Effect of H₂ Concentration on Carbon Deposition Reaction by CO–H₂ Gas Mixture at 773 K to 973 K

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CO–H₂ gas mixture is often used for gas-based DRI process where carbon deposition reaction and Fe₃C metal dusting play negative roles for a stable reduction operation. Fe₃C decomposition leads to the formation of iron particles which is a catalyst for carbon fiber deposition. Because of the parallel occurrence of these reactions, kinetic analysis of them would be complicated. In the present study, to simplify the kinetic analysis, quantitative analysis of carbon fiber deposition was conducted by using thermobalance. A powder iron sample was prepared by reduction of Fe₂O₃ with 100vol%H₂ at 673 K. Carbon deposition on the iron sample was investigated under flowing 100vol%CO, 90vol%CO-10vol%H₂, 75vol%CO-25vol%H₂, 50vol%CO-50vol%H₂, 25vol%CO-75vol%H₂ and 10vol%CO-90vol%H₂ gas mixtures at 773 K, 873 K and 973 K. Results showed that amount of the deposited carbon in the CO–H₂ gas mixture are larger than that in the pure CO gas. The largest amount of deposited carbon was obtained in 75vol%CO-25vol%H₂ gas mixture at 873 K. According to SEM observations and weight change measurements, carbon was deposited in fiber shape on the iron surface and amount of it was increased linearly with an increase in sample’s weight change. The rate constant of carbon fiber deposition was calculated considering Rideal mechanism with focusing on elementary reaction steps. It was found that the rate constant of the hydrogen-oxygen reaction step was the largest indicating a significant effect of hydrogen on promoting carbon deposition 773 K and 873 K. This would be due to the removing oxygen from CO by hydrogen on the iron catalyst.

KEY WORDS: metal dusting; reduced iron; CO–H₂ gas mixture; carbon deposition reaction; carbon fiber deposition.

1. Introduction

In direct reduced iron (DRI) process, natural gas is used as reducing agent to produce iron while in blast furnace the main reductant is coke.¹⁻² DRI, as virgin metal, is mainly charged into EAF process for dilution of tramp elements, such as Ni, Cr, Mo, Cu and Sn in steel. The amount of DRI production has been increased significantly from 0.79 Mt/year in 1970 to 68.4 Mt/year in 2008.¹⁻³ Low equipment cost and high elasticity of production is strong advantage of DRI as one of the promising iron making methods.⁴⁻⁵ Currently, MIDREX is the predominant process for using natural gas. In reformer of the MIDREX, CH₄ and CO₂ from reduction furnace are utilized to produce CO and H₂ as reducing gases. Natural gas reforms over 1273 K in the presence of a catalyst such as Ni. The obtained gases, CO and H₂, heat up to around 1273 K and flow into the reduction furnace again. The reduction reactions are as follows:

Fe₂O₃(s) + 3CO(g) → 2Fe(s) + 3CO₂(g) ..........(1)

The principal reactions in the reformer are as follows;

CH₄(g) + CO₂(g) → 2CO(g) + 2H₂(g) ..........(3)

CH₄(g) + H₂O(g) → CO(g) + 3H₂(g) ..........(4)

Simultaneously, carbon deposition reaction⁶⁻¹¹ in CO–H₂ gas mixture may occur around 673 to 1073 K during cooling step in MIDREX process according to following reactions;

CO(g) + H₂(g) = H₂O(g) + C(s)
ΔG = −127 800 + 197 logT + 78.4T(1)¹³ ..........(5)

2CO(g) = CO₂(g) + C(s)  ΔG = −160 210 + 168T(1)¹³ ..........(6)

The stable operation would have some problems due to carbon deposition reactions, such as sooting on gas path surface and also the deterioration in gas ventilation due to formation of ferrous dusts. In particular, carbon deposition reaction catalyzed by iron would cause complicated reactions such as metal dusting¹⁰ and filamentous carbon deposition.
deposition.\textsuperscript{14,15} Fe\textsubscript{3}C is produced through carbon deposition reaction while metal dusting process leads to decomposition of Fe\textsubscript{3}C into fine iron particles and carbon. The carbon deposition reaction could be accelerated by fine iron particles as a catalyst, and filamentous carbon would generate from each tiny iron particles. The filamentous carbon deposition causes deterioration of permeability in the reaction furnace and wasting of reduction gas. Because carbon deposition reaction would be influenced sensitively by gas composition and reaction temperature, proper control of temperature and atmosphere to suppress carbon deposition is necessary. However, the mechanism of carbon deposition reaction has not been revealed thoroughly due to shortage of reports about the kinetics and reaction mechanism of carbon deposition reaction accompanied with metal dusting reaction.

In this study, the kinetics of carbon deposition reaction with iron catalyst in CO–H\textsubscript{2} gas mixture was investigated to clarify the effect of H\textsubscript{2} concentration at 773 K to 973 K.

2. Experimental Procedure

20 g reagent Fe\textsubscript{2}O\textsubscript{3} powder (−1 μm, purity of 99%), the chemical composition is shown in Table 1, was pressed into a tablet shape (30 mm diameter, 15 mm high), then heated at 1 623 K for 3 600 s under the air atmosphere. The heat treated Fe\textsubscript{2}O\textsubscript{3} was ground to −45 μm grain size using a mortar. In order to obtain reduced iron sample, the prepared Fe\textsubscript{2}O\textsubscript{3} was reduced by 100vol%H\textsubscript{2} at 873 K for 20 minutes in an electric horizontal furnace. Formation of reduced iron was confirmed by XRD analysis and weight change between before and after reduction. To identify surface characteristics of the reduced iron samples, SEM observations were implemented as shown in Fig. 1. Many pores were observed on the surface of reduced iron samples due to the reduction reaction. To quantify the surface characteristics of the reduced iron samples, the specific surface area of the samples was measured by BET method.\textsuperscript{16} For BET analysis, 0.3 g reduced iron sample was used. The specific surface area of the sample is 1.18 (m\textsuperscript{2}/g).

The schematic setup of the carbon deposition experiment is shown in Fig. 2. The total gas flow rate of mixture gas of CO, N\textsubscript{2} and H\textsubscript{2} was 3.33 × 10\textsuperscript{−5} Nm\textsuperscript{3}/s (2 NL/min). Nitrogen gas was introduced 8.33 × 10\textsuperscript{−6} Nm\textsuperscript{3}/s (0.5 NL/min) into the reaction tube (Inner diameter: 35 mm) from the top of the furnace during experiment in order to protect thermobalance. An Al\textsubscript{2}O\textsubscript{3} crucible (9 mm inner diameter, 4 mm height) contained the sample was placed into a Pt basket (18 mm inner diameter, 20 mm height) with ceramic fiber, as shown in Fig. 3. The ceramic fiber was used as heat insulator. The Pt basket was hung on a thermobalance\textsuperscript{17} by Pt wire. The inner diameter of this reaction tube is 35 mm. The initial weight of the reduced iron sample was fixed as 0.028 g, in order not to brim with deposited carbon sample in the Al\textsubscript{2}O\textsubscript{3} crucible. The sample was heated up to experimental temperature in 10 minutes, 773 K, 873 K and 973 K in 100vol%N\textsubscript{2} and then the atmosphere changed to 50vol%CO-50vol%H\textsubscript{2} gas mixture for 30 minutes. The weight change was measured continuously using thermobalance during carbon deposition. After reaction, the sample was cooled to room temperature in 100vol%N\textsubscript{2} in 30 min. Microstructure of the deposited carbon was observed by SEM (SU3500) operated at 20 kV and mineral phase was analyzed by XRD (Smart Lab, Rigaku).

3. Results and Discussion

3.1. The Effect of Temperature and Gas Composition on Carbon Deposition Reaction

Weight change ratio and final weight change ratio were calculated according to Eqs. (7) and (8).

\[
\text{Weight change ratio} = \frac{m}{0.028} \quad (7)
\]

Table 1. Chemical composition of Fe\textsubscript{2}O\textsubscript{3} reagent (mass%).

| Fe\textsubscript{2}O\textsubscript{3} | SO\textsubscript{4} | MnO | SiO\textsubscript{2} |
|--------------------------------|--------------|-----|-----------------|
| 98.5                          | 0.2          | 0.3 | 0.06            |

Fig. 1. Secondary electron image of hematite and Fe sample.

Fig. 2. Schematic view of gas path.

Fig. 3. Schematic illustration of sample.
Final weight change ratio \( m_f / m_0 \) \( = \frac{m_f}{0.028} \) \( \cdots (8) \)

Where \( m \) (g) is the sample weight at time "t" during experiment, \( m_f \) (g) is the amount of weight change after a 1 800 s reaction. To evaluate weight change ratio, the measured weight change is divided by the weight of the reduced iron sample before carbon deposition reaction, which is 0.028 g. Figure 4 shows the sample’s weight change obtained by thermobalance analysis during carbon deposition reaction.

The lowest amount of carbon deposition was obtained in 100vol%CO at each temperature. In addition, the amount of deposited carbon during reaction in CO–H\(_2\) gas mixture was obvious larger than that in the 100vol%CO due to the higher rate of the carbon deposition reaction in the presence of H\(_2\) compared to the pure CO. This result suggests that adding H\(_2\) into CO promotes the carbon deposition reaction according to the Eq. (5). The biggest weight change at 773, 873 and 973 K was obtained in 90vol%CO-10vol%H\(_2\), 75vol%CO-25vol%H\(_2\) and 50vol%CO-50vol%H\(_2\), respectively. It seems for a large amount of carbon deposition, not only sufficient CO is needed to supply required amount of carbon but also presence of H\(_2\) can promote the deposition reaction. Figure 5 shows the effect of temperature on final weight change ratio with different kinds of gas mixtures. From this figure, the largest amount of deposited carbon was obtained at 873 K regardless of gas mixture ratio. In this study, \( \Delta G^o \) of Eqs. (5) and (6) become −24 778 to 3 724 (J) and −30 346 to 3 254 (J) at 773 K to 973 K, respectively. The effect of thermodynamic on the carbon deposition reaction is not so significant because the difference of calculated value of \( \Delta G^o \) was very small. Therefore, it is considered that a drastic increase in the amount of deposited carbon by adding hydrogen depended on a kinetic effect.

XRD patterns of the samples after carbon deposition at 773 K, 873 K and 973 K under different atmospheres are shown in Fig. 6. Cementite and carbon were detected in these patterns. Cementite formation would be due to the reaction of reduced iron with deposited carbon. It was revealed that adequate carbon for cementite formation was deposited on the iron catalyst at 773 K, 873 K and 973 K in the carburizing atmosphere. The diffraction peak of carbon gradually increased according to the amount of carbon deposition reaction. In contrast, the sample conducted at 873 K in 100vol%CO only has the diffraction peak of iron, which also shows the possibility that the surface of each post-reaction sample would vary.

The transformation of iron sample’s surface was provided by carbon deposition reaction and the SEM observations of post-reaction sample are shown in Fig. 7. The deposited carbon is roughly classified into two forms, generating car-

Fig. 4. Sample weight change curves during carbon deposition reaction.

Fig. 5. Effect of temperature on the final weight change ratio of carbon deposition reaction in each gas composition for 1 800 s.
bon fiber or not. The sample which had no or little carbon fiber deposition got formation of carbon on the surface or cementite from XRD analysis as shown in Fig. 6. The membrane carbon phase concealed the pore which was observed in reduced iron sample. On the other hand, the filamentous carbon has growth starting points at fine iron particle, which observed distinctly in the sample which got quite large weight change. According to a previous research by J. Zhang et al, they detected carbon and iron diffraction peaks by transmission electron microscope and energy dispersive X-ray spectrometry analysis of fine iron particles. In the present study, cementite was detected by XRD analysis of the filamentous carbon deposited sample which would be due to the transformation of fine iron particle into cementite during carbon deposition reaction. However, the strong diffraction peaks of iron were obtained in the XRD pattern of the post-reaction sample heated at 873 K in 100vol%CO. It seems the fine iron particles did not get enough carbon to

Fig. 6. XRD patterns of sample after 1 800 s carbon deposition reaction.
compose cementite. Moreover, the smallest weight change ratio was obtained after treatment at 973 K compared to the treatment at lower temperatures, 773 and 873 K in all gas compositions. This result would be related to the sample’s specific surface area. The largest grain size was observed in the sample heated at 973 K in compare with the samples heated at 773 and 873 K. Therefore, it is assumed that specific surface area of the sample heated at 973 K would be smaller than that of the samples heated at 773 and 873 K causing a lower weight change ratio in the sample which heated at higher temperature.

3.2. Phase Transition during Carbon Deposition Reaction

Considering Fig. 4, weight change curves can be divided into three phases. Figure 8 shows schematic illustration of catalyst transfer behavior during carbon deposition reaction. In phase I, reduced iron which is starting material acts as catalyst in the carbon deposition. In phase II, fine iron particles produced by metal dusting acts as catalyst. The period between phase I and phase II is considered as a transition period. However, the transition point from phase I and phase II was not recognized in Fig. 8.
Therefore, reaction rate was calculated based on the weight change curves to clarify the transition point. Rate of the carbon deposition reaction can be presented by the following Eq. (9) which was adapted in the 300 s time interval and the measurement section shifts every 100 s forward.

\[
n_{c,\text{ave}}(n) = \frac{\sum (t_{\text{ave}} - t)(n_{c,\text{ave}}(n) - n_{c}(n))}{\sum (t_{\text{ave}} - t)^2}
\]

Where \( n_{c,\text{ave}} \) (mol) is the average quantity of deposited carbon for each 300 s time bracket and \( n_c \) (mol) is the quantity of deposited carbon at the middle of this time bracket. In order to calculate these values, weight change which was measured by the thermobalance divided by molar mass of carbon. Likewise, \( t_{\text{ave}} \) (s) represent the average of reaction times for each 300 s time bracket and \( t \) (s) is the time at the middle of this time bracket.

**Figure 9** shows relationship between the rate of carbon deposition reaction and reaction time. Reaction rate reached a stable state by treatment for a longer time, especially in the sample which obtained filamentous carbon deposition. It is conceivable that the existing phase and reaction mechanism change continuously, due to the carbon deposition on the iron. In order to analyze the carbon deposition reaction, the experiment was interrupted after 300 s, 600 s, 1000 s and 1400 s treatment at 873 K in 75vol%CO-25vol%H₂. The phase transition of iron after carbon deposition was investigated by XRD analysis and SEM observation.

**Figure 10** shows the XRD results for the iron after treatment for a certain time. As shown in Fig. 10, Fe₃C could be detected in all samples after reaction. The diffraction peaks indicated an increase in the carbon content after 300 s carbon deposition reaction. This increment of intensity would be because of the growing of filamentous carbon. The diffraction peaks belong to carbon increased gradually, as most of deposited carbon would be piled on the sample rather than dissolving into Fe.

**Figure 11** demonstrates the morphological property of reduced iron sample after reaction obtained by SEM observation. Obviously, the surface of reduced iron would be transformed by disappearing of pores which observed before carbon deposition at 300 s. It can be seen that the new layer which was composed of carbon and cementite would overlap the surface of iron. Furthermore, formation of tiny iron particles after 600 s treatment was confirmed and increasing reaction time would make a longer filamentous carbon. SEM observation also indicated that the tiny iron particle lay at the base of carbon fiber and diameter of the both substances would be almost same.

The carbon deposition reaction which is accompanied with nucleating Fe₃C and filamentous carbon has been proposed as metal dusting process as following steps\(^{10}\) (Fig. 12):

i. Carbon is deposited on iron surface by carbon deposition reaction as Eq. (5).

ii. Carbon is transferred into solid solution and carburization occurs.

iii. Up to over saturation, Cementite nucleates and grows, mainly at the surface but also at grain boundaries as Eq. (10).
iv. Locally graphite nucleates on iron and it causes cementite becomes unstable. Cementite decomposes to graphite and tiny iron particles, according to Eq. (11).

\[ \text{Fe}_3\text{C}(s) = 3\text{Fe}(s) + \text{C}(s) \]  

(11)

v. Carbon is transferred into tiny iron particles. The carbon diffuses through the tiny iron particle to some site where graphite nucleation is easy. Then, filamentous carbon grows where graphite growth starts, according to Eqs. (5) and (6).

In consideration of this mechanism, primary reaction which is relevant to composing tiny iron particle would convert into filamentous carbon deposition. Consequently, area of the interface between a gas and tiny iron particles was so large that carbon deposition rate would increase with increasing reaction time. However, carbon deposition rate after 1 000 s reaction was almost stable. This is because generating tiny iron particles would reach utmost. This would be because the reactive interface of iron catalyst was also constant.

3.3. The Effect of H\textsubscript{2} Gas on Carbon Deposition Reaction

Table 2 summarizes the relation between type of carbon deposition and atmosphere. In order to recognize the carbon fiber deposition rate, rate-determining step of the reaction was investigated by dividing carbon deposition reaction into elementary process as follows:\(^5\)

\[ \text{CO}(g) = \text{O}^* + \text{C}(s) \]  

(12)

\[ \text{O}^* + \text{H}_2 (g) = \text{H}_2\text{O}(g) \]  

(13)

\[ \text{O}^* + \text{CO}(g) = \text{CO}_2 (g) \]  

(14)

where O* indicates the oxygen which adsorbs on the surface of iron catalyst.

These reaction rates are expressed as follows:

\[ n_1 = k_1(1 - \theta \theta \theta) P_{\text{CO}} \]  

(15)

\[ n_2 = k_2 \theta \theta \theta P_{\text{H}_2} \]  

(16)

\[ n_3 = k_3 \theta \theta \theta P_{\text{CO}} \]  

(17)
where $k_1$, $k_2$ and $k_3$ indicate the reaction rate constant. $\theta_o$ is the iron surface coverage ratio of oxygen. $P_{H_2}$ and $P_{CO}$ represents the partial pressure of hydrogen and carbon monoxide, respectively. Granting that supplying oxygen from absorbed CO and desorption oxygen by $H_2$ and CO is treated with steady-state, and the carbon deposition rate can be considered as follows;

$$n_{c,c} = n_1 + n_2 + n_3$$

(18)

where $n_{c,c}$ indicates calculated value of carbon deposition reaction. Based on Eqs. (15), (16) and (17), $\theta_o$ is described as follows;

$$\theta_o = \frac{k_1 P_{CO}}{(k_1 + k_2) P_{CO} + k_2 P_{H_2}}$$

(19)

In order to obtain $n_{c,c}$, $\theta_o$ was substituted in the Eq. (19), and $n_{c,c}$ is as following equation.

$$n_{c,c} = \frac{k_1 k_2 P_{CO} P_{H_2} + k_1 k_3 P_{CO}^2}{(k_1 + k_3) P_{CO} + k_2 P_{H_2}}$$

(20)

Measurement value of $n_{c,m}$ which show carbon deposition rate of carbon fiber was obtained from the mean average of carbon deposition rate from 1 500 s to 1 800 s in Fig. 9. Using the $k_1$, $k_2$ and $k_3$ for parameter, $k_1$, $k_2$ and $k_3$ were determined when the residual error between $n_{c,m}$ and $n_{c,c}$ become to minimum. Figure 13 shows relationship between elementary reaction rate constants, $k_1$, $k_2$ and $k_3$, and reaction temperature. From Fig. 13, $k_2$ is larger than $k_3$ at 873 K and 973 K. Therefore, the rate of removing adsorbed oxygen by hydrogen is higher than CO. On the other hand, $k_1$ was larger than $k_2$ and $k_3$ at 773 K, and it means that adsorption of oxygen on iron surface was faster than desorption by $H_2$ and CO at 773 K. Therefore, at 773 K, there was significant difference whether carbon fiber deposit or not, as shown in Table 2. However, further investigation is required to understand the influence of atmosphere on carbon deposition reaction at 773 K.
Figure 14 shows \( n_{c,c} \) and \( n_{c,m} \) versus concentration of CO and \( H_2 \) in the inlet gas. In this figure, white circles indicates \( n_{c,m} \) in carbon fiber deposition, and black ones indicates \( n_{c,m} \) in no carbon fiber deposition. The broken line shows \( n_{c,c} \) under carbon fiber deposition condition. From this figure, measurement \( n_{c,m} \) is good agreement with calculated \( n_{c,c} \) at all temperatures. Adding \( H_2 \) into CO made \( n_{c,m} \) increased drastically because \( k_2 \) was larger than \( k_1 \) and \( k_3 \) at 873 K and 973 K. \( n_{c,c} \) at 873 K and 973 K has peaks around 75vol\%CO-25vol\%H\(_2\) and 60vol\%CO-40vol\%H\(_2\), respectively. On the other hand, \( n_{c,c} \) at 773 K increased with increasing CO concentration in inlet gas without peak. Therefore, at 773 K, it is considered that absorption rate of oxygen on iron surface had larger contribution on carbon deposition than desorption rate of oxygen as shown in Fig. 13.

4. Conclusion

In order to evaluate the effect of \( H_2 \) concentration on carbon deposition reaction, reduced iron sample was used in CO–\( H_2 \) gas mixture at 773 K, 873 K and 973 K. The results of experiments can be summarized as follow:

(1) The thermobalance analysis revealed the weight change of carbon deposition. In perspective of reaction temperature, the biggest weight change was obtained at 873 K. In perspective of gas composition, the biggest weight change was obtained in 90vol\%CO-10vol\%H\(_2\), 75vol\%CO-25vol\%H\(_2\) and 50vol\%CO-50vol\%H\(_2\) at 773 K, 873 K and 973 K respectively.

(2) XRD analysis of samples after carbon deposition reaction implied that Fe\(_3\)C as intermediate product was composed by reduced iron sample and deposited carbon. The part of Fe\(_3\)C which is metastable phase decomposed to carbon and tiny iron particles during carbon deposition reaction, and tiny iron particles behaved new catalysts of filamentous carbon deposition.

(3) The analysis in the view of elementary process of carbon deposition reaction evaluates the filamentous carbon deposition rate, and the reaction velocity constant at 773 K, 873 K and 973 K was obtained. The reaction rate constant of removal O\(^*\) by Hydrogen is bigger than other reaction rate constant at 873 K and 973 K, and adding hydrogen into carbon monoxide would have extremely large effect on carbon deposition reaction.

REFERENCES

1) M. Atushi, H. Uemura and T. Sakaguchi: Kobe Steel Eng. Rep., 60 (2010), No. 1, 5 (in Japanese).
2) Y. Inada: Kobe Steel Eng. Rep., 50 (2000), No. 3, 86 (in Japanese).
3) N. Takamatsu, K. Yonezawa, H. Ueno, W. Tamaki and S. Hayashi: Tetsu-to-Hagané, 100 (2014), 26 (in Japanese).
4) H. Sakamoto, Y. Iguchi and S. Hayashi: Tetsu-to-Hagané, 83 (1997), 175 (in Japanese).
5) D. Kaneko, O. Davies, O. Tsujiya and H. Sako: Tetsu-to-Hagané, 73 (1987), 314 (in Japanese).
6) Y. Nishiyama, T. Doi and K. Moriguchi: J. Jpn. Inst. Met. Mater., 77 (2013), 210 (in Japanese).
7) S. Ando, N. Kurose, T. Shimoo and H. Kimura: J. Jpn. Inst. Met., 49 (1985), 737 (in Japanese).
8) S. Ando, T. Shimoo and H. Kimura: J. Jpn. Inst. Met., 49 (1985), 45 (in Japanese).
9) N. Towhidi and J. Szekely: Metall. Trans., 14B (1983), 359.
10) H. J. Grabke: Mater. Corros., 54 (2003), 736.
11) S. Sawai, Y. Iguchi and S. Hayashi: Tetsu-to-Hagané, 85 (1999), 20 (in Japanese).
12) E. T. Turkdogan, R. G. Olsson and J. V. Vinters: Carbon, 8 (1970), 545.
13) M. Ohtani: Tetsu Yakin Neturikigaku, Nikkan Kogyo Shimbun, Tokyo, (1971), 207 (in Japanese).
14) K. Ishii, Y. Kashiwaya and S. Kondo: J. Jpn. Inst. Met., 50 (1986), 767 (in Japanese).
15) Y. Kashiwaya and K. Ishii: J. Jpn. Inst. Met., 52 (1988), 1103 (in Japanese).
16) S. Braunauser, P. H. Emmett and E. Teller: J. Am. Chem. Soc., 60 (1938), 309.
17) H. Ogi, T. Maeda, K. Ohno and K. Kunitomo: ISIJ Int., 55 (2015), 2550.
18) J. Zhang, A. Schneider and G. Inden: Corros. Sci., 45 (2003), 1329.
19) M. Taniguchi and I. Muchi: Tetsu-to-Hagané, 56 (1970), 162 (in Japanese).