Reduction Kinetics of Fine Hematite Ore Particles with a High Temperature Drop Tube Furnace

Yingxia QU,1)* Yongxiang YANG,2) Zongshu ZOU,1) Christiaan ZEILSTRA,3) Koen MEIJER3) and Rob BOOM2)
1) School of Materials and Metallurgy, Northeastern University, Box 312, No. 3-11, Wenhuax Road, Heping District, 110819, Shenyang, P. R. China.  2) Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands.  3) Tata Steel, PO Box 10000, 1970 CA IJmuiden, The Netherlands.

(Received on December 31, 2014; accepted on February 10, 2015)

Hisarna is a new coal based smelting reduction process, which has the excellent features of using coal and fine hematite ore directly as raw materials instead of coke and pellet. In this context, the reduction kinetics of hematite ore fines in the smelting cyclone was studied in the laboratory scale. The gas-solid and gas-molten particle reduction behaviour were studied with a High-temperature Drop Tube Furnace (HDTF) and a combination of various characterization methods was used to track the kinetic behaviour such as chemical titration, optical microscope and Scanning Electron Microscope (SEM). A series of experiments with different reaction time (210–2020 ms) has been conducted at different temperatures from 1550 K to 1750 K, thus enabling the kinetic study of the partially reduced hematite ore particles. It was found that a quantity of micro pores was formed during the reduction process mainly due to the loss of oxygen. The un-reacted shrinking core model could be used to describe both gas-solid particle reaction and gas-molten particle reaction.

KEY WORDS: Hisarna process; fine hematite ore; reduction kinetics; gas-solid particle reduction; gas-molten particle reduction.

1. Introduction

Hisarna is a new coal based smelting reduction process. It requires significantly less coal usage and thus reduces the amount of CO₂ emissions. Furthermore, it is a flexible process that allows partial substitution of coal by biomass. Without Carbon Capture and Storage (CCS) technology Hisarna is expected to cut CO₂ emissions by 20%, whereas with CCS it can achieve a reduction of up to 80% by 2050.¹ In addition, it uses fine ores instead of pellet or sinter used in the conventional ironmaking process. Hisarna is, in essence, a merger between the smelting cyclone technology of CCF developed by Hoogovens (now Tata Steel) and bath smelting technology of Hismelt developed by Rio Tinto. The pre-reduction degree in the smelting cyclone is around 20% and the final reduction is completed in the bath of the smelting reduction vessel (SRV). The Hisarna pilot plant which has an annual capacity of 60,000 tonnes was built and commissioned at Tata Steel’s IJmuiden steelworks in the Netherlands. In April 2011 the process was piloted for the first time. Industrial scale demonstration will be carried out from 2014–2018. The earliest industrialization of Hisarna, the smelting reduction technology being tested at the IJmuiden steelworks, will be from 2020.

In the past few decades, iron ore fines can be directly used and charged into the ironmaking furnaces with the emergence of a number of the alternative ironmaking technologies²–⁴) (e.g. FIOR, FINMET, Circored and FINEX). It achieves the benefits on both economy and environment. However, the using of fine iron ore particles leads to new challenges on operation and unknowns on reaction mechanism at the same time. Up to now, the intensive experimental studies on iron ore fines have been carried out with laboratory-scale fluidized bed reactor⁵–⁹) and gas conveyed system.¹⁰,¹¹) The experimental studies with the laboratory-scale fluidized bed reactor were successfully applied to analyse the gas-solid particle reduction mechanism in the fluidized bed reactors which are used in the direct reduction processes and the pre-reduction stage of smelting reduction processes. However, the temperature of the fluidized bed reactor cannot go up to and beyond the melting temperature of iron ore, to avoid the agglomeration in the reactor. For this reason, most of the studies with fluidized bed reactor limited the temperature below 1173 K. Therefore, the kinetic study on gas-solid particle reduction of fine hematite ore at higher temperature is still missing. In addition, the gas-molten particle reduction behaviour of fine hematite ore is also not clear. Although high temperature could be obtained with the gas conveyed system, the published experimental results with gas conveyed system focused on the lower part of the blast furnaces and the final stage of smelting reduction processes. So only fine wüstite particles were used in the experiments. In the Hisarna process, the individual hematite ore particles are reduced at very high temperature in the smelting cyclone and experience a series of physical and chemical changes.

* Corresponding author: E-mail: quyingxia800@163.com
DOI: http://dx.doi.org/10.2355/isijinternational.55.952
such as heating up, thermal decomposition, reduction and melting. The kinetic mechanism of the reduction of hematite ore particle is essential for understanding and predicting the reduction process in the smelting cyclone of HISarna process, and is essential for optimising the operation of the pilot plant. Therefore, a kinetic model has been built based on the experimental results at the typical operating conditions of HISarna process, and then the individual rate steps involved in the reactions were discussed to identify the rate controlling step of the overall reaction.

2. Experimental

2.1. Experimental Set-up and Procedures

The experimental set-up used in this study is a drop tube furnace with a unique gas conveyed system. Since the experimental temperature was extremely high in this study, a new name of High-temperature Drop Tube Furnace (HDTF) was used to characterize it. The HDTF mainly consists of 6 components as shown in Fig. 1: an electrically heated tube furnace, a gas pre-heater, a syringe pump particle feeder, a water cooled particle injection probe, a sampling probe with a combination cooling system of gas (N₂) and water, and a sample collector. A honeycomb flow straightener was attached at the tip of the injection probe to achieve a better laminar flow in the hot zone. Both of the injection probe and sampling probe could be moved freely in vertical direction to change the length of hot zone. An Alsint (99.7% Al₂O₃) tube was used as reaction tube which has an inside diameter of 60 mm, outside diameter of 70 mm and length of 1 100 mm. The reaction tube was heated by six SiC heating elements. Due to the cooling load of the sampling probe and injection probe, the common isothermal zone could not appropriately represent the temperature condition in the hot zone. Therefore, the experimental temperature in the hot zone was calculated by the weighted average method.

When the furnace was heated up to the designated temperature, the gas was switched from protection gas of N₂ to the mixed reducing gas. The used gases coming from the gas cylinders were regulated with the mass flow controllers. A small part of the mixed gas was separated as carrier gas which was measured with a mass flow meter. The carrier gas flowed into the container of the syringe pump particle feeder and brought several particles together with it, and then flowed into the water cooled injection probe. The other part of reducing gas flowed into the gas preheater and was heated to 773 K, and then introduced into the furnace directly from the top of the furnace. The reactions took place in the hot zone which started from the tip of the injection probe and ended at the top of the sampling probe. The partially reduced particles and the off-gas after reaction were received by the sampling probe. Finally, the partially reduced particles were collected in the sample collector which had two conical shape chambers to increase the capture ratio of the hematite ore particles.

2.2. Experimental Conditions and Strategies

The hematite ore fines were provided by Tata Steel in Ijmuiden, the Netherlands. The chemical analysis is shown in Table 1. The raw material was prepared with screening and dried to remove the moisture. The particle size was analysed by the technique of laser diffraction on a volume

<table>
<thead>
<tr>
<th>Composition</th>
<th>mass%</th>
<th>Composition</th>
<th>mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.40</td>
<td>MnO</td>
<td>0.10</td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
<td>SiO₂</td>
<td>2.38</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>96.08</td>
<td>H₂O</td>
<td>0.67</td>
</tr>
<tr>
<td>MgO</td>
<td>0.06</td>
<td>Rest</td>
<td>0.28</td>
</tr>
</tbody>
</table>
basis and the volume median diameter was used as the representative diameter. In this study, the typical particle size 45–53 μm was used, and the median diameter was 50 μm which was applied to the calculation of particle’s residence time. The residence times were 210 ms, 700 ms, 970 ms, 1570 ms and 2020 ms, respectively. It was assumed that there were three forces acting on a single particle: gravity force, buoyancy force and drag force as shown in Fig. 1, and then the residence time was calculated with the iteration method by applying Newton’s second law of motion and Stokes law to the particles’ motion through fluids. The iron ore particles were accelerated by the net force in the vertical direction just after the exit of the particle feed system. The formulas are shown in Eqs. (1)–(5). The gas mixture was composed of 42.2% CO and 57.8% CO₂ and the gas flow rate was 4 L/min. The post combustion ratio (PCR) of the reducing gas is 57.8% which is in the typical range of the pilot plant operation. The temperature in the hot zone was varied by the steps of 50 K between 1 550 K and 1 750 K. The particle feed rate was controlled to be 1 g/h to avoid the agglomeration of particles at high temperature.

Net external accelerating force:
\[ m_p \frac{du_p}{dt} = F_D + F_C - F_B \] .......................... (1)

Drag force:
\[ F_D = C_D \times A_p \times \frac{1}{2} \times \rho_g \times \left( u_g - u_p \right) \left( u_g - u_p \right) \] .......................... (2)

Difference of gravity and buoyant force:
\[ F_G - F_B = V_p g \left( \rho_g - \rho_p \right) \] .......................... (3)

Drag coefficient:
\[ C_D = 24 / \text{Re} \] .......................... (4)

Reynolds number of the particle:
\[ \text{Re} = \frac{\rho_g \times \left( u_g - u_p \right) \times d_p}{\mu_g} \] .......................... (5)

Where,
\[ \rho_g, \rho_p \] – Gas density and particle density, kg/m³
\[ u_g, u_p \] – Gas velocity and particle velocity, m/s
\[ m_p \] – Mass of iron ore particle, kg
\[ A_p \] – Cross sectional area of particle, m²
\[ V_p \] – Volume of particle, m³
\[ g \] – Gravitational acceleration, m/s²
\[ d_p \] – Diameter of particle, m
\[ \mu_g \] – Gas viscosity, kg/ms

The reduction degree \( R \) of hematite ore is defined as the ratio of mass loss of oxygen to the total initial mass of oxygen in the hematite ore. The reduction degree of the collected samples was analyzed with chemical titration. With this method, the weight percentage (wt%) of total iron (Fe₂O₃), Fe²⁺ and Fe³⁺ could be obtained, and then the reduction degree was calculated with Eq. (6).

\[ R = \left( 1 - \frac{Fe^{2+} \% + 1.5Fe^{3+} \%}{1.5Fe_{tot} \%} \right) \times 100\% \] .......................... (6)

The morphology of the partially reduced particles were observed with the optical microscope and further investigated with Scanning Electron Microscope (SEM). The optical distinction of solid reactant and product phases is quite easy for hematite and magnetite, but the difference between magnetite and wüstite is barely detectable and the sample has to be etched. A distinction between magnetite and wüstite could be obtained by etching with diluted acid of HCl, whereas wüstite was heavily attacked and the magnetite remain undissolved.

3. Experimental Results

3.1. Results of Reduction Degree

The experimental results of reduction degree at the five temperatures (1 550–1 750 K) are shown in Fig. 2. The reducing gas was composed of 42.2% CO and 57.8% CO₂. The particle size was in the range of 45–53 μm. According to the previous study, the thermal decomposition of fine hematite ore took place in the first 210 ms in the inert gas and no further thermal decomposition reaction could be detected after 210 ms. In the reducing gas, the thermal decomposition and reduction of hematite ore took place simultaneously in the first 210 ms and only reduction took place after 210 ms. In order to study the reduction kinetics of fine hematite ore, the residence time was varied from 210–2 020 ms since the thermal decomposition of hematite has influence on the reduction process in the first 210 ms. Figure 2 clearly shows that the \( R \) of hematite ore goes up with increasing temperature at the same residence time. On the other hand, the \( R \) of hematite ore increases with increasing residence time at 1 550 K–1 700 K, while the \( R \) reaches the equilibrium state at 1 750 K when the residence time is over 970 ms. The results at different temperatures were used in the kinetic analysis in the following section.

3.2. Morphological Observation

Morphological observation is quite necessary for the kinetic study of iron ore reduction since it is helpful in understanding the reaction process. The external appearance of the unreduced particles was observed with optical microscope and SEM as shown in Fig. 3. It can be seen that the particle has an irregular shape and its surface looks smooth and bright under the light of optical microscope. The image from the SEM further reveals the topography of the particle which has a smooth and close-grained structure.
The external appearance of the collected partially reduced particles was also observed by the optical microscope. Since solid particles still kept the irregular shape and molten particles presented the spherical shape, three types of reaction were identified and summarized in Fig. 4: 100% gas-solid particle reduction, mixed reduction (part of gas-solid reduction and part of gas-molten particle reduction) and 100% gas-molten particle reduction. The 100% gas-solid particle reduction took place at 1 550 K and 1 600 K at all the studied residence times and at 1 650 K at the residence times of 210–970 ms. Although some molten particles were achieved in the collected samples at 1 650 K at the residence times over 970 ms and at 1 700 K at the residence time of 210 ms, the solid particles still existed. The 100% gas-molten particle reduction took place at 1 700 K at the residence times over 210 ms and at 1 750 K at all the studied residence times. On the other hand, the generation of molten particles indicates that a considerable amount of FeO was generated in the particles. It is because that the melting temperatures of both Fe₂O₃ and Fe₃O₄ are higher than 1 750 K, while the melting temperature of FeO is around 1 644 K.

3.2.1. External Structure of a Single Reduced Particle

In order to obtain the details of the reaction, it is essential to focus on a single particle for the observation of both its external and internal structure. Figure 5 illustrates the morphological change of the single particles’ surface experienced at 1 550 K, 1 600 K and 1 650 K (zone 1 as shown in Fig. 4). The residence time of the selected samples was 970 ms. The images (a)–(c) in Fig. 5 were taken with optical microscope for the entire particles. It was found that with the increase of temperature, the surface of the reduced particles became coarser and coarser. Big pores could be observed on the particle at 1 650 K. The magnified images for the particles were taken with SEM as shown in Figs. 5(d)–5(f). The magnification of the images is 3000x revealing the details of 1 μm. The particles were from the same experiment with the particles in Figs. 5(a)–5(c). There were not many pores on the particle at 1 550 K, but the particle already had a rough surface. The size of the micro pores which were formed at 1 600 K was smaller than the micro pores which were formed at 1 650 K. The images in Figs. 5(d)–5(f) show the same phenomenon as that shown in Figs. 5(a)–5(c). The formation of the micro pores in the particles during the reduction process was caused by the loss of oxy-

Fig. 3. Morphological observations of unreduced particle, (a) with optical microscope, (b) with SEM, 1000x.

Fig. 4. Identified reaction types from the shape of the partially reduced particles in the samples at 1 550–1 750 K, particle size: 45–53 μm, reducing gas: 42.2% CO + 57.8% CO₂.

Fig. 5. Morphological observations of reduced particles at 970 ms: with optical microscope: (a) T = 1 550 K, (b) T = 1 600 K, (c) T = 1 650 K; with SEM 3000x: (d) T = 1 550 K, (e) T = 1 600 K, (f) T = 1 650 K.

Fig. 6. Exterior appearance of spherical particle produced at 1 650–1 750 K, with SEM (a) 1200x, (b) 3000x.
gen and the construction of iron oxides during the melting process. The pulverization of iron ore particles at high temperature was not observed. The main reason is that the iron ore used in this study does not contain crystallization water.

For the gas-molten particle reduction, the particle experienced not only reduction but also melt in the reactor and formed a sphere. Since all the spherical particles in zone 2 and 3 in Fig. 4 have the same appearance, one example at 1750 K is given in Fig. 6. The details of the surface of the spherical particle were photographed with SEM since SEM can produce very high-resolution images and give a clear three-dimensional appearance of the sphere. It can be observed that a lot of micro pores densely distributed on the spherical particle. The micro pores were caused by the gas formation and evolution near the solidified liquid particles, due to reduction reactions. In molten state, the formed gas (CO₂) will have to transfer out of the surface from inside the droplet. Local bubbling may occur, and together with the dissolved gas molecules which can lead to the micro pores upon cooling and solidification.

3.2.2. Internal Structure and Phase Distribution in a Single Particle

The kinetic model was determined based on observing the structural changes inside the partially reduced particles, and this method has been widely used for the kinetics study of iron ore reduction. The polished sections of the partially reduced particles were observed with optical microscope as shown in Figs. 7–11. The experimental conditions were the same with that shown in Fig. 4. At the temperature below 1650 K, the light areas are the phases of hematite and the dark areas are the phases of magnetite. It was found that the peripheral part of hematite particle was reduced to magnetite by reducing gas and the un-reacted hematite core remained inside. The unreacted core of hematite became smaller with increasing residence time and temperature. At 1650 K and above, the polished section of the particles presented an identical colour at all the studied residence times. It means that almost all the hematite in the particle was reduced to magnetite and wüstite. After 30 seconds etching time, the wüstite could be heavily attacked by a mixture of
hydrochloric acid (HCl 37%) and ethanol. Three typical examples at 1,650 K, 1,700 K and 1,750 K which were observed with optical microscope are given in Fig. 12. The dark area is wüstite and the light area is magnetite. The size of the un-reacted core (magnetite) of the individual particles became smaller with the increase of reduction degree. At 1,750 K, all the area of the polished section of the molten particle was attacked by HCl and had an identical colour. It means that these particles were reduced to wüstite completely. The results indicate that the reduction progressed topochemically at all the studied temperatures from 1,550–1,750 K and one interface un-reacted shrinking core model can describe all the cases in this study. Furthermore, from Figs. 7 to 11, it was found that the micro pores generated not only at the surface of particles as shown in Figs. 5–6, but also formed inside the particles during the reduction process. The formation of micro pores during the reduction process greatly facilitated the diffusion of reducing gases from the outer surface of the particle to the reaction interface.

4. Kinetic Analysis

4.1. Reduction Mechanism

A kinetic model can describe a particular reaction type and translate that mathematically into a rate equation. In this study, the reduction kinetics was further studied based on the one interface un-reacted shrinking core model according to the morphological observation. The system of the un-reacted shrinking core model involves three phases: the gaseous phase, the product layer and the un-reacted core. The removal of oxygen takes place at the interface between the product layer and the un-reacted core. The reduction mechanism of hematite ore was obtained and the kinetic data of activation energy ($E_a$) and reaction rate constants ($k$) were calculated, which could be used for the further mathematical modelling of HIsarna process.

Generally, in heterogeneous reaction systems, mass transfer (like diffusion from the bulk of the fluid phase towards the interface) and chemical reaction usually proceed in series. If the reaction rate is entirely controlled by the chemical
kinetics, the rate is usually characterized as “microkinetic”. On the other hand, physical phenomena also influence the reaction rate when the diffusion rate is not much higher than the chemical reaction rate. This reaction rate is usually termed as “macrokinetic”, and accounts for both chemical and physical phenomena.\(^{19}\) From the macrokinetics viewpoint, the reduction proceeds through the following steps occurring successively during the reaction:

i. transport of gaseous reactant (CO/H\(_2\)) from bulk gas to exterior surface of the ore particle through a gaseous boundary layer.

ii. diffusion of gaseous reactant (CO/H\(_2\)) through the product layer to the reaction interface.

iii. chemical reduction reaction of iron oxide with gas reactant (CO/H\(_2\)).

iv. Diffusion of gaseous product (CO\(_2\)/H\(_2\)O) outward through the product layer.

v. transport of the gaseous product (CO\(_2\)/H\(_2\)O) from the exterior surface of the particle to the bulk gas through the gaseous boundary layer.

From the microkinetics viewpoint, the interfacial chemical reaction (step iii) can be further interpreted as follows. One example of chemical reaction mechanism from hematite to magnetite is helpful to understand the process.

iii-a) Reaction on atomic scale at the interface of iron oxides:

Hematite-magnetite:

\[
Fe_2O_3 + 3CO = 2Fe^{3+} + 6e^- + 3CO_2 \quad \text{......... (7)}
\]

iii-b) Mass transport of cations (Fe\(^{3+}\)) and electrons inside the hematite or magnetite matrix along the interface of hematite-magnetite or magnetite-wüstite (solid state diffusion)

iii-c) nucleation and growth of reaction products at the interface of iron oxides:

Hematite-magnetite:

\[
2Fe^{3+} + 6e^- + 8Fe_2O_3 = 6Fe_3O_4 \quad \text{......... (8)}
\]

The elementary steps of interfacial chemical reaction of iron oxide reduction have already been proposed by Hayes and Griesveson.\(^{20}\) Firstly, the reduction gas picks up oxygen and frees the cations and electrons, and then the cations and electrons move inside the hematite or magnetite matrix along the interface, which is also called solid state diffusion. Finally, the nucleation and growth of magnetite or wüstite can take place. The \(E_a\) of each step from both macrokinetics and microkinetics have been calculated by many investigators.\(^{21-25}\) The typical ranges of \(E_a\) of different rate controlling steps have been summarized by Strangway.\(^{26}\) It was found that the \(E_a\) of step iii-b) were higher than 90 kJ/mol, while the \(E_a\) of all the other steps in macrokinetics and microkinetics were lower than 90 kJ/mol. In the study of Tabirou,\(^{16}\) it was stated that the \(E_a\) of mass transport of cations and electrons inside the matrix along the interface (step iii-b)) could be as high as 400 kJ/mol. It is closely related to the defect structure of the solid reactant. William\(^{27}\) gave some examples of the mass transport of Fe atoms: the \(E_a\) of Fe in \(\alpha\)-Fe is 251 kJ/mol, the \(E_a\) of Fe in \(\gamma\)-Fe is 284 kJ/mol.

The reaction rate constant \(k\) can be calculated depends on the rate controlling step. Based on the un-reacted shrinking core model, the mathematical formulations for gaseous diffusion, chemical and mixed control reactions were described elsewhere\(^{14,26,28}\) and are listed as follows:

Chemical control:

\[
1 - (1 - R)^{\frac{1}{3}} = F(R) = kt \quad \text{.......... (9)}
\]

Diffusion control:

\[
1 - \frac{2}{3} R - (1 - R)^{\frac{2}{3}} = G(R) = kt \quad \text{.......... (10)}
\]

Mixed control:

\[
\frac{I}{F(R)} = t_d \left[ 3F(R) - 2F(R)^2 \right] + t_c
\]

\[
t_d = \frac{\rho_0 r_0^2}{6D_e (C_0 - C_e)} \quad t_c = \frac{\rho_0 n_0 K_e}{k_1 (1 + K_e) (C_0 - C_e)} \quad \text{......... (11)}
\]

Where,

\(r_0\) – initial particle radius, m

\(t\) – residence time, s

\(R\) – overall reduction degree, between 0 and 1

\(k_1\) – the forward reaction rate constant, m/s

\(D_e\) – effective diffusion coefficient, m\(^2\)/s

\(\rho_0\) – initial oxygen density, mole/m\(^3\)

\(C_0\) – reducing gas concentration at the particle surface, mole/m\(^3\)

\(C_e\) – equilibrium concentration of reducing gas, mole/m\(^3\)

\(K_e\) – gas equilibrium constant

4.2. Kinetic Data

The reaction kinetics of gas-solid particle reduction, mixed reduction and gas-molten particle reduction in Fig. 4 should be discussed separately. The mixed reduction in zone 2 must have the features of both gas-solid particle reduction in zone 1 and gas-molten particle reduction in zone 3. Since the ratio of the solid particles to the molten particles in the collected samples of the mixed reduction was difficult to be quantified, the kinetic data was not obtained. The fully molten particles were obtained only at two temperatures: 1700 K (700–2020 ms) and 1750 K (210–2020 ms). In addition, the reduction degree reached the equilibrium state rapidly at 1750 K, therefore the kinetic data of gas-molten particle was not clear based on the current obtained experimental results and it will be studied further in the near future. The experimental results of gas-solid particle reduction in Fig. 2 (zone 1 in Fig. 4) were dealt with Eqs. (9)–(11). If the plot of \(F(R)\) versus \(t\) gives a straight line, the rate controlling step is chemical reaction. If the plot of \(G(R)\) versus \(t\) gives a straight line, the rate controlling step is gaseous diffusion. If it is a mixed control, the plot of \(t/F(R)\) versus \(3(F(R) - 2F(R)^2)\) would give a straight line. The kinetic plots and the correlation coefficients of the plots at the three temperatures are shown in Fig. 13. The correlation coefficients were used elsewhere,\(^{18,25}\) which was helpful in judging the linear relationship of lines. It was found that the kinetic plots of chemical control at the three temperatures have the best linear relationship compared to gaseous diffusion control and mixed control. Therefore, the rate controlling step of gas-solid particle reduction can be regarded as the chemical reaction control.

The reaction rate constants were further calculated based on
on the rate controlling step from the slopes of the plots. The straight plots of $F(R)$ versus $t$ were drawn with the least square method and the reaction rate constants were calculated as shown in Fig. 14. It shows that $k$ goes up with the increase of temperature. At 1 550 K, the reaction rate constant is $0.75 \times 10^{-2}$ s$^{-1}$. At 1 600 K, the value is more than twice as great as that at 1 550 K, which is $1.60 \times 10^{-2}$ s$^{-1}$. At 1 650 K the reaction rate constant of $2.67 \times 10^{-2}$ s$^{-1}$ is more than 3 times as great as the result at 1 550 K.

The effect of temperature on the reaction rate constant is expressed by the Arrhenius equation which can be converted to Eq. (12). The Arrhenius equation can be obtained from experimental data at different temperatures by calculating the pre-exponential factor ($A$) and activation energy ($E_a$).

\[
\ln k = \frac{-E_a}{RT} + \ln A \quad \text{(12)}
\]

The plot of $\ln k$ versus $1/T$ was drawn in Fig. 15(a), with which $A$ was calculated from the intercept and $E_a$ was calculated from the slope. The $E_a$ was calculated to be 270.0 kJ/mol and the $A$ was 9.36 $\times$ $10^6$ s$^{-1}$. Finally, the reaction rate constant can be expressed by Eq. (13).

\[
k = 9.36 \times 10^6 \exp \left( \frac{-270000}{RgT} \right) \quad \text{(13)}
\]

In order to give more evidence for the reaction mechanism of gas-solid reduction, $E_a$ was also calculated by the Friedman’s method that belongs to model-free method.\(^{18,29}\) This method is a differential method as shown in Eq. (14). A plot of $\ln(\text{d}R/\text{d}t)$ versus $1/T$ gives $E_a$ from the slope since $R$ is regardless of the model. With the results of $R$ of gas-solid particle reaction as shown in Fig. 2, the corresponding relationship between the natural logarithmic rate of reduction ($\text{d}R/\text{d}t$) and the reciprocal of absolute temperature ($1/T$) was drawn in Fig. 15(b). The $E_a$ calculated from the slope of the plot is 271 kJ/mol which is slight higher than the result 270 kJ/mol calculated from model-fitting method. Therefore, from the microkinetics viewpoint, the rate controlling step is the mass transport of cations and electrons at the reaction interface.

\[
\ln \left( \frac{\text{d}R}{\text{d}t} \right) = \ln \left( A \Phi(R) \right) - \frac{E_a}{RgT} \quad \text{(14)}
\]
5. Conclusions

The reduction mechanism of fine hematite ore particles at high temperature has been investigated through the kinetic analysis. The reduction of hematite ore particles at the studied conditions which are also the typical conditions of the pilot plant of HIsarna process can be divided into three stages according to the physical state of the collected particles: gas-solid particle reduction, mixed reduction and gas-molten particle reduction. The gas-solid particle reduction took place at 1550 K and 1600 K at all the studied residence times of 210–2020 ms, and at 1650 K at the studied residence times of 210–970 ms. The mixed reduction took place at 1650 K at the residence times of over 970 ms and at 1700 K at the residence time of 210 ms. The gas-molten particle reduction took place at 1700 K at the residence times of over 210 ms and at all the studied residence times at 1750 K.

The kinetic model has been built based on the morphology study, the results of which showed that the un-reacted shrinking core model could describe both gas-solid particle reaction and gas-molten particle reaction. The rate controlling step of gas-solid particle reduction at the typical operating conditions of smelting cyclone has been obtained by the model-fitting method, and then confirmed by the model-free method. The activation energy of the gas-solid particle reaction was about 270 kJ/mol. The results revealed that the reaction rate controlling step of gas-solid reduction was chemical control from the macrokinetics viewpoint, and the rate controlling step was the mass transport of cations and electrons at the reaction interface from the microkinetics viewpoint. The activation energy and rate controlling step of gas-molten particle reduction were still not clear based on the current experimental data and will be investigated in the following study. On the other hand, through morphology study, it was found that a quantity of micro pores was formed during the reduction process mainly due to the loss of oxygen from the particles and the construction of iron oxides during the melting process. The micro pores largely facilitated the diffusion of gaseous from the outer surface of particle through the product layer to the reaction interface. The results of kinetic analysis offered a good understanding of the melting and reduction behaviour of fine hematite ore particles in the smelting cyclone and provided kinetic data for the further mathematical modelling of the HIsarna process. It will eventually help in the scaling up the pilot plant of the process, together with the CFD reactor model. According to the identified rate controlling step in this study, the operating parameters of the smelting cyclone could be adjusted to intensify the reduction process.

Acknowledgments

This research was carried out at Delft University of Technology and was financially supported by the Materials innovation institute M2i (www.m2i.nl) under the project M41.5.09327. The authors would like to express their thanks to Mr. Jan van der Stel and Mr. Jeroen Link from Tata Steel (IJmuiden) for fruitful discussions and providing process data for this study. The first author acknowledges the China Scholarship Council (CSC) for providing the scholarship during this research at Delft University of technology.

REFERENCES