Kinetics of Cementite Formation from Reduced Iron in CO–H₂–H₂S Mixtures under Pressurized Conditions

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In the present authors’ previous study, the rate of iron carbide formation from completely reduced iron ore was gravimetrically measured in CO–H₂–H₂S mixtures of sulfur activity 0.035 to 0.6 at the total pressure of 0.1 to 0.6 MPa and at the temperature of 773 to 1 023 K. From the experimental results under the wide conditions, it was derived that the rate of iron carbide formation was controlled by the carburization reaction on the pore surface of reduced iron. In this study, the integrated rate equation for the first order reaction, \( -\ln(1 - f) = (g(T) - 1) \), was applicable to cementite formation curves, \( f \) versus \( t \) relation, in the range of iron carbide formation, i.e. \( f < 0.6 \). The value of \( g(T) \) is proportional to the total pressure of carbon monoxide, \( p_{CO} \), in the reaction gas containing hydrogen more than 20 %. From the dependency of \( g(T) \) on \( p_{CO} \), it was assumed that the rate controlling elementary reaction for the carburization of reduced iron is the dissociative adsorption of carbon monoxide on the pore surface. Following the elementary reaction, the rate equation for the carburization was derived substituting the adsorption isotherm for sulfur; \( g(T) = K_{CO} \left( \frac{p_{CO}}{p_{CO} + a_{CO} + \frac{K_{S}}{T}} \right) \). The relation between \( p_{CO} \) and the rate equation was applied to the data for \( g(T) \) to obtain \( K_{CO} \) and \( K_{S} \). At the individual temperatures, the good linear relation \( f(T) = \frac{1}{2} \) to obtain \( K_{CO} \) and \( K_{S} \). The rate equation substituted with the values of \( K_{CO} \) and \( K_{S} \) for the carburization simulated reasonably well the carbide formation curves in the range \( f < 0.6 \).

KEY WORDS: iron carbide; cementite; formation curve; first order reaction; carburization rate; partial pressure; carbon monoxide; dissociative adsorption; rate equation; sulfur; adsorption isotherm.

1. Introduction

Production of iron carbide started in Trinidad in 1994.1) Since then, fundamental studies2)–17) concerning iron carbide production from iron ore have been actively performed. Since iron carbides are thermodynamically meta-stable, however, it is not formed until the carbon activity of the reaction gas is increased beyond unity. Therefore, the decomposition of iron carbides and the precipitation of free carbon may become serious problems. On the formation of iron carbide, therefore, no reliable kinetic study has been conducted until quite recently. The present authors2)–15) have found out that almost pure iron carbides are producible by preventing not only the decomposition of iron carbide but also the precipitation of free carbon by adding a little amount of H₂S to CO–H₂ mixtures. Thus, reduced iron can be converted completely to carbides at sulfur activities less than unity, i.e. without any formation of FeS.

In our previous studies,7)–9,13) the rate of carbide formation from completely reduced iron ore in H₂–H₂S mixtures was accurately measured in CO–H₂–H₂S mixtures by gravimetric technique at 973 K. But, the measurements of the carbide formation rate were made only under total pressures 0.1013 MPa (1 atm) or less.

In this study, the experimental results concerning the iron carbide formation reported in the previous study,18) which was conducted by using new equipment of a high-pressure type usable up to 1 MPa, is theoretically analyzed and a reaction mechanism is proposed. Based on the proposed reaction mechanism, the rate equation for the formation of cementite, which is one of the two iron carbides, i.e. \( \theta \)-iron carbide (cementite, Fe₃C) and \( \chi \)-iron carbide (Fe₅C₂), formed from reduced iron in CO–H₂–H₂S mixtures, is derived. The rate of formation of Fe₃C will be soon reported.

2. Rate Analysis and Discussions

2.1. Analysis of the Rate of Cementite Formation from Completely Reduced Iron

The reactions for the carburization of completely reduced iron ore to form iron carbides are the following parallel reactions, i.e. (1) and (2), and consecutive reactions, i.e. (1) or (2), (3) and (4).

\[
\begin{align*}
2CO(g) &= [C] + CO_2(g) \quad \text{(1)} \\
CO(g) + H_2(g) &= [C] + H_2O(g) \quad \text{(2)}
\end{align*}
\]

\[
\begin{align*}
2CO(g) + 2H_2O(g) &= [C] + H_2(g) \quad \text{(3)} \\
2CO(g) + H_2O(g) &= [C] + H_2(g) + CO_2(g) \quad \text{(4)}
\end{align*}
\]
A model for the formation of cementite is shown in Fig. 1. The formation of cementite (Fe₃C) proceeds through the following steps: i) diffusion of the reaction gas components in bulk gas phase, ii) diffusion in gas film on a thin bed of reduced iron particles, iii) diffusion in the bed, iv) diffusion in he particles, v) carburization reactions on interior pore surface of the particles, vi) the diffusion of carbon in metallic iron of the particles, and vii) cementite formation on the interface between metallic iron and cementite. The carburization experiments were conducted in so much flow of the interface between metallic iron and cementite. The carburization reactions were not observed during the conversion of iron to iron carbides. Thus, it was assumed that the ratio of the specific pore surface area in m² kg⁻¹ (initial reduced-iron)⁻¹, A_p, of un-reacted reduced iron at f_p to the initial specific surface area, A_p₀, of reduced iron at f_p=0 in m² kg⁻¹ (initial reduced-iron)⁻¹ is equal to 1−f_p,  

\[ \frac{A_p}{A_p_0} = 1 - f_p \]  

Further assuming that the carburization reactions proceed on the pore surface of un-reacted reduced iron, the rate of the carbide formation as the rate of carbon take-up per unit mass of reduced iron, \( df_p/df \), is expressed by Eq. (6),  

\[ df_p/df = A_p \varphi'(p,T) d_p \]  

where \( \varphi'(p,T) \) is the carburization rate per unit surface area in kg(C) m⁻²s⁻¹, \( d_p \) the ratio of the mass of carbon relative to the mass of metallic iron in cementite in kg(C) kg⁻¹ (initial reduced-iron)⁻¹, \( p \) the dimensionless partial pressure of gaseous component i in Pa/10¹³²⁵Pa, \( T \) the reaction temperature in K and \( t \) the reaction time in s. Defining an overall carburization rate, \( g(p,T) \), as a function of component’s partial pressures, temperature and the initial specific surface area by Eqs. (7), (8) is finally derived as the rate equation for the carburization,  

\[ g(p,T) = A_p \varphi'(p,T) d_p \]  

\[ df_p/df = g(p,T)(1 - f_p) \]  

Integrating Eq. (8) under the initial condition of \( f_p = 0 \) at \( t = 0 \), the integrated rate equation for the first-order reaction was derived as,  

\[ -\ln(1 - f_p) = g(p,T)t \]  

Equation (9) was applied to the carbide formation curves, which were gravimetrically measured in the reac-
tion of completely reduced iron ore with CO–H₂–H₂S mixtures of the total pressures up to 0.6 MPa. Typical examples of the rate analysis by \(-\ln(1-f_q) versus t\) are shown in Fig. 3. Through the points in the range \(f_q<0.6\), a straight line with good linearity can be drawn for each carbide formation curve. In fitting the straight line through the data points, the points very close to \(t=0\) were excluded because of anticipated larger error by gas exchange from nitrogen to the reaction gas. From the gradients of the lines, the values of \((p, T)\) were evaluated. The points in the range of \(f_q>0.6\) deviate somewhat upwards from the linear equation with respect to time. In all the studies in fluidized bed which were conducted to produce iron carbides in CO–H₂–H₂S mixtures, Fe₅C₂ was always observed to start being formed in the later stage of \(f_q<0.5\) or 0.6. Considering the results, it would be reasonable that the deviation from the linear relation in Fig. 3 may be attributable to the formation of \(\chi\)-phase iron carbide (Fe₅C₂).

2.2. Dependency of Carburization Rate, \(g(p, T)\), on the Composition and Total Pressure of Reaction Gas Mixtures

The variation in the value of \(g(p, T)\) with the composition of the reaction gas and the total pressure is shown in Fig. 4 (a), 4(b) and 4(c), respectively at 873, 923 and 973 K. At the individual temperatures and individual total pressures, the value of \(g(p, T)\) is the maximum around 20% hydrogen and, with departing from there on either side, the value of \(g(p, T)\) decreases gradually. Furthermore, in the composition range of more than 20% hydrogen, the values of \(g(p, T)\) at individual temperatures and individual total pressures are about on a line drawn through the point \(p_{H_2}/p_{T}=1\) and \(g(p, T)=0\) although, at 873 K, one point deviates largely from the line. Observing the data at fixed compositions, on the other hand, the value of \(g(p, T)\) increases with increasing the total pressure.

The relationship between the value of \(g(p, T)\) and the partial pressure of carbon monoxide is summarized in Fig. 5 for all the experiments conducted in CO–H₂–H₂S mixtures at various total pressures at 873, 923 and 973 K. According to the results, the value of \(g(p, T)\) is proportional to \(p_{CO}\) in the compositions containing more than 20% of hydrogen, i.e. less than 80% of carbon monoxide, with sulfur activity \(a_s=0.5\) at the individual temperatures. But, with further decreasing the content of hydrogen down to less than 20% in CO–H₂–H₂S mixtures, the value of \(g(p, T)\) gradually decreases deviating the proportional relation to the partial pressure of carbon monoxide. This deviation is seen about the points which locate at relatively higher pressures of carbon monoxide, i.e. relatively lower pressures of hydrogen, at the individual total pressures. In other words, the points locating at right hand side of the points in the individual total pressure range shows a tendency to deviate downwards from the linear relation.

2.3. Mechanism of Carburization Reactions for Cementite Formation from Reduced Iron

The kinetics of carburization and decarburization of iron in CO–CO₂, CO–H₂ and CH₄–H₂ gas mixtures were studied by Grabke et al. Turkdogan et al. Fruehan et al.
and so on. In their studies, however, it is only the initial carburization rate at nearly zero carbon content that the rate was theoretically and quantitatively analyzed. Even formulating the initial rate as a function of the composition and total pressure of the carburizing gas, and temperature is too complicated to be thoroughly established. In this study, the assumption is made on the basis of the experimental results that the carburization of iron in CO–H₂–H₂S mixtures may control the rate of carbide formation from reduced iron. Grabke et al. 19–22) showed that the elementary reactions for the carburization of iron in CO–CO₂ mixtures as

\[
\text{CO} \rightarrow \text{[C]} + \text{O(ad)} \quad \text{(10)}
\]

\[
\text{O(ad)} + \text{CO} \rightarrow \text{CO}_2 \quad \text{(11)}
\]

and in CO–H₂ mixtures as

\[
\text{CO} \rightarrow \text{[C]} + \text{O(ad)} \quad \text{(12)}
\]

\[
\text{O(ad)} + \text{H}_2 \rightarrow \text{H}_2\text{O} \quad \text{(13)}
\]

The carburization rate in CO–He gas mixtures increased more strongly than proportional relation to the partial pressure of carbon monoxide in correspondence to the reaction (11). And the rate in CO–H₂ gas mixtures increased in proportion to the partial pressure of carbon monoxide in correspondence to the reaction (12).

In this study, from the dependency of the value of \( g(p, T) \) on the 1.0 power to the partial pressure of carbon monoxide in correspondence to the reaction (12). On the other hand, in the gas mixtures containing less than 10% of hydrogen, the rate of carbide formation slows down in spite of the increase in the partial pressure of carbon monoxide where the dependency of \( g(p, T) \) on \( p_{\text{CO}} \) becomes to be proportional to the power greater than 1.0 to \( p_{\text{CO}} \) as can be seen in Fig. 5 and Fig. 6, which is rearranged in a logarithmic–logarithmic relation from Fig. 5. That is, in higher contents of hydrogen, removing the adsorbed oxygen, O(ad), by the reaction (13) is very fast and the rate of the reaction (12) controls the rate of iron carbide formation. But, as the content of hydrogen decreases, removing the adsorbed oxygen becomes gradually slower to reach the rate controlling condition of oxygen removal by the reactions (11) and (13), ultimately only reaction (11). In this limiting condition, the reaction (13) may come to be controlled by the feed rate and/or diffusion rate of hydrogen.

In the present authors’ previous study 13) which was conducted in CO–H₂–H₂S mixtures under the total pressure of 0.03 to 0.1 MPa by mixing nitrogen to the reaction gas, the value of \( g(p, T) \) was proportional to 1.7 power to the total pressure of the gas mixtures containing 20% and more of hydrogen. The reason why the pressure dependence of \( g(p, T) \), i.e. to 1.7 power, was much greater than that in the present study, i.e. to 1.0 power, is not clear. But two reasons are supposed. One is the much narrower total pressure range, i.e. 0.03 to 0.1 MPa, compared the range in the present study, i.e. 0.1 to 0.6 MPa. Another possible reason may be the incomplete reduction of iron ore particles in H₂–H₂S mixtures. Even a little amount of remained wustite could severely affect the rate of iron carbide formation.

2.4. Derivation of Carburization Rate Equation and Determination of Rate Constants

In the condition containing more than 20% hydrogen, assuming that the reaction (12) controls the carbide formation rate, the rate Eq. (14) was derived,

\[
g(p, T) = k_{\text{CO}}(p_{\text{CO}} - a_c p_{\text{H}_2}/K_2 p_{\text{H}_2}) \theta \quad \text{(14)}
\]

where \( a_c \) is the carbon activity in iron in equilibrium with cementite, \( K_2 \) the equilibrium constant for the reaction (2) and \( \theta \), the surface coverage of vacant adsorption site on the pore surface of reduced iron.

Sulfur is one of the oxygen group elements in the periodic table of elements, which oxygen group elements com-
monly possess the surface-active nature. And the rate retarding effect of sulfur is well known with the reactions such as carburization, decarburization, nitrogenization, denitrogenization, the water gas shift reaction and so on which proceed on the surface of metals such as iron, nickel and so on. According to Grabke et al., the surface coverage of sulfur, $q_S$, on metallic iron is expressed by a Langmuir adsorption isotherm and the coverage of vacant site, $q_{H2S}$, is expressed by Eq. (15)

$$q_{H2S} = \frac{1}{1 + K_S a_S}$$ ........................(15)

where $K_S$ is the adsorption coefficient of sulfur. The adsorbant other than sulfur is hardly conceivable in the carbide formation from reduced iron in CO–H2–H2S mixtures.

In this study, the iron ore particles were reduced in H2–H2S mixtures and, after flushing the atmosphere in the reaction tube with nitrogen, the reduced iron particles were carburized in CO–H2–H2S mixtures with the same sulfur activity as in the reduction step. Consequently, it may be reasonably assumed that sulfur adsorbed on the interior pore surface of reduced iron is in equilibrium with the reaction gas mixture. On the sulfur adsorbed surface of reduced iron which was also saturated with cementite, the carburization reactions of the reactions (2) and/or (1) proceeded. Therefore, the adsorption isotherm of Eq. (15) for sulfur was thought to be applicable to the carburization reactions in this study. Substituting Eq. (15) in Eq. (14), Eq. (16) was derived,

$$g(p_r,T) = k_{CO}(p_{CO} - a_Cp_{H2}/K_S p_{H2})/(1 + K_S a_S)$$ ......(16)

Rearranging Eq. (16) in the condition $p_{H2}=0$, the following equation was derived,

$$p_{CO}/g(p_r,T) = (K_S/k_{CO}) a_S + 1/k_{CO}$$ ...............(17)

The plot in the relation between $p_{CO}/g(p_r,T)$ and $a_S$ for the data at 823 to 973 K is shown in Fig. 7. At each temperature, there can be seen a good linear relation though the linearity is slightly poor for the data at the highest temperature 973 K. From the gradients and the segments at $a_S=0$ of the straight lines, the values of $k_{CO}$ and $K_S$ were estimated. The temperature functions for $k_{CO}$ and $K_S$ are shown in Fig. 8.

From the linear relation in $\ln k_{CO}$, versus $1/T$ and $\ln K_S$ versus $1/T$, the temperature functions of the Arrhenius type for $k_{CO}$ and $K_S$ are determined excluding the data at 973 K. The determined equations are represented,

$$k_{CO} = 4.93 \times 10^2 \exp(-41 \text{kJ} \cdot \text{mol}^{-1}/RT)$$ ......(18)

$$K_S = 1.50 \times 10^{-7} \exp(47 \text{kJ} \cdot \text{mol}^{-1}/RT)$$ ......(19)

The activation energies for $k_{CO}$ and $K_S$ were 41 and −47 kJ/mol, respectively. The former value is positive, but the
latter is negative. Grabke and Tauber reported the activation energy 200 kJ/mol for the rate constant of the carburization of α-iron with CO–H₂ mixtures in the temperature range from 873 to 1098 K. The main reason of the difference is the decrease in the specific surface area of reduced iron with increasing temperature in this study. With respect to the value of \( K_S \), they reported \( K_S \) at 1123 K while the value calculated from Eq. (19) at 1123 K is 2.3. The reason why the value obtained in this study is much less than their value might be attributed to the difference in the physical properties of iron, i.e. iron foil with Grabke et al. and the very reactive iron with this study, which was iron reduced from iron oxide at the low temperatures with hydrogen.

Finally the carbide formation curves from reduced iron were simulated by applying the rate Eqs. (16) and (9), where the Eqs. (18) and (19) were used as for the values of \( k_{CO} \) and \( K_q \). Typical comparison is shown in Fig. 9 for the carbide formation from the reduced iron in the conditions of 80%CO–H₂–H₂S mixture of \( x_S =0.5 \) at 873 K. In the later period \( f_0 >0.8 \), all the experimental curves gradually deviate from the calculated ones. This can be explained by the fact that, in this study, the kinetics have been established taking into account only the formation of cementite, i.e. the initial period of the carbide formation \( f_0 <0.6 \). Now, the kinetics for the formation of \( \chi \)-iron carbide is being developed. As for the formation of cementite in the conditions of 0.4 MPa or less, the simulation is good enough to simulate the carbide formation, but the simulation is a little poor in the condition of 0.6 MPa, which is the most deviated case from the experimental ones of all the simulated curves, in the various conditions. In Fig. 3, the rate analysis was conducted excluding the very initial points. This is one apparent reason of the derivation, which indicates that the calculated curves should be slightly moved to right hand side. Considering it, the simulation by Eqs. (16), (18) and (19) can be used for the simulation of cementite formation from completely reduced iron.

In the studies by Grabke et al., the activity of carbon and partial pressures of the carburizing gases appear as their linear polynomial expression in the denominator of the carburization rate equation. But, in this study, the sulfur activity is the only derivative species present in the denominator and the other gases or their derivative species are not there. The reason is discussed below.

According to Grabke et al., the reactions and the rate equation for the carburization in CO–He mixtures was represented as follows,

\[
CO(gas) = O(ad) + C(in Fe) \quad (20) \\
O(ad) + CO(gas) \rightarrow CO_2(gas) \quad (21) \\
O(ad) + H_2(gas) \rightarrow H_2O(gas) \quad (22)
\]

\[
v_{20} = k_1(1 - \theta_o)P_{CO} - k'_1\theta_o \rho_C \quad (23)
\]

\[
v_{21} = k_2\theta_{ad} P_{CO} \quad (24)
\]

Where \( v_{20} \) and \( v_{21} \) are the carburization rate of reactions (20) and (21), \( k_1 \) and \( k'_1 \) the rate constants of the forward and backward reactions for the reaction (20), and \( k_2 \) the rate constant for the reaction (21). Using the condition for stationary state, \( v_{20} = v_{21} \), the surface coverage of the vacant site, \( \theta_{ad} \), can be calculated

\[
\theta_{ad} = k_1 P_{CO} (k_1 P_{CO} + k'_1 P_{CO} + k'_2 \rho_C) \quad (25)
\]

And \( \theta_o \) is introduced in Eq. (24) to derive the carburization rate, \( v \).
\[ v = k_1 k_2 p_{CO} (k_3 p_{CO} + k_4 p_{CO} + k_5 a_s) \]  \hspace{1cm} (26)

For the initial rate of the carburization at \( a_s = 0 \) and with the assumption \( k_1 \gg k_2 \)

\[ v = k_2 p_{CO} \]  \hspace{1cm} (27)

In CO–H\(_2\) mixtures, the rate of reaction (22) is

\[ v_{22} = k_3 \theta_{a} p_{H_2} \]  \hspace{1cm} (28)

where \( k_3 \) is the rate constant for the reaction (22). The steady state condition for the carburization in CO–H\(_2\) is

\[ v_{20} = v_{21} + v_{22} \]  \hspace{1cm} (29)

because the adsorbed oxygen is removed not only with H\(_2\) but also CO. The rate equation results

\[ v = (k_1 k_2 p_{CO} + k_4 k_5 p_{CO} p_{H_2}) (k_3 p_{CO} a_s + k_2 p_{CO} + k_3 p_{H_2}) \]  \hspace{1cm} (30)

With the assumption \( k_1 p_{H_2} \gg k_2 p_{CO}, k_2 p_{CO} \) the following equation is obtained

\[ v = k_1 p_{CO} \]  \hspace{1cm} (31)

The carburization rate equations, Eqs. (27) and (31), were derived in the conditions of CO–H\(_2\)–H\(_2\)S mixtures not containing H\(_2\)O, where \( \frac{\theta_{a}}{p_{CO}/T} \), \( \frac{\theta_{s}}{p_{CO}/T} \), and \( \frac{\theta_{o}}{p_{CO}/T} \) were determined from the linear relation between \( p_{CO}/T \) and \( a_s \). The temperature functions of the Arrhenius-type for \( k_{CO} \) and \( K_{a} \) were determined, i.e. Eqs. (18) and (19).

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