Rate of Iron Carbide Formation from Reduced Iron in CO–H₂–H₂S Mixtures under Pressurized Conditions

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Under pressurized conditions up to 0.6 MPa, the rate of the iron carbide formation from completely reduced iron in CO–H₂–H₂S mixtures was measured by gravimetric technique. The fractional conversion for carbide formation, f_θ , was defined as the weight gain divided by the weight of carbon for the complete conversion to cementite. First, the compositions of the partially reacted samples were analyzed by Mössbauer absorption spectroscopy. Then, the fractional conversion calculated from the composition, f_θ^M , was compared with f_θ . The value of f_θ agreed reasonably with that of f_θ^M in the range $f_\theta < 0.8$, from which the gravimetric method is proved to be valid to the measurements for the rate of iron carbide formation. The carbide formation curves, f_θ versus t relation, were not influenced by the weight of the sample and the flow rate of the reaction gas in the conditions; 50 mg, more than 3.33×10^{-6} m³/s. Cross sectional view indicated the homogeneous distribution of cementite regions in the reduced iron particles partially converted to cementite. On the other hand, the rate was very sensitive to the conditions of the carburization reaction on the pore surface. The rate increased with increasing the content of carbon monoxide up to 80 to 90 %, where the rate was the maximum, and then gradually decreased with further increasing the content. The rate increased with the total pressure, but decreased with the activity of sulfur. The rate controlling step of the iron carbide formation was discussed on the basis of the experimental results. The rate controlling step was assumed to be the carburization reactions on the pore surface of reduced iron particles.

KEY WORDS: iron carbide; cementite; reduced iron; gravimetric measurements; carbon monoxide; hydrogen; hydrogen sulfide; pressurized condition; sulfur activity; rate controlling step.

1. Introduction

Production of iron carbide as an alternative iron source was first examined several decades ago¹⁾ and commercialized first in the world in Trinidad in 1994.²⁾ Since then, several fundamental studies^{3–18)} concerning its production from iron ore have actively been performed. However, iron carbides are thermodynamically meta-stable and can not be formed until the carbon activity of the reaction gas increases beyond unity, where free carbon can easily precipitate. On the formation of iron carbide, therefore, no reliable kinetic study has been conducted up to now. Recently, Hayashi *et al.*^{4–6)} have found out that nearly pure iron carbides of Fe₃C and Fe₅C₂ can be produced by preventing not only the decomposition of iron carbide but also the precipitation of free carbon by adding only a little amount of H₂S to CO–H₂ mixtures. The following conclusions have been obtained in our previous studies.^{4–6,8–10)} The optimum temperature range is from 823 to 1123 K. Pressurizing is very effective to improve the gas utilization degree and to increase the formation rate. Reduced iron can be converted completely to carbides at sulfur activities less than unity, *i.e.* without formation of FeS.

In our previous studies,¹⁴⁾ the rate of carbide formation from completely reduced iron ore in H₂–H₂S mixtures was accurately measured in 4–80% H₂–CO–H₂S mixtures at 973 K by gravimetric technique. But, the measurements were made only in the total pressure of the atmospheric pressure or less.

In this study, new equipment of a high-pressure type usable up to 1 MPa was made. The rate of carbide formation from iron ore reduced completely was measured in CO–H₂–H₂S mixtures at high pressures of 0.6 MPa or less. From the experimental results, the rate controlling step was discussed.

2. Experimental Procedures

High-pressure equipment used in this study is schematically shown in Fig. 1. In the high-pressure vessel, a thermobalance, a dual type of reaction tube and an electric furnace were set. Weight gain of reduced iron by carburization was measured by the thermobalance (Cahn, C-1000) with accuracy of ± 1 μ g. The pressures inside and outside the reaction tube were manually controlled by the two pressure control valves for the reaction gas in the tube and nitrogen

Fig. 1. Schematic representation of the apparatus for the gravimetric measurements under pressurized conditions.

Table 1. Composition of the iron ore used (mass%).

T.Fe	FeO	SiO ₂	Al ₂ O ₃	CaO	S	C.W
68.23	0.42	0.89	0.43	0.01	0.003	1.43

C.W.=combined water

in the furnace. The flow rate of each component gas of the reaction gas mixtures was precisely controlled within less than 1% error by individual mass-flow controller to simultaneously achieve a given composition and a given total flow rate. The reaction tube was composed of an inner silica tube of 25 mm inside diameter and an outer silica tube of 35 mm inside diameter with closed bottom end. The reaction gas flowed upward in the inside reaction tube after heated during flowing down between the dual tubes. As sample, particles in a size range 0.15–0.21 mm of hematite iron ore as a pellet feed with the composition shown in Table 1 were used in the present study. In most experiment, the iron ore particles of 50 mg were put evenly on a flat horizontal disk of silica glass fiber filtration paper of 13 mm diameter, which disk was fixed in a holder of 0.3 mm platinum wire for the disc. At the beginning of the experiments, the pressure was raised to a given one ranged in 0.1–0.6 MPa by nitrogen gas and then, the furnace temperature was raised to a given one ranged in 773–1 023 K in nitrogen flow. Then, the iron ore particles were completely reduced in H₂–H₂S mixtures with a given sulfur activity ranged in 0.03–0.7. The sulfur activity a_S was defined as the ratio (p_{H_2S}/p_{H_2}) in the reaction gas divided by the ratio (p_{H_2S}/p_{H_2}) in equilibrium with Fe and FeS. Correct measurements of weight gain by carbide formation could be established only by complete reduction, which prevented the weight loss by reduction of remained wustite. After flushing the atmosphere with nitrogen for 300 s, the reduced iron ore was carburized in CO–H₂–H₂S mixtures with the same sulfur activity at the same temperature as in the reduction step.

The total flow rate of the reaction gas mixtures was varied in the range of $1.66\text{--}8.33 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ (273 K and 101 325 Pa) and most experiments were conducted at a high flow rate of $3.33 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$. Just after carbide formation reaction was completed or interrupted, the atmosphere was exchanged with nitrogen, the pressure dropped down to the atmospheric, the furnace removed from the tube, and the

sample quenched in nitrogen flow as quickly as possible. Finally the sample was dropped into acetone for preventing even any slight re-oxidation. The sample was quantitatively analyzed by X-ray diffraction. In calculating the composition from the peak intensity of the spectrum, the coefficients of weight ratio W_i/W_{Fe_3C} divided by the peak height ratio I_i/I_{Fe_3C} for component i–Fe₃C binary standard samples were used. The index i denotes Fe, Fe₅C₂, FeO, Fe₃O₄ or Fe₂O₃. Also, some samples obtained in the experiments with 200 mg iron ore were chemically analyzed for carbon and sulfur by the combustion method for the check of free carbon precipitation.

The reaction extent for the conversion of reduced iron to iron carbides, f_θ , is defined as;

$$f_\theta = \Delta W / [W_0(TFe/100)(M_C/3M_{Fe})] \dots \dots \dots (1)$$

where TFe is the total iron percent in the iron ore, W_0 the initial weight of the iron ore sample, ΔW the weight gain by carburization, and M_C and M_{Fe} the molecular weight of carbon and iron, respectively. In the calculation of f_θ , it was assumed that the entire weight gain was made by carbon taken in the carbides formed. Also, some samples partially converted to cementite were mounted in epoxy resin, and their cross sections were microscopically observed after etching with an alkali solution of sodium picric acid for 200 s at about 320 K, iron carbides being distinctly dyed to light brown.

3. Experimental Results

3.1. Verification of the Validity of Gravimetric Measurements for the Rate of Carbide Formation from Reduced Iron

During the carbide formation, the reaction of the reduced iron in 80%CO–H₂–H₂S mixture with sulfur activity $a_S=0.5$ under 0.2 MPa at 873 K was interrupted at several conversion extents to cementite. The samples were quantitatively analyzed by Mössbauer absorption spectroscopy to get the composition. From the weight gain and the composition, two values of the conversion extent, i.e. f_θ and f_θ^M , were obtained for one sample, where f_θ^M was calculated from the composition by the following equations,

$$f_\theta^M = f_\theta^M(\theta) + f_\theta^M(\chi) = (w_\theta + 1.2w_\chi) / (w_m + w_\theta + w_\chi) \dots \dots (2)$$

$$f_\theta^M(\theta) = (w_\theta) / (w_m + w_\theta + w_\chi) \dots \dots \dots (3)$$

$$f_\theta^M(\chi) = (1.2w_\chi) / (w_m + w_\theta + w_\chi) \dots \dots \dots (4)$$

where w_θ , w_χ and w_m are the mass fractions of iron in cementite (Fe₃C), χ -iron carbide (Fe₅C₂) and metallic iron in the samples, respectively. The value of 1.2 equals the ratio of the number of carbon atom to the number of iron atom for Fe₅C₂ divided by the ratio for Fe₃C, i.e. (2/5)/(1/3)=1.2. The relation between f_θ and f_θ^M is shown in Fig. 2. In the range of f_θ at least less than 0.8, the fractional conversion to cementite which was calculated from weight gain, f_θ , is equal to the fractional conversion to cementite which was calculated from composition analyzed by Mössbauer absorption spectroscopy, f_θ^M , which means that the weight increase corresponds directly to the weight increase of carbon in iron carbides. Within the range of f_θ less than 0.6, especially, the weight gain corresponds to the formation of ce-

mentite, i.e. $f_{\theta} = f_{\theta}^M(\theta)$.

3.2. Influence of Gas Diffusion in Particle and Particle Bed on the Rate of Iron Carbide Formation

In considering the reaction mechanism of iron carbide formation, the direct observation of the morphology of partially reacted samples is very important. A typical metallographic cross-section of reduced iron particles partially reacted with 80%CO–H₂–H₂S mixture with $a_s=0.3$ under 0.6 MPa at 973 K is shown in Fig. 3. The region of cementite is distributed almost uniformly throughout the particle, not being confined to the peripheral part of the particle. These results indicate that the gas diffusion resistance in particles of the reduced iron ore is negligible.

On the other hand, the weight of iron ore particles was varied in the range from 25 to 200 mg. On the silica filtration paper disc as the sample holder, the iron ore particles were scattered in a few layers for 25 mg to about several layers for 200 mg. The influence of the sample weight on the carbide formation curves was checked in 80%CO–H₂–H₂S of the flow rate $3.33 \times 10^{-5} \text{ m}^3/\text{s}$ with $a_s=0.5$ under 0.6 MPa at 973 K is shown in Fig. 4. Increasing the weight

Fig. 2. A typical carbide formation curve from weight gain f_{θ} compared with f_{θ}^M as the sum of $f_{\theta}^M(\theta)$ calculated from the content of Fe_3C and $f_{\theta}^M(\chi)$ from the content of Fe_5C_2 , which were quantitatively analyzed by Mössbauer absorption spectroscopy.

from 25 to 50 mg does not retard the rate. By further increasing the weight from 50 to 100 mg, the rate is slightly retarded in the later stage, and by further increasing from 100 to 200 mg, the carbide formation starts to be clearly retarded. Gas diffusion resistance in the layers of the particles of 25 to 50 mg was negligible even in the condition of 0.6 MPa and 973 K. Hereafter, the experiments were conducted mainly using the particles in the size range of 45–53 μm and the weight of 50 mg. The thickness of the iron ore bed on the sample plate was one to two layers of 0.15–0.21 mm particle per 50 mg.

3.3. Influence of Flow Rate of Reaction Gas on the Rate of Iron Carbide Formation

The influence was investigated in 80%CO–H₂–H₂S with $a_s=0.5$ under the total pressure 0.6 MPa, i.e. the maximum total pressure where the rate was the maximum in this study, at 973 K. The composition of the reaction gas was set to be 80%CO–H₂–H₂S mixture, where the rate was also the maximum in the atmospheric pressure. In the conditions, the carburization curves in a wide range of flow rate at 973 K are shown in Fig. 5. In the figure, no explicit tendency for the flow rate to affect the carburization rate is observed. In our previous study,¹⁷⁾ the rate of carbide formation from completely reduced limonite ore was not influ-

Fig. 4. Influence of the weight of iron ore particles on the rate of carbide formation at 973 K.

Fig. 3. Cross section of a reduced iron particle partially converted to cementite in 80%CO–H₂–H₂S mixture of 0.6 MPa with $a_s=0.5$ at 973 K ($f_{\theta}=0.45$); red part is cementite and white part is metallic iron.

ended by the flow rate in the range more than 1.66×10^{-5} Nm^3/s although the rate was much faster than the rate of completely reduced hematite ore, which was used in this study, due to the larger specific surface area. These results indicate that the concentration drop in the reaction gases by the product gases and the concentration drop by the gas diffusion resistance in gas film on the layer of iron ore particles are negligible. In below, the experiments were conducted in the conditions of the total flow rate $2.5\text{--}3.33 \times 10^{-5}$ m^3/s^{-1} (1.5–2.0 NL/min) including under the pressure as high as 0.6 MPa.

At the beginning of carburization of completely reduced iron, nitrogen gas flow, which pressure had been controlled by a pressure control valve was exchanged with a reaction gas mixture, which pressure had been controlled by the

Fig. 5. Influence of the total flow rate of the reaction gas on the rate of carbide formation at 873 K.

Fig. 6. Influence of the composition of the reaction gas on the rate of carbide formation at 873 K.

other pressure control valve. Therefore, some pressure difference between the two manually controlled pressure control valves seemed to have yielded some disturbance in the very initial part of the carbide formation curves. Excluding the very initial part, thus, only the main part of the curves e.g. $f_\theta < 0.05$, was analyzed.

3.4. Influence of Composition of CO–H₂–H₂S Mixtures on the Rate of Carbide Formation

In our previous studies^{8–10,14–18)} conducted at the atmospheric pressure, the rate of iron carbide formation in CO–H₂–H₂S mixtures showed the maximum rate around the composition of 80%CO–H₂–H₂S mixture at 973 K. From the results, it was suggested that the carburization reaction strongly depends on the composition of the carburization gas, and the reaction (5), not the reaction (6), may be the main carburization reaction in CO–H₂–H₂S mixtures.

In pressurized conditions in this study, the influence of the composition of CO–H₂–H₂S mixtures with sulfur activity 0.5 at total pressures 0.1, 0.2, 0.4 and 0.6 MPa at 873 and 923 K is shown in Figs. 6 and 7, respectively. In this study, the experiments at 0.1 MPa, at which pressure the results were reported in the previous studies,^{8–10,14,15,17,18)} were again conducted. At each of the total pressures, with increasing hydrogen content from 4 or 10%, the carbide formation rate increases up to around 20%, where the rate shows the maximum, but with further increasing the hydrogen content, on the contrary, the rate gradually decreases. The same dependency on the composition was observed in

Fig. 7. Influence of the composition of the reaction gas on the rate of carbide formation at 923 K.

Fig. 8. Influence of the total pressure on the rate of carbide formation at 873 K.

Fig. 9. Influence of the total pressure on the rate of carbide formation at 973 K.

the author's previous study¹⁴⁾ conducted at 0.1 MPa total pressure. Throughout all the experiments in this study, the carbide formation rate was the maximum at the composition of around 80%CO-H₂-H₂S mixture under the total pressure up to at least 0.6 MPa at temperatures from 873 to 973 K.

The similar dependency on the composition of CO-H₂ mixtures not containing H₂S was observed concerning the carbon deposition on reduced iron oxides by Olsson and Turkdogan.¹⁹⁾ The rate of carbon deposition showed a strong hydrogen content dependency with the maximum around 5% hydrogen at 673 K, a normal dependency with the maximum around 30% at 873 K and a weak dependency with the maximum about 20–60% at 1073 K. This

shows that the sequence of elementary reactions in the process of the iron carbide formation from reduced iron is very similar to that in the carbon deposition on reduced iron.

3.5. Influence of Total Pressure on the Rate of Iron Carbide Formation in CO-H₂-H₂S Mixtures

The influence of the total pressure in the reaction gas on the carbide formation rate was investigated in the fixed compositions 80%CO-H₂-H₂S of $a_s = 0.5$ at 873 K and 60%CO-H₂-H₂S mixture of $a_s = 0.5$ at 973 K. The typical results are shown in Figs. 8 and 9. At each temperature, the rate of the carbide formation increases clearly with increasing the total pressure. Also in the other compositions of CO-H₂-H₂S mixture, the pressure dependence of the rate

was the same. If the dependency of the rate on the total pressure can be quantitatively treated, it may be critical in clarifying the reaction mechanism for the carbide formation from reduced iron in CO–H₂–H₂S mixtures. The carburization reactions for the iron carbide formation in CO–H₂ mixtures are the two carburization reactions of the reactions (5) and (6). The dependency on the total pressure is reasonable because, according to the equilibrium constants of these reactions; $K_{\text{COH}_2} = a_{\text{C}} p_{\text{H}_2\text{O}} / p_{\text{CO}} p_{\text{H}_2}$ and $K_{\text{COCO}} = a_{\text{C}} p_{\text{CO}_2} / p_{\text{CO}}^2$, the activity of carbon of the reaction gas is proportional to the total pressure at fixed compositions.

3.6. Influence of Sulfur Activity of CO–H₂–H₂S Mixtures on the Rate of Iron Carbide Formation

In this study, weight gain by the conversion of reduced iron to iron carbides was gravimetrically measured. The gravimetric technique stands on the principle that sulfur depresses both the decomposition of iron carbide and, at the same time, the precipitation of carbon even in high carbon potential reaction gas mixtures. In 80%CO–H₂–H₂S mixture with sulfur activities from 0.3 to 0.7 at 0.1 MPa at 873 K, the carbide formation curves from reduced iron ore are shown in Fig. 10. The carbide formation rate gradually decreases with the increase in the sulfur activity. In Iguchi *et al.*'s previous study,¹⁴⁾ the sulfur's effect which decreases the rate with increasing its activity has been also observed at 0.1 MPa at 973 K. As observed above, sulfur has not only the positive effect on iron carbide formation by depressing the decomposition of iron carbides, but sulfur also has the negative effect on it by strongly decreasing the rate. The effect of sulfur described in this section is similar to the effect of sulfur on the carburization, decarburization, nitrogenization, denitrogenization, water gas shift reaction and etc by Grabke *et al.*,^{20–23)} but sulfur being useful for the production of iron carbide was first reported in the studies by Hayashi *et al.*^{4–6)} With reference to this, Olsson and Turkdogan¹⁹⁾ wrote that sulfur can depress the precipitation of free carbon and stabilize meta-stable cementite in CO–H₂ and CO–CO₂ mixtures.

3.7. Influence of Temperature on the Rate of Iron Carbide Formation in CO–H₂–H₂S Mixtures

The influence of temperature on the rate of carbide formation in 80%CO– and 60%CO–H₂–H₂S mixtures with $a_{\text{S}}=0.5$ is shown in Figs. 11 and 12. In the temperature range up to 973 K with 60%CO–H₂–H₂S mixture and up to 923 K with 80%CO–H₂–H₂S mixture investigated in study, the carbide formation rate increases with increasing the temperature in either of the compositions. The temperature of 1073 K is thought to be the highest temperature for the treatment of iron ore in fluidized bed and at more than 1083K, the operation is encountered by various difficulties due to the sticking phenomena of reduced iron particles. Iguchi *et al.*¹⁵⁾ indicated that the iron carbide formation rate increased with the temperature up to 1073 K in the carbide formation in fluidized bed using Robe River limonite as sample. In CH₄–H₂ mixtures not containing sulfur, Nakagawa *et al.*³⁾ reported that the content of cementite, which was the only one carbide formed in the gas mixtures, reached the maximum at 1023 K, *i.e.* about 90% with balanced free carbon precipitated, in the reduction and carbide formation in one step from hematite iron ore. The

Fig. 10. Influence of sulfur activity of the reaction gas on the rate of carbide formation at 873 K.

Fig. 11. Influence of the temperature on the rate of the carbide formation.

Fig. 12. Influence of the temperature on the rate of the carbide formation.

maximum content of cementite decreased with increasing and decreasing the temperature from 1023 K.

4. Discussion on the Rate Limiting Step

The reactions for the carburization of completely reduced iron ore to form iron carbides are the reactions (5) to (8). The reactions (5) and (6) are the parallel reactions and reactions (5) or (6), (7) and (8) are consecutive reactions.

The formation of cementite (Fe_3C) proceeds through the following steps; (i) the transport of the reaction gas components by forced convection in bulk gas phase, (ii) the diffusion of the reaction gas components in gas film on a thin bed of reduced iron particles, (iii) the diffusion of the reaction gas components in a thin bed of the particles, (iv) the diffusion of the reaction gas components in the particles, (v) the carburization reactions on interior pore surface of the particles, (vi) the diffusion of carbon in metallic iron in the particles, and (vii) the cementite formation on the interface between metallic iron and cementite.

With respect to the steps other than the step (v), the resistance to the diffusion of the reaction gas components and the formation of iron carbides may be neglected due to the following reasons. For step (i) and (ii); the total flow rate of the reaction gas did not affect the rate of carbide formation (Fig. 5). For step (iii) and (iv); the weight of the reduced iron particles did not affect the rate (Fig. 4). The rate of iron carbide formation was nearly proportional to the total pressure of the reaction gas. The cementite region was distributed uniformly in the particles (Fig. 3). If the rate were controlled by this step, the rate would be independent of the total pressure. For step (vi) and (vii); the composition and the sulfur activity of the reaction gas gave very strong affects on the rate of iron carbide formation (Figs. 6 and 7, and 10).

The following experimental results support the almost exclusive control of the step (v). The rate of iron carbide formation was nearly proportional to the total pressure of the reaction gas (Figs. 8 and 9). The rate of the reduction of the iron ore particles in H_2 was much faster than the rate of the iron carbide formation by about one order. Even taking into account the differences between the diffusion coefficients of H_2 and CO , and between the equilibrium constants of the reactions; $\text{FeO}+\text{H}_2=\text{Fe}+\text{H}_2\text{O}$ and the reaction (2).

In the previous study¹⁴⁾ where the iron carbide formation rate from reduced iron particles in $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures was studied at the atmospheric pressure, it was concluded that the rate of the carburization reactions control the iron carbide formation rate. Although increasing the total pressure of the reaction gas mixtures theoretically increases the resistance of gas diffusion relative to the resistance of chemical reactions, the situation of the carburization reactions control does not change in the iron carbide formation from the reduced iron particles.

5. Conclusions

Under the total pressure up to 0.6 MPa, depressing the decomposition of iron carbides and the precipitation of free carbon have been successfully achieved by adding H_2S , corresponding to $a_s=0.3\text{--}0.6$, where a_s was defined to be $(p_{\text{H}_2\text{S}}/p_{\text{H}_2})/(p_{\text{H}_2\text{S}}/p_{\text{H}_2})_{\text{Fe/FeS}}$, to the CO-H_2 mixtures. Utilizing the effect of sulfur, the conversion rate of reduced iron to iron carbides was measured by the gravimetric technique in $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures. And the following results were ob-

tained.

(1) The fractional conversion of reduced iron to iron carbide measured by the gravimetric method agreed with that calculated from the composition analyzed by Mössbauer absorption spectroscopy in the range of f_θ at least less than 0.8. Namely, the gravimetric method has proved to be valid as a technique for measuring the rate of iron carbide formation from reduced iron in $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures.

(2) In the reduced iron particles partially converted to cementite in the reaction gases, formed cementite regions are distributed uniformly in the particles. The carbide formation rate did not change with the weight of iron ore particles in the range 25 to 50 mg, further it did only slightly to 100 mg. From these results, the gas diffusion resistance in the particles and the thin bed of them was so small to be negligible.

(3) The rate of iron carbide formation was much less than the rate of reduction rate in $\text{H}_2\text{-H}_2\text{S}$ mixtures and did not depend on the flow rate of the $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures even at the highest total pressure 0.6 MPa.

(4) The carbide formation rate was very sensitive to the composition of $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures and the rate was the maximum around the composition of 80% $\text{CO-H}_2\text{-H}_2\text{S}$ mixture.

(5) The carbide formation rate increased with increasing the total pressure of fixed compositions of 80% $\text{CO-H}_2\text{-H}_2\text{S}$ and 60% $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures.

(6) The carbide formation rate decreased with increasing the sulfur activity from 0.3 to 0.6 in 80% $\text{CO-H}_2\text{-H}_2\text{S}$.

(7) The carbide formation rate increased with increasing the temperature within the range of 773 to 973 K in 80% $\text{CO-H}_2\text{-H}_2\text{S}$ and within the range of 773 to 10123 K in 60% $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures.

(8) The rate of the iron carbide formation from reduced iron ore particles in $\text{CO-H}_2\text{-H}_2\text{S}$ mixtures is controlled by the carburization reactions on the pore surface of the particles provided that the following conditions are satisfied; the sample weight less than 50 mg, the total flow rate of the reaction gas more than $3.33\times 10^{-5}\text{ m}^3/\text{s}$, and under the total pressure 0.6 MPa or less.

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