Decarburization Rates of Liquid Iron by H$_2$O in High Sulphur Concentration Range

By Yasushi SASAKI** and G. R. BELTON***

Recently, Shigeno et al.1) studied the decarburization of liquid iron between 1 573 and 1 773 K by H$_2$O at high sulphur concentrations. Previously, Sain and Belton2) measured the rates of decarburization of liquid iron by CO$_2$ and found that there was a small residual rate at the apparent sulphur saturation. The residual reaction rates were also found in the reaction of nitrogen with liquid iron.3) In this communication, the work of Shigeno et al. was examined if the residual rate was also existed, and if possible, to derive the chemical reaction rate constant by taking into account of the residual rates.

Unfortunately, most of the rates measured by Shigeno et al. were under the effect of the mass transport process even at high sulphur concentrations. But some results of the low sulphur concentrations might be analyzed as a mixed controlled system. In this case, the apparent rate might be expressed on the assumption of Sugino et al. by

$$\text{Rate} = \frac{P k_{ap}}{k_p} \ln \left(1 + \frac{P_{H_2O}}{P_{H_2O}}\right) \quad \ldots \ldots \ldots (1)$$

and

$$\frac{1}{k_{ap}} = \frac{1}{k_p} + \frac{1}{k_d} \quad \ldots \ldots \ldots (2)$$

where,

- $P$: the total pressure (atm)
- $k_{ap}$, $k_p$, $k_d$: the apparent and chemical rate constants at a particular sulphur concentration respectively (mol/m$^2$ sec atm)
- $P_{H_2O}$: the partial pressure of H$_2$O at the bulk gas phase
- $m$: the mass transport coefficient
- $P_{H_2O}$: the partial pressure of H$_2$O at the interface.

From Eq. (3), if the $P_{H_2O}$ was obtained, $k_d$ was easily calculated. In this case, it is possible to assume that the $P_{H_2O}$ is equal to the partial pressure of a decarburization reaction (4).

$$C + H_2O = H_2 + CO \quad \ldots \ldots \ldots (4)$$

By substituting the calculated $P_{H_2O}$ to Eq. (3), $k_d$ can be evaluated. The results are shown in Table 1.

$$\nu/(1 - \nu) = K_s(a_s) \quad \ldots \ldots \ldots (5)$$

where, $\nu$: the fractional coverage of sulphur
- $K_s$: termed the adsorption coefficient for sulphur
- $(a_s)$: the activity of sulphur, taken to be the weight percent of sulphur in the carbon saturated alloy.

Secondly, sulphur is supposed to block the reacting sites. The apparent chemical reaction rate constant is expressed by

$$k_d = (1 - \nu) k_t \quad \ldots \ldots \ldots (6)$$

where, $k_t$: the chemical reaction rate constant on the other symbols have their usual meanings. It was reported that the rate was fully controlled by the mass transport process at low sulphur concentration of 0.0001 (wt%). In this case, the rate may be expressed by

$$\text{Rate} = \frac{P k_d}{k_t} \ln \left(1 + \frac{P_{H_2O}}{P_{H_2O}}\right) \quad \ldots \ldots \ldots (3)$$

where, $P_{H_2O}$: the partial pressure of H$_2$O at the interface.

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| Table 1. Calculated $k_d$ in Eq. (3). |
| Temperature (K) | 1573 | 1673 | 1773 | 1873 |
| $k_d$ (mol/m$^2$-sec-atm) | 12.7 | 18.99 | 19.48 | 19.9 |

Table 2. Calculated apparent rate constant (k$_{ap}$).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Sulphur (wt%)</th>
<th>Apparent rate (g/m$^2$-sec)</th>
<th>$k_{ap}$ (mol/m$^2$-sec-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1573</td>
<td>0.7 ~0.8</td>
<td>0.54</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>0.07</td>
<td>1.55</td>
<td>8.50</td>
</tr>
<tr>
<td>1673</td>
<td>0.07 ~0.8</td>
<td>1.55</td>
<td>8.51</td>
</tr>
<tr>
<td></td>
<td>0.3 ~0.4</td>
<td>1.9</td>
<td>10.42</td>
</tr>
<tr>
<td></td>
<td>0.07</td>
<td>2.4</td>
<td>13.16</td>
</tr>
<tr>
<td></td>
<td>0.045</td>
<td>2.6</td>
<td>14.26</td>
</tr>
<tr>
<td>1773</td>
<td>0.7 ~0.8</td>
<td>1.84</td>
<td>10.69</td>
</tr>
<tr>
<td></td>
<td>0.4 ~0.5</td>
<td>2.25</td>
<td>12.00</td>
</tr>
<tr>
<td></td>
<td>0.07</td>
<td>2.6</td>
<td>14.26</td>
</tr>
</tbody>
</table>

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** Formerly Department of Metallurgy, University of Newcastle, N.S.W. 2308, Australia. Now at New Materials Research Laboratories, Nissin Steel Co., Ltd., Koya-shinmachi, Ichikawa 272.
the bare surface (mol/m²·sec·atm). With the combination of Eqs. (5) and (6)
\[ k_s = k_t/(1 + K_s(a_0)) \] .....................(7)
At the high sulphur concentration, \( K_s(a_0) \) has a very large value. This reduce to
\[ k_s = k_t/K_s(a_0) \] .....................(7')
The rate constant as a function of reciprocal of the activity of sulphur are represented in Fig. 1. Within the experimental scatters, it seems that there is a linear dependence of \( k_t \) on the reciprocal of the sulphur concentrations, but with a residual rate at \( 1/(a_0) \to 0 \). Actually, the number of data is too few for evaluating the precise rate constant, but the fundamental feature will not be changed. Accordingly, an apparent chemical reaction rate constant can be written in the form
\[ k_c = k_t/K_s(a_0) + k_R \] .....................(8)
where, \( k_R \): the residual reaction rate constant (mol/m²·sec·atm).
This experimental expression is also established at the case of decarburization with CO₂ and with the same values for \( K_s \) as those given by the low sulphur concentration data. Therefore, it would be reasonable to assume that the values for \( K_s \) given by the low sulphur concentration data can be used for the decarburization with H₂O.

From the slope in Fig. 1, \( k_t \) can be evaluated if \( K_s \) is known. Sain and Belton measured the values of \( K_s \) under the carbon saturated condition. The work of Shigeta et al., however, was not under the carbon saturated condition. But, at this moment, there are little reliable information to estimate the \( K_s \) under the particular carbon content. Therefore, in this communication, the values of Sain and Belton are used as a first approximation.

\[ \log K_s = 3.600/T + 0.57 \] .....................(9)
The evaluated values of \( k_t \) (mol/m²·sec·atm) are shown in Table 3 and in Fig. 2 as a Arrheius form with the rate constants originally calculated by Shigeno et al. The value of \( K_R \) (mol/m²·sec·atm) can be obtained from the interception in Fig. 1 and are also represented in Table 3. The ratio of \( K_R/k_t \) is about 0.03, and this is nearly the same order of 0.016 obtained by Sain and Belton.

The calculated \( k_t \) in this communication is about 1/10 of that of reported by Shigeno et al. It can be supposed that their very large values mainly came from the negligence of the residual rate. They calculated \( k_t \) from the following equation which was obtained by combining Eqs. (2) and (7').
\[ 1/k_{ap} = 1/k_d + K_s(a_0)/k_t \] ...............(10)
But if Eq. (8) is used instead of Eq. (7'), the corresponding relation of Eq. (10) is expressed by
\[ 1/k_{ap} = 1/k_d + K_s(a_0)/(k_t + K_s(a_0)K_R) = 1/k_d + K_s(a_0)/(k_t(1 + K_s(a_0)(k_R/k_t))) \] ...............(11)

They evaluated the \( k_t \) by using the data in a range of 0.2 to 0.7 wt% of sulphur. Then the value of the term \( K_s(a_0)(k_R/k_t) \) is about 5 to 10. Therefore, the negligence of this term misleads to about 6 to 11 times larger value of \( k_t \).

Table 3. Calculated chemical rate constant (\( k_t \)) and residual rate constant (\( k_R \)).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( k_R ) (mol/m²·sec·atm)</th>
<th>Rate constant ( k_t ) (mol/m²·sec·atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1573</td>
<td>0.2</td>
<td>33.21</td>
</tr>
<tr>
<td>1673</td>
<td>1.24</td>
<td>50.9</td>
</tr>
<tr>
<td>1773</td>
<td>1.71</td>
<td>46.22</td>
</tr>
</tbody>
</table>

Fig. 1. Apparent rate constants (\( k_{ap} \)) as a function of the reciprocal sulphur activity.

Fig. 2. Temperature dependency of the chemical rate constants (\( k_t \)). Closed circles are the rate constants estimated by Shigeno et al.
When Eq. (7) is used, the rate of decarburization is supposed to be zero at the sulphur saturation. But, the experimental results suggest that there is a small residual rate at the apparent sulphur saturation. This means that the surface coverage of sulphur does not increase with the sulphur concentration after some high sulphur concentration and becomes practically constant. Without taking account of this constant unsaturated coverage, the estimation of coverage at high sulphur concentration by using Eq. (7) leads to nearly saturated coverage (≈1.0). Therefore, the calculated rate at bare surface using the values of this nearly saturated coverage will have a quite large value.

They also measured the rate of decarburization of iron with CO$_2$. In this case, the obtained rate constants were nearly the same to that reported by Sain and Belton within the factor of 2. Shigeno et al. calculated the rate constants by using the data of less than 0.1 wt% of the sulphur content. At this case, the value of $K_s(a_0)$ is about 1~1.5. Namely, the error due to the neglect of the residual rates were small. As previously mentioned, iron was not saturated with carbon in the work of Shigeno et al. In this case, $K_s$ would be smaller than that with the carbon saturation. This would increase the small error of the evaluation of $k_t$. Therefore, to establish the reliable value of $k_t$, it is necessary to carry out more precise measurements under the well-determined experimental conditions.

REFERENCES
3) M. Inouye and T. Choh: Trans. ISIJ, 8 (1968), 134.