Effect of Hydrogen Addition on Reduction Kinetics of Iron Oxides in Gas-injection BF

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The gas-injection BF is a new iron-making technology with injecting gas instead of the traditional pulverized coal injection and recycling the BF top gas through the gasifier. Compare with traditional BF, there is a larger amount of reducing gas such as CO and H2 in gas-injection BF. Effect of H2 addition on reduction kinetics of iron oxides in gas-injection BF was investigated by Thermogravimetric Analysis. The result shows that the reduction rate of iron oxides rise with the increase in both temperature and H2 content. By contrast with the H2 content increasing from 10% to 15% at 700°C and 900°C, the improvement of reduction rate is more obvious when addition from 15% to 20% at the same temperature. For comparison, it shows an opposite result in the condition of 1 000°C. In addition, the efficiency of H2 on reduction rate can be neglected as the content is less than 5%. The reaction mechanism was obtained according to the unreacted core model. In the condition of 30% CO+10% H2, both the diffusion rate and interfacial reaction rate reveal an increasing trend with the increase of temperature, of which the degree of improvement in diffusion rate is more significant, which leads to the interface reaction gradually being the controlling step. The same case occurs with the increase of H2 at 900°C. Under the condition of experiment, the activation energy decreases with H2 addition, which illustrates that the reduction of iron oxides become more easily to perform with the rich hydrogen in gas-injection BF.

KEY WORDS: reduction kinetics; hydrogen content; unreaction core model; reduction rate.

1. Introduction

The blast furnace (BF) is the main process of the iron and steel industry, which emits over 70% of the CO2 and consumes the most energy.1) The traditional blast furnace relies on the coke seriously and the coke rate contributes to a great extent of the whole production cost. Most of the new trends in blast furnace technology focused on developing a new coke alternative such as natural gas injection, pulverized coal, waste plastic, biomass, coke oven gas and other hydrocarbons injection.2–9) The utilization of these sources, however, depends strongly on the developed technologies and wealthily district resources.10) In addition, top gas recycling blast furnace (TGR-BF) have received an increasing interest in recent decades in order to reach the strict targets of energy conservation as well as low emission of CO2.10,11) Top gas recycling and tuyere injection of oxygen are the primary technologies studied in the ULCOS project.12) Currently, a number of studies on TGR-BF have been carried out, such as the analysis of flow and combustion of reducing gas in tuyere, CO2 emission and energy consumption.11,13–15) Nonetheless, the clear limitation for the development of above technology is that how to capture and disposal CO2 of BF top gas, which implies the additional cost as $56/tCO2.16) Currently, pulverized coal injection (PCI) is still the main means for reducing coke rate.17) The highest amount of pulverized coal injection reported is approximately 250 kg/thm while the amount of coke is similar as previous. However, the impact of chemical properties of the coal should be not left out, which may cause problems for complete combustion within raceway, gas permeability in the shaft, dirtying of deadman zone and, as a consequence, irregular furnace operation and decreasing productivity.11,18) The gas-injection BF is a new iron-making technology with injecting gas into tuyeres and recycles the BF top gas through the gasifier, which can provide a new gas source and effectively translates CO2 in BF top gas into CO as a lower cost. Compared with traditional BF with PCI, the gas injection technology could simplify the iron making process and recycle the BF top gas, which can contribute to lower emissions and high productivity. The technological process as follows: BF top gas as the gasifying agent is injected into gasifier→coal gasification occurs in the gasifier→H2-rich gas is produced→H2-rich gas is heated in gas heating device→the high temperature gas and hot air are injected into the furnace through the tuyere. The technological process is shown in Fig. 1.

In addition, the inferior coal possessing the properties high-volatile and high-ashes can be utilized in the gas-
making process which not only make the blast furnace smelting get rid of high-quality coke, but also make the hydrogen content in gas injected increase to improve the BF production efficiency.

In the gas-injection BF, the reduction behavior of iron oxides will be dominated by the high concentration of reducing gas such as CO and H2. This paper focuses on the effect of hydrogen addition on the reduction kinetics of iron oxides aiming to clarify the reaction mechanism and determine the optimum hydrogen content in gas-injection BF.

2. Experimental Method

The pellets produced by industry process were taken as testing samples. The chemical compositions are shown in Table 1.

The schematic layout of experimental apparatus which can measure the iron mass continuously is shown in Fig. 2. The rated power and the highest heating temperature are 8 kW and 1200°C, respectively. The output of the balance was fed to a strip chart recorder to record the weight changes as a function of time.

In the reduction experiment, 500 g pellets with the size of 10–12.5 mm were put into the reduction reactor. Then the reduction reactor was heated up at the rate of 10°C/min in electric furnace. The pellets were heated up to the required temperature and subsequently kept for 30 min to minimize the temperature fluctuation. During the whole process of heating and holding, nitrogen as the shielding gas was filled into the reduction tube at a rate of 5 L/min. After that, reducing gas mixtures were used to reduce the pellets with the flow rate of 15 L/min as shown in Table 2. The reducing gases were replaced by nitrogen after the reaction and the reduction tube was taken out from the furnace to cool down until room temperature.

3. Results and Discussion

3.1. Effect of H2 Content on Reduction Behavior of Iron Oxides

The reduction of ferric oxides in the blast furnace experiences three steps: Fe2O3→Fe3O4→FeO→Fe. The FeO reduction is the most difficult step and the requisite atmosphere condition is the strictest. FeO reduction with CO is an exothermic reaction while FeO reduction with H2 is an endothermic reaction, and the reduction behavior of iron oxides in mixed atmospheres of CO–H2 is complex. On the basis of the results obtained from thermodynamic calculation, the highest H2 content is set to 20% to ensure the exothermicity during the reduction of FeO in gas-injection BF.

3.1.1. Effect of H2 Addition on Weight Loss of Pellets

The weight loss of sample under different H2 contents at 700°C is shown in Fig. 3. It can be clearly seen that the weight of sample decreases continuously along with the reduction time, and at the same reaction time, the weight loss of sample exhibits a positive correlation with H2 content. In addition, there is a large weight loss of sample at the initial stages of reduction, followed by a slowing down in the weight loss until the end of reduction. XRD analysis of samples before and after reduction at 700°C under different atmospheres was carried out and the results are shown in Fig. 4. It is observed that the pellet is mainly composed of hematite, magnesium ferrites oxide (MgFe2O4) and iron silicon oxide phase (Fe2.45Si0.55O4) before reduction. In contrast, metallic iron is the predominant phase after reduction, furthermore, a small amount of Fe0.9Si0.1, Al0.7Fe3Si0.3, MgFe2O4 and Fe2.95Si0.05O4 are also identified. In addition, the peak of reduced products becomes remarkable as H2 content enhances, while that of both Fe2O3 and FeO greatly weaken.

![Fig. 1. Process of gas-injection BF.](image1)

![Fig. 2. Schematic diagram of reduction experimental.](image2)
even disappear, which reflects that H₂ addition in atmosphere can improve the reduction efficiency of the pellets.

3.1.2. Effect of H₂ Addition on Reduction Degree and Rate

The relationship between the reduction degree of pellets and the reduction time under different H₂ contents at 700°C, 900°C and 1 000°C are obtained as Figs. 5(a), 5(c) and 5(e) respectively. And the functional relation of the reduction degree and reduction time is found to fit the logarithmic function by trial and error method, which also shows that the reduction of pellets is in accordance with the first order reversible reaction. The reduction rate was obtained by solving the first order differential equations of reduction degree, and the results are shown in Figs. 5(b), 5(d) and 5(f) respectively.

As can be seen from Fig. 5, the reduction rate is faster and the reduction degree increase rapidly at the initial stages of reduction, and then become less pronounced in the later stage due to the resistance of thick product layer. The addition of H₂ has a positive effect on the reaction extent. From Figs. 5(a) and 5(b), the reduction degree can reach to 87.32% after 2.5 h with 30% CO+20% H₂ while that is only 60.41% with 30% CO+5% H₂ at 700°C, and the reduction rate of former should be about 2 times than the latter. The results prove that the hydrogen is a kind of much more effective reducing gas than CO even though the temperature is lower than 847°C, which originates from the molecular size of H₂ (collision diameter 2.915 Å) less than that of CO (collision diameter 3.590 Å) as well as the diffusion coefficient of H₂ in solid more than 3 times than CO diffusion coefficient.

As shown in Figs. 5(b), 5(d) and 5(f), the reduction rate of iron oxides increase with the increase in both temperature...
and H\textsubscript{2} content, while in different extents of H\textsubscript{2} content, the increase rate of reduction is different when H\textsubscript{2} content goes up in the same range. When the H\textsubscript{2} content less than 5\%, it has a weak effect on the reduction rate. The reduction rate increase most obviously with the increase of H\textsubscript{2} from 15\% to 20\% at 700\°C and 900\°C. With regard to 1 000\°C, there is a greater impact on the increase of reduction rate with the increase of H\textsubscript{2} content from 10\% to 15\% than from 15\% to 20\% and the reduction rate increase slowly above 15\%, which could illustrate that content of H\textsubscript{2} is no longer the primary factor for regulating the increase of reduction rate when it’s above 15\%, and thus the H\textsubscript{2} content in gas-injection BF should be lower than 15\%.

### 3.1.3. Effect of H\textsubscript{2} Addition on Microstructure of Pellets

The micro distribution of Fe element with the H\textsubscript{2} addition is shown in Fig. 6. It's not hard to see Fe elements clusters into classes of spherical or bulk with 30\%CO+0\%H\textsubscript{2}, and continue to aggregation and growth. According to the classical nucleation theory, only more than the critical radius (r*) can the nuclei exist stably. Unstable nucleus would spontaneously move to stable nucleus resulting in grain aggregation and growth to reduce the surface energy. Comparing Figs. 6(a) and 6(b), H\textsubscript{2} addition enhances the rate of the nucleation and grain growth. Furthermore, a large of ferric crystal nucleus could be homogeneous distribution along with lots of the iron ion saturated appearing among the original nucleus and growing throughout the old phase with H\textsubscript{2} addition, which results in a dense metallic layer forming. Comparatively speaking, the reduction process with 30\%CO +0\%H\textsubscript{2} is accompanied with a metallic phase migration and for the reason that the critical radius is larger and the aggregation and growth of grain will rely on the stable crystal nucleus.

### 3.2. Effect of Temperature on Reduction Behavior of Iron Oxides

Figure 7 groups the isotherms of pellets reduction at different temperature. As can be seen from Fig. 7, the higher temperature in the range 700–1 000\°C corresponds to the more efficient reaction, which is due to the reduction of FeO by H\textsubscript{2} being the endothermic reaction and the reduction ability of H\textsubscript{2} strengthening with the increase of temperature. From Fig. 7(b), when the H\textsubscript{2} content is 5\%, it makes little contributions on the reduction rate with the increase of temperature, which could conclude that the H\textsubscript{2} content is the reduction restriction factor for the reaction instead of temperature when H\textsubscript{2} content is less than 5\%. So the H\textsubscript{2} content in the gas-injection BF should be more than 5\%.

When the H\textsubscript{2} content reaches to 20\%, the degree and rate of reduction at 900\°C are close to that at 1 000\°C. Obviously it could conclude that H\textsubscript{2} is no longer the limiting factor for reduction reaction once its content above 20\%, and the H\textsubscript{2} content in gas-injection BF should be lower than 20\%.

The XRD patterns of the samples at the atmosphere of CO=30\%, H\textsubscript{2}=10\% under different temperatures are shown in Fig. 8. The main phase of pellets is metallic iron, Fe\textsubscript{0.9}Si\textsubscript{0.1}, Al\textsubscript{0.1}Fe\textsubscript{2}Si\textsubscript{0.3}, MgFe\textsubscript{2}O\textsubscript{4} and it also contains a small amount of Fe\textsubscript{3}O\textsubscript{4}FeO which not been reduced and Fe\textsubscript{2.95}Si\textsubscript{0.05}O\textsubscript{4} at 700\°C. With the increase of temperature, however, Fe\textsubscript{3}O\textsubscript{4} and FeO greatly are reduced, and then the diffraction peaks of MgFe\textsubscript{2}O\textsubscript{4} and Mg\textsubscript{2}SiO\textsubscript{4} remarkably weaken, which presents that iron oxides are reduced firstly and followed by the reduction of MgFe\textsubscript{2}O\textsubscript{4} and Mg\textsubscript{2}SiO\textsubscript{4}.

### 3.3. Kinetic Model for Reduction of Iron Oxides

The kinetic modeling for the reduction of iron oxides is very important for understanding the kinetics of the reduction process which will help to increase productivity and to improve the gas utilization in gas-injection BF. While the kinetic models for the reduction of iron oxides with H\textsubscript{2} or CO have been largely investigated by many researchers, the kinetics of the reduction with H\textsubscript{2}–CO mixtures is rather limited. What is more the reduction kinetics of iron oxides with H\textsubscript{2}–CO mixtures was generally simulated and predicted by mathematical modeling. K. Piotrowski investigated the kinetics of hematite (Fe\textsubscript{3}O\textsubscript{4}) to wustite (FeO) based on Johnson-Mehl-Avrami-Erofe’ev equation. They found that this initial stage of the reaction process could be interpreted as a both phase-boundary-controlled reaction. A. Bonalde proposed grain model that considers the particle size and porosity to describe the reduction of hematite pellets with Midrex gas. And the predictions of the model were compared with the experimental results. It is very important to develop an optimum model in the investigation of a specific technology. In this paper, in order to explore the mechanism of iron ore reduction and to identify the optimal addition amount of H\textsubscript{2} in gas-injection BF, the kinetic model is established based on the theory of unreacted shrinking core model which is vastly used for kinetics of iron ore reduction. In addition, the water gas shift reaction is also taken into account in this kinetics model.

A series of reactions occurring in succession during the process of ferric oxides reduction in the blast furnace above 570\°C: Fe\textsubscript{3}O\textsubscript{4}→Fe\textsubscript{2}O\textsubscript{3}→FeO→Fe\textsubscript{2}O\textsubscript{3}+H\textsubscript{2}→FeO→Fe. In the reduction series, the transformations of Fe\textsubscript{2}O\textsubscript{3}→FeO and Fe\textsubscript{3}O\textsubscript{4}→FeO are much easier than that of FeO→Fe, thus the two former reactions can be ignored in the kinetics analysis. In addition, the water gas shift reaction will also take place besides for the reduction of iron oxides, which will restrict the gas utilization in gas-injection BF. The FeO reduction in the gases mixture and the water gas reaction can be expressed as follows:

\[
\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \quad \ln K_{\text{FeO}}^\theta = 1.94 - 2.818.14 / T \quad \ldots \ldots (1)
\]

\[
\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O} \quad \ln K_{\text{FeO}}^\theta = -2.92 + 2.742.36 / T \quad \ldots \ldots (2)
\]
CO + H₂O = CO₂ + H₂  \ln K_w = -4.03 + 4.49275/T  \quad (3)

K′ in the gases mixture of Eqs. (1) and (2) can be presented as follows:

\[ K′ = \phi_{\text{H}_2} K_{\phi_{\text{H}_2}} + \phi_{\text{CO}} K_{\phi_{\text{CO}}} \]  \quad (4)

Where \( \phi_{\text{H}_2} \) and \( \phi_{\text{CO}} \) is mole fraction of H₂ and CO respectively.

The FeO reduction equilibrium constant (\( K^\theta \)) in the kinetic model of interface reaction is the minimum of \( K′ \) and \( K_w \) as described by following:

\[ K^\theta = \min(K′, K_w) \]  \quad (5)

The \( K^\theta \) for different reduction conditions can be obtained by Eq. (5) and results are shown in Table 3.

The effect of H₂ addition on the reduction kinetics of iron oxides can be analyzed by the shrinking core model of unchanging size, the kinetic equation and its integral form are presented as follows:\(^{33}\)

\[
\frac{dR}{dt} = 3(c^0 - c^*) \left( \frac{1}{k_g} \left(1 - \frac{R}{R_{\text{crit}}} \right)^{\frac{2}{3}} \right) \left( \frac{D_{\text{eff}}}{1 + K^\theta} \right)^{\frac{1}{3}} \left( \frac{k_g}{1 + K^\theta} \right) \left( c_0 \rho_o \right) \]  \quad (6)

\[
I = \frac{\rho_o \rho_f}{(c^0 - c^*)} \left( \frac{R}{3k_g} + \frac{R}{6D_{\text{eff}}} \left[ 1 - \left(1 - \frac{R}{R_{\text{crit}}} \right)^2 \right] \right) \]  \quad (7)

Where \( R \) is the reduction extent of pellets, \( t \) is the reduction time, \( D_{\text{eff}} \) is effective diffusion coefficient, \( k_g \) is mass transfer coefficient of gas boundary layer, \( K^\theta \) is the equi-

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**Fig. 8.** XRD patterns of the samples with H₂=10% at different temperatures.

**Table 3.** \( K^\theta \) under different reduction conditions.

<table>
<thead>
<tr>
<th>T/°C</th>
<th>30%CO+0%H₂</th>
<th>30%CO+5%H₂</th>
<th>30%CO+10%H₂</th>
<th>30%CO+15%H₂</th>
<th>30%CO+20%H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.27</td>
<td>0.27</td>
<td>0.31</td>
<td>0.33</td>
<td>0.35</td>
</tr>
<tr>
<td>900</td>
<td>0.17</td>
<td>0.20</td>
<td>0.23</td>
<td>0.26</td>
<td>0.29</td>
</tr>
<tr>
<td>1000</td>
<td>0.14</td>
<td>0.18</td>
<td>0.22</td>
<td>0.25</td>
<td>0.28</td>
</tr>
</tbody>
</table>
librium constant, \( r_0 \) is characteristic initial radius of pellets, \( \rho_0 \) is oxygen density in pellets, \((c^0-c^\ast)\) is the concentration gradient of reducing gas.

In the reaction process, the gas flow rate is 7.32 cm/s. The effect of external diffusion can be negligible as the gas flow rate is above 5 cm/s. Therefore, it is presumed that the reaction rate might be controlled by three mechanisms: 1) the intrinsic interfacial chemical reaction (Eq. (8)), 2) the diffusion including internal diffusion of reactant and product gas species through solid product layer (Eq. (9)), and 3) the combination of 1) and 2) presented by Eq. (10).

\[
t = k_1 \left[ 1 - (1-R)^3 \right] \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ Quad...
As shown in Fig. 9, the slopes of diffusion-controlled line are 0.10178, 0.28482 and 0.42849 while the slopes of chemical-controlled line are 0.12652, 0.265 and 0.34251 at 700°C, 900°C and 1000°C respectively. The apparent rate constant of internal diffusions increases more obviously than the apparent rate constant of chemical reaction with the increase of temperature. Therefore, rate-controlling step will transform from mixed model to chemical reaction with the increase of temperature.

Figure 10 shows the functions using the experimental results for interfacial chemical reaction control and internal diffusions controls respectively at 900°C with different H₂ addition.

It can be seen from Fig. 10, H₂ addition has a significant effect on reduction mechanism. Similar to the effect of temperature (Fig. 9), the gap between the two control curves gradually becomes smaller with the increase of H₂, and the two control curves intersect when H₂ addition is above 10%. The rate-controlling step of iron oxides reduction has been determined by comparing the value of R². This conclusion can be drawn that the rate-controlling step should be the mixed model when the H₂ addition is below 10%, and that should be the interfacial chemical reaction when the H₂ addition is above 10%. And there is transformation of reduction mechanism when H₂ addition is 10% (Fig. 10(c)). The reduction rate is controlled by the interfacial chemical reaction within 1.75 h (Fig. 10(d)), and then controlled by the mixed model in the later stage. The results indicate that, in the gas-injection BF, the rate-controlling step will transform from mixed model to chemical reaction model with the increase of H₂ addition, which is deduced from the case that the apparent rate constant of internal diffusions...
increases more obviously than the apparent rate constant of chemical reaction.

The rate-controlling step of iron oxides under different conditions has been shown in Table 4. The reduction rate is mainly controlled by the mixed model composed of interfacial reaction and internal diffusions without H₂ addition. However, when the H₂ addition is 5%–20%, there is a transition from mixed controlled model to chemical-controlled model with the increase of temperature and H₂ addition.

At 900°C, the relative resistance of internal diffusion decrease with the increase of H₂ addition for the reason that the diffusion coefficient of H₂ in solid is 3 times than that of CO diffusion coefficient. In addition, the phase of poor reduction, such as MgFe₂O₄ and FeₓSiyO₄, will faster generate with the increase of temperature and H₂ addition in the gases, which cause the relative resistance of interfacial chemical reaction increase during the process of the reduction.

3.3.2. Effect of H₂ Addition on Arrhenius Activation Energy

The best fitting model can be further used to derive the kinetic parameters of reaction rate constant (k) and effective diffusion coefficient (Dₑ) as shown in Table 5.

The activation energy can be obtained from the Arrhenius equation (Eqs. (11)–(14)) by using the results of k and Dₑ in Table 5.

\[
D_e = D_0 e^{-E_{e0}/RT} \quad \text{(11)}
\]
\[
k = A e^{-E_a/RT} \quad \text{(12)}
\]
\[
\ln D_e = -E_{e0}/RT + \ln D_0 \quad \text{(13)}
\]
\[
\ln k = -E_a/RT + \ln A \quad \text{(14)}
\]

Where \( E_{e0} \) and \( E_a \) are the activation energy of internal diffusion and chemical reaction respectively, A is pre-exponential factor, R is molar gas constant.

The activation energy can be obtained according to the plots of lnk and lnDe0 vs. 1/T as shown in Table 6 by using the two element regression method.

From the Table 6, we can see the activation energy values decrease with the increase in H₂ content, resulting in the reaction rate increasing at a given temperature, which indicates that the reduction of iron oxides would easily occur with the H₂ addition in the reducing mixture.

4. Conclusion

(1) Both the reduction extent and rate of pellets increase with the increase of temperature and H₂ addition in gases, no matter is the temperature below or above 810°C. However, the effect is different when the H₂ content increases in the same range. The reduction rate increases most obviously with the increase of H₂ from 15% to 20% below 900°C. However, there is a greater impact on the reduction rate with the increase of H₂ content from 10% to 15% than that from 15% to 20% at 1000°C. In addition, when the H₂ content is less than 5%, it has little effect on the reduction rate. Considering the effect of H₂ addition on the reduction rate, the H₂ content should be 5%–15%.

(2) The controlling step of reduction rate is obtained...
according to the shrinking core model. The results show that, when the H₂ addition is 5%–20%, there is a transition from mixed controlled model to chemical-controlled model with the increase of temperature and H₂ addition.

3) The relative resistance of internal diffusion gradually increases during the process of reduction with the increase of product layer. At the same temperature, the relative resistance of internal diffusion decreases with the increase of H₂ addition. In addition, the phase of poor reduction, causes the relative resistance of interfacial chemical reaction increases during the process of the reduction.

4) The activation energy value decreases considerably with H₂ addition in reducing mixture, which indicates that the reduction of iron oxides would easily occur with the H₂ addition in the reducing mixture.

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