating rates coincide. For the reduction degree of 0.1, the reaction follows a mixed control model. When the reduction degree was 0.2, the model function followed two-dimensional...
diffusion, and the reaction was consistent with the function curve shown in Figure 11 (2). The experimental data followed the curve of function in Figure 11 (9) when the reduction degree was in the range of α = 0.3–0.9. The reaction mechanism was controlled by three-dimensional diffusion. H₂ could not be represented by either model when it first came in contact with iron ore fines, so it was a mixed control model, which in turn quickly changed to two-dimensional diffusion, and was mostly reduced by three-dimensional diffusion.

Figure 11. Standard curves and experimental data based on Malek method for samples.

3.3. Influence of Different Parameters on Industrial Applications

The reduction process of iron oxide particles by H₂ is very complex, and the factors affecting the reduction kinetics of iron oxide are mainly related to external conditions and the material itself, which can be changed to effectively improve the reduction rate and have an impact on the production of industrial applications.

Owing to the dependence of the kinetic mechanism on the reduction temperature, the temperature of the reduction is higher. The reduction temperature is the most significant factor limiting the rate step; a higher temperature facilitates the diffusion rate and the phase boundary reactions. According to the thermodynamic equilibrium diagram, the driving force of reduction increases with increasing temperature when H₂ is used as the reducing agent. Therefore, a higher temperature has a positive effect on the thermodynamics and kinetics. For CO as a reducing gas, the reduction driving force decreases with an increase in temperature. Therefore, H₂ has a higher reduction capacity than CO in the high temperature zone, which increases the reduction rate of iron oxide and industrial productivity. Because H₂ reduction replaces partial carbon reduction, the amount of carbon reduced per ton of iron and the proportion of direct reduction can be reduced, and the production of CO₂ can also be reduced.

The structural characteristics of the ore itself also affect the reduction rate. Owing to the small molecular size of H₂ and fast diffusion rate, the contact area of H₂ with the same particle size ore is increased, the diffusion resistance is low, and the reduction rate is high compared to CO. A high porosity burden allows for better diffusion of reducing gases to the reaction interface. The sinter has a high internal porosity and pore structure of different sizes, and there is little difference in the reduction effect between H₂ and CO. However, the lump and pellets had a relatively dense structure. Because of its strong diffusion ability, it is easier for H₂ to permeate into the structure than CO₂, which strengthens the reduction kinetics, resulting in lower reduction smelting time and higher production efficiency.

4. Conclusions

The isothermal and non-isothermal reduction behavior and mechanism of iron ore fines with H₂ were studied, and the reaction kinetics were analyzed by continuously
recording the weight change of the TG equipment. The results obtained include the following aspects:

(1) Under isothermal conditions, temperature plays a vital role in the reduction process. The activation energy was 27–93 kJ mol\(^{-1}\). The rate-controlling step was gaseous diffusion and interfacial chemical reaction mixed control in the initial stages, and interfacial chemical reaction and solid diffusion in the final stages. The reduction of the samples was expressed by the model function \(F_1\) (instantaneous nucleation and unidimensional growth) toward \(R_2\) (bidimensional shape) through the \(\ln-\ln\) and sharp analyses.

(2) In the non-isothermal reduction experiment, the heating rate significantly affected the reaction rate. The average activation energy calculated by the KAS method was 26 kJ mol\(^{-1}\). The reaction mechanism was analyzed using the Malek method. The models for the non-isothermal kinetics of the reduction of iron ore fines include mixed control, two-dimensional diffusion, and three-dimensional diffusion, depending on the stage of the reduction process.

(3) The reduction of the sample under isothermal conditions can be described by a unidimensional growth at the initial stage of reduction and the 2D shrinking layer reaction mechanism at a later stage. Under non-isothermal conditions, the reduction of the sample is described, in turn, by the mixing control, 2D reaction, and 3D reaction.

(4) The use of H\(_2\) as a reducing agent changes the conditions of the iron oxide reduction reaction, the reduction rate, and the morphology of reduction products, leading to significant changes in its reaction kinetic process. Basic theoretical research on the future large-scale use of H\(_2\) in the ironmaking process is needed to really achieve low-carbon ironmaking.

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