Carburization of Iron by Ar–CO–H₂ at 1523 K

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The rate of carburization of iron in Ar–50%CO–10%H₂ gas mixture at 1523 K have been gravimetrically investigated. It is found that the Ar–CO–H₂ system carburizes faster than Ar–CO, because H₂ combines faster with adsorbed oxygen than does CO. Based on the established results of H₂O and CO₂ dissociation rate, the rate constant (k₃) of the recombination reaction of H₂ and adsorbed oxygen (O ad) is calculated. It was found that k₃ is about 37.5 times larger than that (k₁) of CO and O ad, while the measured k₃ in the present study is only 2.5 times larger than k₁. With the increase of carbon content, the corresponding equilibrium pH₂O* at the reacting surface of Fe–C melt becomes sufficiently small. Accordingly the produced H₂O easily reaches to the equilibrium pressure of pH₂O* due to the very fast recombination reaction of the H₂ and O ad. This is the reason that the addition of H₂ has small contribution to the overall carburization reaction after liquid phase is formed. Take into account the effect of the produced H₂O, rate of carburization (v) in CO–H₂ atmospheres is given by the equation: v = k₁pCOθ₁ + k₃pH₂θ₂(1 – pH₂O/pH₂O*), where θ₂ is the fractional coverage by adsorbed oxygen, pH₂O is the partial pressure of formed H₂O at the interface.

KEY WORDS: carburization; CO–H₂ mixture; liquid Fe–C phase; CH₄ formation; high carbon iron.

1. Introduction

Carburization reaction has a very important role in the BF process and scrap melting processes. Many studies for carburization with CO gas for solid iron have been carried out,1–5) while for liquid iron, especially for high carbon Fe–C melt, has not been well studied despite of its importance. Recently the carburization reaction rate measurement was carried out to investigate the role of the liquid phase on the carburization process.6) It was concluded that the rate of the carburization reaction after the formation of the liquid Fe–C phase was controlled by the surface chemical reaction of:

\[ \text{CO} + \text{O ad} \rightarrow \text{CO}_2 \] ..............................(1)

with the subsequent reaction:

\[ \text{O ad} + \text{C ad} \rightarrow \text{CO} \] ..............................(2)

being sufficiently fast to be at virtual equilibrium. The subscript “ad” indicates the species that is adsorbed on the surface. It was also found that the carburization rate was significantly decreased once the liquid phase was formed.

Generally speaking, high carburization reaction rate is desirable from a viewpoint of melting process efficiency and cost, even after the liquid phase is formed. To continue the melting process, carbon must be supplied from the surface of high carbon Fe–C melt. The following reaction on the molten metal,

\[ \text{O ad} + \text{H}_2 \rightarrow \text{H}_2\text{O} \] ..............................(3)

is well-known to be much faster than that of the reaction (1).7–9) Therefore, the addition of H₂ to the CO gas may enhance the carburization rate which is already reported by several researchers.1–3) Most of these results, however, were based on the initial carburization rate or that under the low carbon content of less than 0.1 mass%. So it is not certain whether the same enhance effect can be expected for the carburization process with high carbon Fe–C melt of more than 3.4 mass%.

The present study for the carburization reaction of iron by CO–H₂ gas mixture was undertaken to evaluate the effect of H₂ addition on the carburization rate of the high carbon Fe–C melts by CO. The carburization rates have been measured gravimetrically at 1523 K and the growing phenomena of liquid Fe–C layer are also studied.

2. Experimental Details

The general experimental technique was essentially the same as that used in the previous study6) except for S content and H₂ addition. An iron plate (20×20×5 mm) was buried in Al₂O₃ powder contained in an alumina crucible (i.d. 30 mm) and heated by SiC furnace. The reacting Ar–CO–H₂ gas mixture was jetted to the surface through an alumina tube (i.d. 0.4 mm) held approximately 10 mm above the surface of the metal.

The Ar–CO–H₂ gas mixtures were prepared by mixing the deoxidized high purity gases of Ar and H₂, after drying, by passing through columns of magnesium percolate and, for CO, by passing through ascarite. Mass flow controllers were used to control flow-rates and gas compositions. All the experiments were carried out at 1523 K under flowing of Ar–50%CO–10%H₂. The typical impurity content (in mass%) of iron is: O, 0.04, C, 0.02, Al, 0.007, S, 0.005.
Relatively high S content compared with the previous study\(^6\) was intended to decrease the chemical reaction rate by blocking the available reaction sites. The specimen was prepared by surface grinding and metallographically polishing the upper surface.

The pre-weighed (about \(20 \times 10^{-3} \text{ kg}\)) sample was slowly brought to the aimed temperature under purified Ar flowing. The inlet tube was adjusted to the appropriate height and then the reaction gas, which had been preset, was introduced over the sample. After the predetermined reaction time, experiments were terminated by switching back to argon and the sample was pulled down to the lower part of the furnace allowing to cool to room temperature. During the experimental period, the exhausted gas composition was analyzed by using QMS. The weight gain of carbon during an experiment was determined by measuring the total weight gain of the sample. The carburized samples were sectioned and the cross sectional area and also the reaction surface area were observed by the optical microscope and SEM.

3. Results

To evaluate the effect mass transfer in gas phase, the dependence of the carburization rate on the gas flow rate was determined by preliminary experiments with total gas flow rates varying from \(3.3 \times 10^{-6}\) to \(23.3 \times 10^{-6} \text{ m}^3/\text{s}\). The reaction rates were independent of the total flow rate for the carburization in CO–Ar at the flow rate of more than \(6.66 \times 10^{-6} \text{ m}^3/\text{s}\). With Ar–CO–H\(_2\), the reaction rates still slightly increase with flow rates until \(11.66 \times 10^{-6} \text{ m}^3/\text{s}\) and became almost independent after \(23.3 \times 10^{-6} \text{ m}^3/\text{s}\). Further increase of flow rate over \(23.3 \times 10^{-6} \text{ m}^3/\text{s}\) make the reaction rate decrease, plausibly due to the temperature decrease of sample. Accordingly a more extensive range of flow rate condition was not investigated and all experiments with the H\(_2\) addition were carried out at the total flow rate of \(23.3 \times 10^{-6} \text{ m}^3/\text{s}\). It means that the results in the present study were still possibly under the effect of gas phase mass transfer. The effect of gas phase mass transfer on the carburization rates will be discussed later.

3.1. Reaction Rates

The weight gain of iron in Ar–50%CO–10%H\(_2\) with total flow rate of \(23.3 \times 10^{-6} \text{ m}^3/\text{s}\) as a function of time was measured at 1523 K as shown in Fig. 1 including that with Ar–50%CO as a reference. For all runs with and without H\(_2\), the liquid phase was observed after at least 15 min of the carburization time. The liquid phase formation was confirmed by the observation of the surface and the sectioned area of the surface region. The measured weight gains are also plotted logarithmically as a function of time in Fig. 2 where the lines are drawn with a slope of 2/3. From Fig. 2, it may be assumed that the weight gain after liquid phase formation (after 15 min) was proportional to \(t^{2/3}\) within experimental scatter that expressed experimentally by the following equation.

\[
W_g = k_{app} t^{2/3}
\] .................................(4)

where \(W_g\) is the weight gain, \(k_{app}\) is an apparent rate constant and can be a function of pCO and pH\(_2\). Apparent carburization rates can be evaluated by differentiating the Eq. (4).

\[
dW_g/dt = (2/3)k_{app} t^{-1/3}
\] .................................(5)

Calculated weight gain (in the unit of mg) curves based on the Eq. (4) are also presented by solid lines in Fig. 1.

The dependence of the carburization rate on the fractional surface coverage by the adsorbed oxygen (\(\theta_0\)) will be discussed later. The carbon concentration of the liquid phase will gradually increase with time. The carbon concentration of the liquid phase will be more than 3.4 mass\%.\(^{10,11}\) The slight increase of carbon concentration at the high carbon condition easily enhances the activity of carbon significantly.\(^{11}\) Thus, correspond with the slight increase of the carbon concentration, \(\theta_0\) will decrease relatively large amount since the reaction (2) is under the equilibrium condition. Thus the power of 2/3 dependence can be qualitatively explained based on the gradual decrease of \(\theta_0\) with time. Unfortunately, it is very difficult to measure the surface carbon concentration continuously. To understand the detail of the power of 2/3 dependence, the further work is needed to provide quantitative information of variation of the surface carbon concentration with time.
At the liquid–solid interface, the carbon concentration in the solid phase side is constant under the constant temperature. Therefore, the carbon diffusion rate in the solid phase is independent from the chemical reaction rate if the solid phase diffusion process is rate-limiting. With the addition of H₂, the weight gain increased about 50% compared with that without H₂ at the same reaction time as shown in Fig. 1. It simply means that the solid phase diffusion process is not rate-limiting. If the liquid phase diffusion process is assumed to be rate-limiting, the carbon concentration at the liquid surface will be equal to the saturated carbon concentration, since the reaction rate must be much faster than the diffusion rate. Then the liquid phase diffusion rate should be independent from the surface carbon concentration since the liquid phase diffusion process is also not the rate-limiting process in the present study.

3.2. Liquid Phase

The cross sectional view of the sample carburized by CO for 1 800 s is shown in Fig. 3. The small holes were observed between the surface layer and the matrix. The liquid phase was easily recognized by this distinctly different structure. The average thickness of liquid phase layer shown in Fig. 3 is about 5 µm although the thickness of the liquid phase layer is not evenly distributed. The liquid phase thickness of the most of samples were observed to be less than 5 µm and also uneven. The thin and uneven thickness made it very difficult to evaluate the reliable thickness of the liquid phase. Therefore, the variation of thickness due to the change of experimental conditions was not discussed in the present study.

Once the liquid phase was formed, the surface of the sample became corrugated so the formation of liquid phase was easily recognized by naked eye observation of the surface. Based on the surface observation, it was found that the liquid layer generally covered the whole area of samples. Some samples had no corrugated surface area at the corners. The effect of uncovered area by the liquid phase on the reaction rate was neglected, since those areas are less than 10% of total area.

3.3. Formation of CH₄

The typical variation of the mass spectroscopic intensity of CH₄ with time was shown in Fig. 4. H₂ gas was introduced at the time of 0 in Fig. 4. After the introduction, the intensity of CH₄ increased about 1 order and was held almost constant during the carburization process. To evaluate the amount of produced CH₄, the relation between the mass spectroscopic intensity ratio of I_{CH₄}/I_{Ar} and the flow rate ratio of Q_{CH₄}/Q_{Ar} was established by introducing the gas mixtures of different ratio of CH₄/Ar. The calibration gas mixtures were prepared by diluting CH₄ gas with appropriate amount of pure Ar gas. It was found that there is a good linear dependency between the I_{CH₄}/I_{Ar} and the Q_{CH₄}/Q_{Ar}. Using this relation, the average pCH₄ as shown in Fig. 4 is found to be about 1×10⁻⁶ Pa and is likely to be negligible. Therefore, the CH₄ formation during carburization process will be confirmed to have a little influence on the total carburization rate. The details of the method to evaluate the gas composition by using QMS is described everywhere.12–14)

4. Discussion

4.1. Carburization Rates of Iron by CO–H₂

The reaction mechanism of the carburization reaction of solid iron with CO and with CO–H₂ was reasonably established.1–3) Namely, under the condition that the chemical reaction process is the rate-limiting step, the carburization reaction with CO–H₂ can be expressed according to the following reaction sequence:

\[
\begin{align*}
CO & \rightarrow O_{ad} + C_{ad} \quad \text{(2)} \\
CO + O_{ad} & \rightarrow CO_2 \quad \text{(1)} \\
H_2 + O_{ad} & \rightarrow H_2O \quad \text{(3)} \\
C_{ad} & \rightarrow C \quad \text{(6)}
\end{align*}
\]

where C is the dissolved carbon and the reaction (3) can be further broken down to the elementary steps:

\[
\begin{align*}
H_2 & \rightarrow 2H_{ad} \quad \text{(7)} \\
O_{ad} + 2H_{ad} & \rightarrow H_2O \quad \text{(8)}
\end{align*}
\]

The reaction (7) has been known to be very fast and at virtual equilibrium. Therefore, it is not possible to distinguish
between (3) and (8) where both give the same rate law and only the reaction (3) is considered.

Shatansky and Grabke\textsuperscript{11} initially assumed that the reaction (2) would be the rate-limiting step based on the very large rate constants for forward and reverse reactions of (3). Later, Kapersma and Shay\textsuperscript{3} carried out the carburization of iron with CO–H\textsubscript{2}–N\textsubscript{2} gas mixture with varying pH\textsubscript{2}/pN\textsubscript{2} by keeping the constant pCO. Their results clearly showed that the carburization rate increased with the increase of pH\textsubscript{2}. This result indicates that the reaction (2) is faster than that of (3), which means that the reaction (2) is not the rate-limiting step. Thus the carburization reaction of solid iron with CO–H\textsubscript{2} is confirmed to be controlled by the adsorbed oxygen removal reaction of (3).

Several works\textsuperscript{6,15–17} for the carburization of molten iron with CO have been carried out. Unfortunately, most of these results\textsuperscript{15–17} were found to be under the effect of mass transfer process. In the previous work,\textsuperscript{6} based on the established chemical reaction rate constant of CO\textsubscript{2} dissociation on the liquid iron, it was confirmed that the rate of the carburization reaction after the formation of the liquid Fe–C phase was controlled by the reaction of:

\[
CO + O_{ad} \rightarrow CO_2 \tag{1}
\]

As already mentioned, no work of the carburization of molten iron with CO–H\textsubscript{2} has been reported. Also the rate of CO dissociation on the liquid iron has not yet been established. Itoh \textit{et al.}\textsuperscript{19} investigated the reaction of levitated molten iron droplet with CO at more than 2073 K. They found that the reaction (2) dominantly occurred initially until the concentration of C and O reached to the line of C–O concentration relation that was determined by the equilibrium gas composition with the condition of CO\textsubscript{2} + CO = 1 (atm). After that, the carburization was proceeded by the reaction (1) with the reaction (2) being at virtual equilibrium. They discussed that the initial rate might be still under the effect of liquid phase mass transfer. Even so, it was clearly shown that the reaction (2) is much faster than (1). Most interesting finding was that the carbon and oxygen were dissolved in the melt by equimolar amount before they reached to the equilibrium. It means that the oxygen and carbon supply rate by CO dissociation is so fast that the contribution of the oxygen removal by the reaction (1) is negligible. Deviation from the equimolar ratio of C/O is seemed to be less than 1% from their observed result. Therefore, the rate of reaction (2) may be about 100 times faster than that of the reaction (1). Later it will be discussed that the reaction rate constant of the reaction (3) is found to be about 35 (at 1523 K) to 15 (at 1873 K) times larger than that of the reaction (1). Compared with these values, it can be said that the reaction (2) is much faster than the reaction (3) on the liquid iron surface. Namely, under the condition that the chemical reaction is rate-limiting, the adsorbed oxygen removal reaction of (3) will be most plausibly the rate-limiting step for the carburization of the molten iron with CO–H\textsubscript{2}. Kishi and Roberts\textsuperscript{18} reported that CO rapidly dissociated on iron films even at 350 K. This result also strongly support that the dissociation of CO can be indeed very fast reaction at high temperature. Actually there are no particular reasons to consider that the reaction (3) suddenly becomes faster than the reaction (2) after the liquid phase formation.

Thus for the carburization reaction of iron with CO–H\textsubscript{2}, applying that the dissociation reaction rate of (2) and (6) is significantly faster than those of reactions (1) and (3), and also neglecting their backward reactions, the forward carburization rate (\(v\)) can be expressed by:

\[
v = k_1pCO\theta_0 + k_3pH_2\theta_0
\]

\[
= k_1pCO(1 + k_3pH_2/k_1pCO)\theta_0 \tag{9}
\]

where \(\theta_0\) is the fractional coverage by oxygen. \(k_1\) and \(k_3\) represent forward rate constant of reactions (1) and (3) respectively. \(\theta_0\) can be determined from the general equilibrium adsorption isotherm,

\[
\theta_0/(1 - \theta_0 - \theta_3) = K_0a_O \tag{10}
\]

\[
\theta_3/(1 - \theta_0 - \theta_3) = K_3a_S \tag{11}
\]

where \(\theta_3\) is the fractional coverage by sulfur and \(K_0\) and \(K_3\) are the absorption coefficient for oxygen and sulfur respectively. \(a_O\) and \(a_S\) are the activity for oxygen and sulfur. The values of \(K_0\) and \(K_3\) will be changed by the standard state of activity. Combined Eqs. (10) and (11), \(\theta_0\) is expressed by:

\[
\theta_0 = K_0a_O/(1 + K_3a_O + K_3a_S) \tag{12}
\]

Since the CH\textsubscript{4} production rate is very small, the contribution of CH\textsubscript{4} formation to the over-all carburization rate was neglected in the Eq. (9). Based on the Eq. (9), the increase of the carburization rate with the addition of H\textsubscript{2} can be attributed to the term of \(k_3pH_2/k_1pCO\). From the ratio of the apparent carburization rate with and without H\textsubscript{2} addition at 60 min, the apparent ratio of \(k_3/k_1\) is determined to be about 2.5. Namely, the rate constant of reaction (3) is about 2.5 times larger than that of (1).

Shatansky and Grabke\textsuperscript{11} and also Fruehan\textsuperscript{3} measured carburization rate of solid iron by CO–He and CO–H\textsubscript{2} mixture. By using initial carburization rates, both concluded that the rate constant for CO–H\textsubscript{2} was about a factor of five greater than that for carburization in CO alone. Kapersma and Shay\textsuperscript{3} studied the carburization of solid iron at 1198 K and concluded that carburization rate constant for CO–H\textsubscript{2} was 44 times larger than that for CO alone. But their rate equation contained several doubtful bases and their value was not reliable, rather \(k_3/k_1\) of 9.5 is evaluated using their initial carburization rates. All these data\textsuperscript{1,2,4} were obtained for the low carbon solid iron surface, where there is no studies on the carburization of high carbon liquid iron in CO–H\textsubscript{2} mixtures as far as we know.

The rate constants of CO\textsubscript{2} and H\textsubscript{2}O dissociation on the molten iron, \(k_2\) and \(k_4\) respectively, have been well established as a function of temperature.\textsuperscript{9,19–24} Recently Sasaki and Belton\textsuperscript{20} measured the apparent first-order rate constant ratio for the dissociation reaction of CO\textsubscript{2} and H\textsubscript{2}O with liquid iron at 1823 to 1973 K by using the steady state method. The average values of \(k_2/k_1\) from their work\textsuperscript{9} are reproduced in Fig. 5 comparatively those of other studies\textsuperscript{9,19–21} for the H\textsubscript{2}O and CO\textsubscript{2} decarburization. From Fig. 5, the value of \(k_2/k_1\) at 1573 K is estimated to be about 10. If the reaction:

\[
CO + O_{ad} \rightarrow CO_2 \tag{1}
\]
is considered, equilibrium will occur when:

$$k_1 pCO \theta_0 = k_2 pCO_2 (1 - \theta_0 - \theta_3) ...............(13)$$

Thus,

$$k_2/k_1 = (pCO/ pCO_2) \frac{K_{H_2O}}{K_{CO_2}} ...............(14)$$

where $k_2$ is the rate constant of the backward reaction of (1), $K_0$ is the adsorption coefficient of oxygen with respect to the (pO2)$^{1/2}$ and $a_0$ is the activity of oxygen presented by (pO2)$^{1/2}$ with the standard state of 1 atm$^{1/2}$. $K_0$ is the adsorption coefficient of oxygen and $K_{CO_2}$ is the equilibrium constant for the reaction$^{25}$:

$$CO_2 = CO + 1/2 O_2 .................(15)$$

Equilibrium in the H$_2$O–H$_2$ reaction may be also expressed as:

$$k_3 pH_2 \theta_0 = k_4 pH_2O (1 - \theta_0 - \theta_3) ...............(16)$$

Hence,

$$k_4/k_3 = (pH_2/ pH_2O) \frac{K_{H_2O}}{K_{CO_2}} ...............(17)$$

where $k_4$ is the rate constant of the backward reaction of (3) and $K_{H_2O}$ is the equilibrium constant for the reaction$^{25}$:

$$H_2O = H_2 + 1/2 O_2 .................(18)$$

Combined Eqs. (14) and (17),

$$k_3/k_1 = K_{CO_2}/K_{H_2O} k_4/k_2 ...............(19)$$

Substituting the required values into Eq. (19), the value of $k_3/k_1$ at 1523 K is easily calculated to be about 35.7. Namely, the rate constant of the forward reaction of (3) at 1523 K is about 35.7 times larger than that of the reaction (1) and is significantly large compared with the measured value of 2.5. This difference strongly suggests that the carburization reaction with CO–H$_2$ after the liquid phase formation will not be controlled by the chemical reaction at the surface and possibly be influenced by the gas phase mass transfer process. In view of the experimental scatters shown in Fig. 5, and the accumulated error in the thermodynamic data used in the calculation, the value of 35.7 may change slightly, but its fundamental feature will not be changed.

### 4.2. Evaluation of H$_2$O Formation

The calculated H$_2$O/H$_2$ and CO$_2$/CO equilibrated with Fe–C system at 1523 K as a function of carbon content is shown in Fig. 6. This figure shows that the equilibrated H$_2$O/H$_2$ and CO$_2$/CO ratio are about $10^{-3}$ for the Fe–C melt with the carbon content of more than 3.5 mass%.

The CO and H$_2$ gas supply rate in the present condition are $11.66 \times 10^{-6}$ m$^3$/s and $2.33 \times 10^{-6}$ m$^3$/s or about 0.03 and 0.006 mol/min respectively. The experimental average production rate of CO$_2$ estimated from the results obtained in Fig. 1 is about $1 \times 10^{-5}$ mol/min. Thus the nominal conversion ratio of CO$_2$/CO is about $3 \times 10^{-4}$. Compared with the equilibrium CO$_2$/CO ratio at 35.7 mass% C, the conversion ratio of CO$_2$/CO is 1/3 of the equilibrium one. If we assume that the reaction rate constant of reaction (3) is 35.7 times larger than that of (1) and take into account the pH$_2$ of 10 kPa, the supposed production rate of H$_2$O will be 1.5$\times$10$^{-4}$ mol/min. Then the calculated conversion ratio of H$_2$O/H$_2$ is about 0.025 and is well above the equilibrium H$_2$O/H$_2$ ratio.

In the present experimental condition, the H$_2$O production in the reaction (3) certainly cannot be neglected for the total carburization reaction. Then the previous assumption that the chemical reaction is the rate-limiting step may need some corrections. Thus the rate equation, Eq. (9), can be modified by taking account of the backward reactions as:

$$v = k_1 pCO \theta_0 - k_2 pCO_2 (1 - \theta_0 - \theta_3)$$

$$+ k_1 pH_2 \theta_0 - k_4 pH_2O (1 - \theta_0 - \theta_3)$$

$$= k_1 pCO \theta_0 (1 - ((pCO_2/pCO)/(pCO_2/pCO)^*)$$

$$+ k_1 pH_2 \theta_0 (1 - ((pH_2O/pH_2)/(pH_2O/pH_2)^*)$$

$$..............(20)$$

where (pCO$_2$/pCO)* and (pH$_2$O/pH$_2$)* are the equilibrium pCO$_2$/pCO and pH$_2$O/pH$_2$ ratios for the particular $\theta_0$ on the Fe–C melt. As already mentioned, (pCO$_2$/pCO)/(pCO$_2$/pCO)* is 1/3 and can be neglected as a first approximation. Then,

$$v = k_1 pCO \theta_0 + k_1 pH_2 \theta_0 (1 - ((pH_2O/pH_2)/(pH_2O/pH_2)^*)$$

$$.........................(21)$$
Since the value of equilibrium conversion ratio of \((\text{pH}_2\text{O}/\text{pH}_2\text{})^3\) is less than \(1\times10^{-3}\), \(\text{pH}_2\text{}/\text{pH}_2\text{~}^3\) is reasonably assumed to be 1. Then Eq. (21) can be converted to the following form,

\[
V = k_1\text{pCO}\theta_0 + k_3\text{pH}_2\theta_0(1-\text{pH}_2\text{O}/\text{pH}_2\text{O}^*) \tag{22}
\]

Substituting the value of \(\text{pH}_2\), \(\text{pCO}\) and the calculated \(k_1/k_3\) in the present condition into Eq. (21), the value of \(\text{pH}_2\text{O}/\text{pH}_2\text{O}^*\) is calculated to be about 0.93 which indicate that the reaction (3) is almost under equilibrium. At the same time, it is reflected that the addition of \(\text{H}_2\) to \(\text{CO}\) has no dominant effect on the total carburization process in the present study.

Based on these discussions, it can be said that the carburization rate of iron by \(\text{CO}\) may be enhanced by the \(\text{H}_2\) addition with the iron of very low carbon condition but not for that with high carbon content. With increase of carbon content, the corresponding equilibrium oxygen potential (or equilibrium \(\text{pH}_2\text{O}^*\)) at the reacting surface become sufficiently small. Therefore, the produced \(\text{H}_2\text{O}\) easily reached to the equilibrium pressure due to the very fast reaction of (3). As a result, the addition of \(\text{H}_2\) has little contribution to the overall carburization reaction of high carbon Fe–C alloy.

By supplying the high gas flow rate of \(\text{H}_2\), \(\text{pH}_2\text{O}/\text{pH}_2\text{O}^*\) ratio may be decreased. However, this condition to conquer the gas phase mass transfer resistance may not be practically attained. This is because the increase of \(\text{H}_2\) flow rate easily decreases the surface temperature of sample and rather blows off the liquid phase layer at the surface. To confirm the effect of \(\text{H}_2\) on the carburization experimentally, another approach such as carburization of levitated molten Fe–C droplet under high gas flow rate must be carried out.

5. Conclusions

The rate of carburization of iron in \(\text{Ar}–50\%\text{CO}–10\%\text{H}_2\) gas mixture at 1 523 K have been gravimetrically investigated. The following results were obtained.

(1) The liquid and solid diffusion processes are not rate-limiting, since the addition of \(\text{H}_2\) increases the weight gain about 50% compared with that without \(\text{H}_2\).

(2) The liquid phase formation in \(\text{Ar}–\text{CO}–\text{H}_2\) atmosphere is observed at least after the carburization time of 15 min.

(3) The \(\text{CH}_4\) formation during the carburization process is confirmed to have little influence on the total carburization rate.

(4) The observed rate constant of the reaction (3) is experimentally determined to be about 2.5 times higher than that of reaction (1), while it is calculated to be about 37.5 times larger from the reported rate constant ratio of \(k_2/k_4\).

(5) The carburization rate of iron by \(\text{CO}\) may be enhanced by the \(\text{H}_2\) addition under low carbon condition but not for high carbon condition. Since the produced \(\text{H}_2\text{O}\) may reach to the corresponding \(\text{pH}_2\text{O}^*\) at the reacting surface with increase of the carbon content.

(6) Taking into account the effect of the produced \(\text{H}_2\text{O}\), the carburization rate \((v)\) in \(\text{CO}–\text{H}_2\) atmospheres is deduced to be given by the equation:

\[
v = k_1\text{pCO}\theta_0 + k_3\text{pH}_2\theta_0(1-\text{pH}_2\text{O}/\text{pH}_2\text{O}^*).
\]

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