Synthesis of Iron Carbide by Reaction of Iron Ores with H₂–CO Gas Mixtures Bearing Traces of Sulfur

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Particles of hematite ores in a porcelain boat were reduced and carburized at $823 \sim 1\,223$ K by H₂–CO mixtures under low sulfur pressures where metallic iron remained stable. Within major of these various conditions nearly one hour reaction could convert their particles completely to iron carbides such as mostly Fe₃C. It was found that traces of gaseous sulfur makes iron carbides enough stable rather than free carbon or metallic iron. Their conversion yields were insensitive to inlet H₂/CO mole ratio and ore type. Total sulfur contents in products obtained for lower sulfur pressures were as low as conventional reduced irons.

KEY WORDS: iron carbide; iron ore; H₂–CO gas mixture; gaseous reduction; carburization; gaseous sulfur.

1. Introduction

Utilization of iron carbides like cementite Fe₃C as an alternative iron source charged into an electric furnace is currently being demonstrated worldwide with much attentions.[1-3] This is probably because many of benefits mentioned below are considered for this utilization: (1) High quality iron scraps tend to be deficient; (2) The carbides also contain much carbon as heat source; (3) Non-pyrophoricity unlike reduced iron; (4) Rapid melting by injection can be expected due to fines; (5) Lower nitrogen level in steel can be realized; (6) Poor tramp elements in carbides is available to revive a large amount of low grade scraps.

In order to produce the iron carbides like Fe₃C, some pilot plants such as the Stelling Process[4] or the Iron Carbide Process[1-3] have been examined to react iron ores with natural gas in a fluidized bed, which were operated at relatively lower temperatures. At present, a commercial scale plant for producing carbides is under start up at Trinidad.[3] However, this process needs long residence times for the production, leaves a little residual iron oxides and has ore type dependence. Therefore, other economical processes having high productivity are desired to be further developed.

On these circumstances, we have just recently carried out a laboratory research using usual H₂–CO gas originated from fossil fuel and found out the possibility of an attractive process for producing easily iron carbides more stably at wider temperatures such as $873 \sim 1\,173$ K. This process has a feature operating under low sulfur pressures and has nearly one order of magnitude greater productivity than the above conventional method. In this paper, our fundamental test results to produce iron carbides from iron ores with H₂–CO gas in a small boat are reported.

2. Experiment

The chemical compositions of four types of iron ores A ~ D employed in this work are shown in **Table 1**. The ores were screened between $0.15 \sim 0.21$ mm diameters. Only ore B has a feature containing much gangues.

A batch of particles of 0.8 g weighed in a porcelain boat was reacted with H₂–CO gas mixtures under atmospheric pressure in a 22 mm inner diameter silica reactor heated isothermally at $823 \sim 1\,223$ K by a SiC element. The gas flow rate and the composition are in the range of H₂/CO = 100/200, 200/200, 200/100, and 200/50 ((cm³/min)/(cm³/min)). Using a H₂–0.2 or 2 vol% H₂S gas cylinder, gaseous sulfur H₂S was added into these gases in the proportion of $P_{H_2S}/P_{H_2} = 6.3 \times 10^{-5} \sim 4.8 \times 10^{-3}$, which are also represented as the sulfur activity in inlet gas, a_S. The value a_S is defined on the basis of gas ratio $(P_{H_2S}/P_{H_2})_e$ at Fe/FeS equilibrium[5,6] as listed in **Table 2**. The Goto method[7] enabling to evaluate thermal equilibrium states of chemical reactions confirmed that the calculated values a_S nearly equal to inlet ones under the present experimental conditions.

$$a_S = (P_{H_2S}/P_{H_2})/(P_{H_2S}/P_{H_2})_e \quad \cdots\cdots\cdots\cdots (1)$$

X-ray powder diffraction patterns of specimens after

Table 1. Chemical composition of iron ores. (mass%)

Name	Key	T.Fe	FeO	SiO₂	Al₂O₃	CaO	S
San Ishidro	Ore A	68.23	0.42	0.89	0.43	0.01	0.003
Hamersley	Ore B	62.38	0.07	4.47	2.63	0.04	0.009
MBR	Ore C	68.10	0.13	0.94	0.51	0.04	0.002
Carajas	Ore D	69.13	0.14	0.47	0.76	0.01	0.001

reaction were taken using a Cobalt target. The obtained results were identified referring to ASTM cards. The content of existing solid phase i F_i (mass%) was determined semi-quantitatively using the strongest diffraction peak height for each material. Several samples after reaction were compacted with resin, whose cross sections were observed by an optical microscopy. Carbon and sulfur contents in products were determined by means of combusting typical samples with oxygen.

3. Experimental Results

X-ray analysis of products identified the existence of phases Fe_3C, $Fe_{2.5}C$, Fe_2C, and C other than usually existing phases Fe_3O_4, FeO, and Fe, referring to ASTM cards. Their strongest peaks are shown in **Table 3** for carbides or carbon. **Figure 1** shows some examples of X-ray diffraction patterns for the given conditions. As seen in Fig. 1(a), only Fe_3C exists with traces of free

Table 2. Gas ratio $(P_{H_2S}/P_{H_2})_e$ at Fe/FeS equilibrium.[5,6]

Temp.(K)	873	973	1073	1173	1273
$(P_{H_2S}/P_{H_2})_e \times 10^4$	3.56	9.43	21.1	39.0	58.3

Table 3. ASTM card, crystal system, and diffraction peak of materials detected in this work.

Material	Number of ASTM card	Crystal system	Strongest peak	
			hkl	2θ(deg)
Fe_3C	35–772	Orthorhombic	031	52.7
$Fe_{2.5}C$	36–1248	Monoclinic	510	51.7
Fe_2C	20–508	Monoclinic	510, 021	51.5
			31–2, 40–2	52.3
C	26–1079	Hexagonal	003	31.0

carbon and metallic iron. In Fig. 1(b), $Fe_{2.5}C$ and Fe_2C are also appeared besides Fe_3C with traces of C, Fe, and FeO. Because all diffraction peaks reflected from Fe_2C phase shifted toward less angles by nearly $2\theta = 0.5$ degree and the strongest peak by crystal planes $hkl = 31$-2, 40-2 overlapped each other with that by $hkl = 510$ of $Fe_{2.5}C$ phase, these two higher iron carbides could not be divided definitely. Therefore, the content of these carbides was evaluated only as their summation $F_{Fe_{2.5}C + Fe_2C}$ (mass%).

Figure 2 shows variation of products with reaction time for ore A under the condition of $H_2/CO = 200/200$, $P_{H_2S}/P_{H_2} = 6.3 \times 10^{-4}$, $a_S = 0.30$, and 1 073 K. At 10 min the metallic iron content became maximum. Hereafter iron carbide Fe_3C increased with decreasing metallic iron. At 60 min product contents reached $F_{Fe_3C} = 93.2$ and $F_C = 5.3$ mass% with both chemically determined contents of less 0.028 mass% S and 6.4 mass% C close to 6.7 mass% C in the form Fe_3C. The stability of the carbide was enough excellent even after adding 60 min reaction in the same gas. Through entire reaction periods, free carbon was hardly precipitated.

Figure 3 shows variation of products with reaction time for ore A under the condition of $H_2/CO = 200/200$, $P_{H_2S}/P_{H_2} = 0$ or 4.2×10^{-4}, $a_S = 0$ or 1.18, at 873 K. In $a_S = 0$, much free carbon were precipitated with less Fe_3C, great degradation of ore particles and huge swelling of samples in a boat. However, in $a_S = 1.18$, iron carbides were preferred without free carbon and degradation of ores. At 240 min the contents of products reach $F_{Fe_3C} = 50.0$, $F_{Fe_{2.5}C + Fe_2C} = 35.6$, $F_C = 2.7$, $F_{Fe} = 9.6$, and $F_{FeO} = 2.1$ mass% with chemical contents of 7.8 mass% C and 0.22 mass% S. At 360 min, amount of higher iron carbides $Fe_{2.5}C$ and Fe_2C increased as shown already in Fig. 1(b). These $Fe_{2.5}C$ and Fe_2C phases were also

Intensity (CPS)

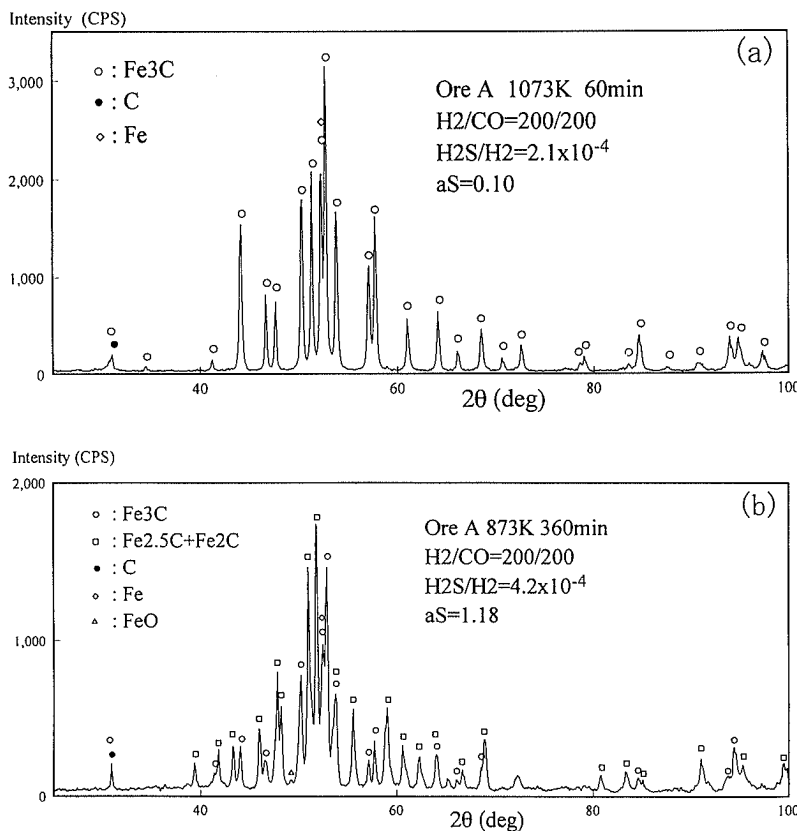o : Fe3C
● : C
◇ : Fe

Ore A 1073K 60min
H2/CO=200/200
H2S/H2=2.1x10⁻⁴
aS=0.10

2θ (deg)

(a)

Intensity (CPS)

o : Fe3C
□ : Fe2.5C+Fe2C
● : C
◇ : Fe
▲ : FeO

Ore A 873K 360min
H2/CO=200/200
H2S/H2=4.2x10⁻⁴
aS=1.18

2θ (deg)

(b)

Fig. 1.
Examples of X-ray diffraction patterns.
(a) 1 073 K, $F_{Fe_3C} = 50.0$, $F_C = 5$, $F_{Fe} = 2.1$ mass%, chemically 8.9 mass% C, 0.015 mass% S, (b) 873 K, $F_{Fe_3C} = 40.2$, $F_{Fe_{2.5}C + Fe_2C} = 52.0$, $F_C = 2.8$, $F_{Fe} = 3.9$, $F_{FeO} = 1.1$ mass%, chemically 9.7 mass% C, 0.29 mass% S.

appeared appreciably for other two conditions of $P_{H_2S}/P_{H_2}=4.2\times10^{-4}$, $a_S=0.45$ at 973 K and $P_{H_2S}/P_{H_2}=1.1\times10^{-3}$, $a_S=0.75$ at 1023 K, under high carbon potentials with $H_2/CO=200/200$. These conditions are subscripted as stars in later Fig. 4.

Figure 4 summarizes the contents (mass%) of both iron carbides (mostly Fe_3C) and free carbon obtained after 60 min reaction of ore A with $H_2/CO=200/200$ or 200/50 as functions of values a_S and temperatures. In this work, the results with $F_{Fe_3C}>80$ mass% and those with $F_{Fe_3C}>45$ mass% together with $F_C<11$ mass% are called the most favorite area and the favorite area for producing iron carbides, respectively. In the figure, star

marks represent the conditions identifying appreciable existence of higher iron carbides $Fe_{2.5}C$ and Fe_2C.

Exclusive of high sulfur conditions, it was found that the conditions of $a_S=1.0\sim2.0$ at $823\leq T<923$ K, $a_S=0.7\sim2.0$ at 923 K, and $a_S=0.05\sim1.0$ at $923<T\leq1223$ K are more favorable for producing iron carbides and the conditions of $a_S=0.10\sim1.0$ at $973\leq T\leq1123$ K are most favorable.

As shown in **Fig. 5**, sulfur content in products after reaction increased with inlet a_S. It was confirmed that the conditions with low sulfur contents above 0.015 mass% S can produce iron carbides stably with the complete conversion. At $a_S>1$, the content was as high
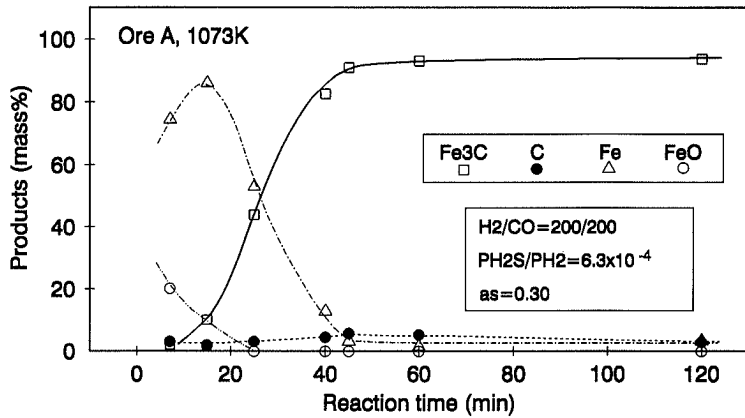

Fig. 2.
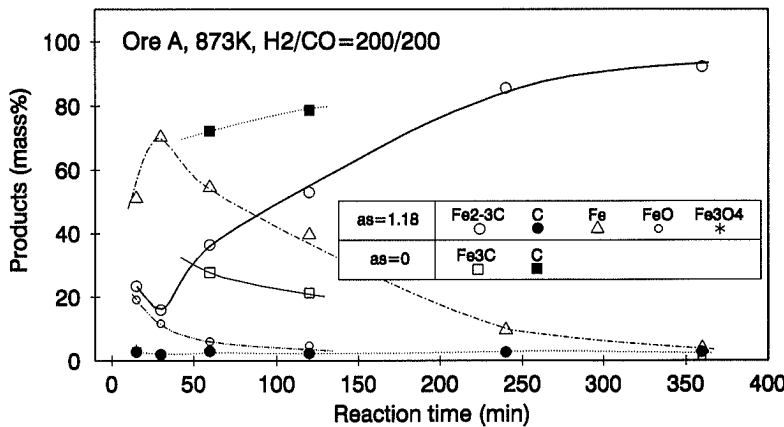Reaction time dependence of product contents at 1073 K.

Fig. 3.
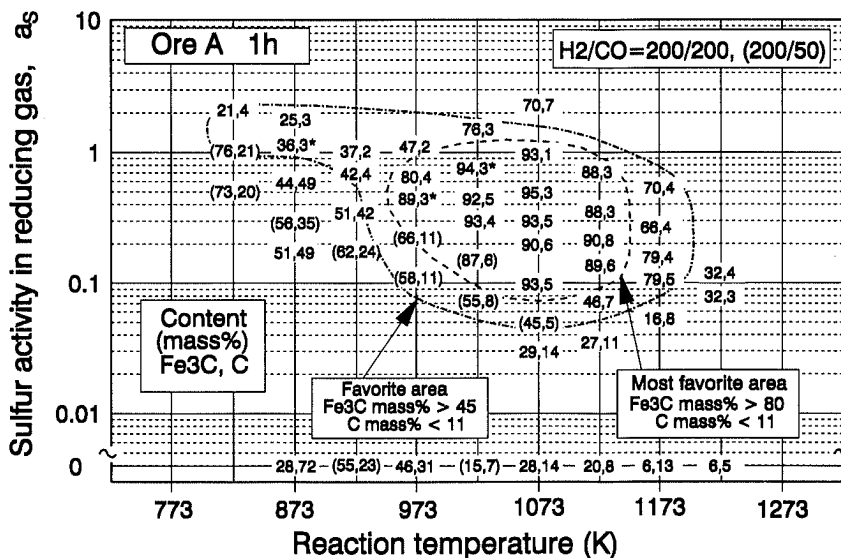Reaction time dependence of product contents at 873 K.
(Exp. cond.: same as Fig. 1(b))

Fig. 4.
Influence of a_S and temperature on product contents.
(*: a little $Fe_{2.5}C$ and Fe_2C beside Fe_3C)

as 2.63 mass% S due to fairly formation of FeS despite reaching a high value of $F_{Fe_3C} = 70.2$ mass%.

Figure 6 shows dependence of H_2/CO mole ratio on product contents obtained for 60 min reaction of ore A at 1 073 K. Below $H_2/CO = 200/100$, the contents of iron carbides were in the level of 90 mass% with free carbon less than 0.4 mass% analyzed chemically.

As shown in **Fig. 7**, product contents for 60 min reaction at 1 073 K did not depend on four kinds of ores A~D, keeping more than 90 mass%.

It is known that a picric acid dissolved in hot alkali water solution can etch only cementite selectively, not

metallic iron, to convert a bright optical reflection image into dark one. The optical microscopically observation after such ecthing indicated that the bright areas showing
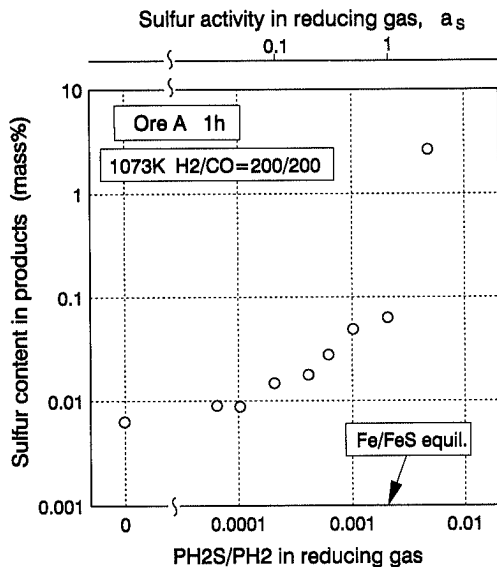

Fig. 6. Influence of H_2/CO ratio in reducing gas on product contents.

Fig. 5. Relation between a_s and sulfur content in product at 1 073 K.
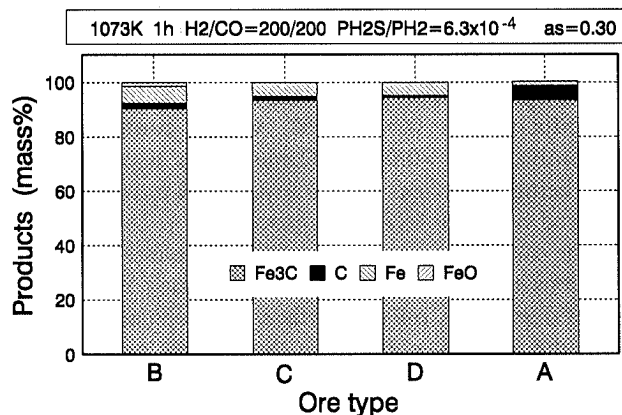

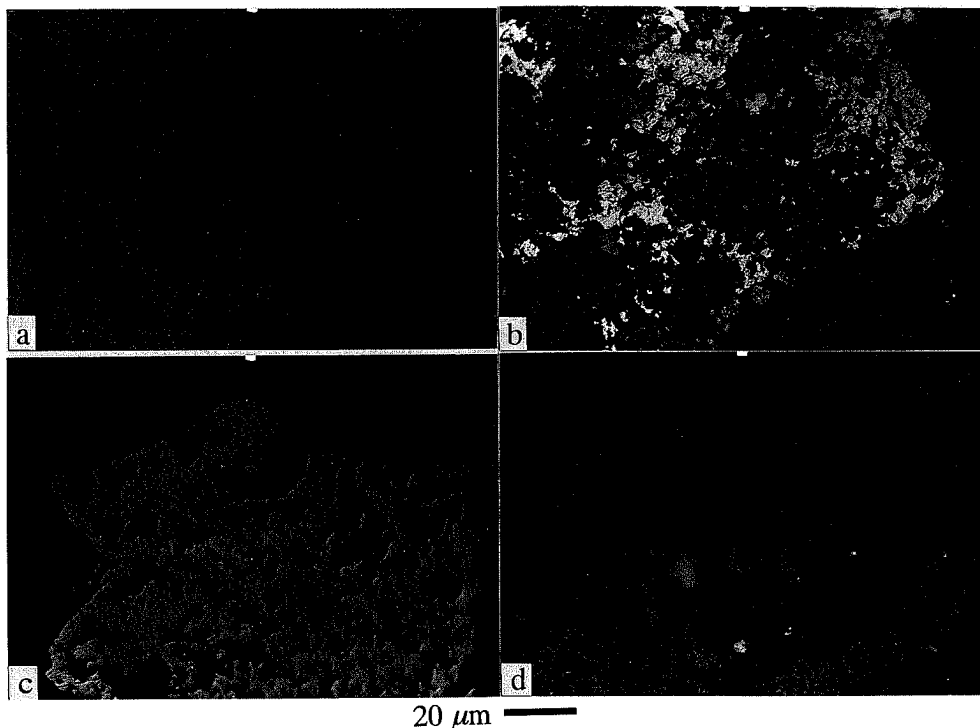**Fig. 7.** Influence of ore type on product contents.

$20 \mu m$

Fig. 8. Optical micrographs of cross sections of products with or without etching the same areas.
(1 073 K, ore A, $H_2/CO = 200/200$, $P_{H_2S}/P_{H_2} = 2.1 \times 10^{-4}$, $a_s = 0.10$) (a),(b) 20 min, $F_{Fe_3C} = 31.7$, $F_C = 1.9$, $F_{Fe} = 65.6$, $F_{FeO} = 0.8$ mass%, (c),(d) 60 min, $F_{Fe_3C} = 92.9$, $F_C = 5$, $F_{Fe} = 2.1$ mass%, (a),(c) no etching, (b),(d) etching.

both metallic iron and iron carbide phases decreased with reaction times as compared in **Figs. 8(a)~8(d)**, where the conditions of ore A, $H_2/CO = 200/200$, $P_{H_2S}/P_{H_2} = 2.1 \times 10^{-4}$, $a_S = 0.10$, 1 073 K, and 20 or 60 min are quoted. The latter condition gave a dark image because of almost completely conversion from iron ore into carbides.

4. Discussion

As indicated in Figs. 2 and 3, in the earlier stage of reaction the reduction of hematite to metallic iron proceeds and subsequently the metallic iron is carburized by CO to form iron carbides rather than free carbon under the small existence of gaseous sulfur.

For the case without sulfur, a large quantity of free carbon were formed with less iron carbides at lower temperatures, as shown in Fig. 3 or 4, because the employed gas mixtures have higher carburizing ability. On the other hand, the addition of sulfur into reaction gas mixtures suppressed greatly carbon precipitation and preferred iron carbides stably under wider experimental conditions. This influence could be observed from fairly lower sulfur potentials with relatively low sulfur contents in products near 0.02 mass%, whose contents were comparable to $S = 0.01 \sim 0.02$ mass% in usual sponge irons, being fairly less than 0.2 mass% S in iron pellets produced by the FASTMET process.[8]

In the case without sulfur, carburization into bulk iron will occur through fresh iron surface along with much carbon deposition on the surface. It is considered that when the carbon content in bulk iron exceeds the solubility, carbides may be formed interiorly. On the other hand, it is generally known that sulfur is a surface active element to form ad-layer of sulfur anions on iron surface. In the existence of sulfur, the ad-layer may cause fairly decrement of the carburization rate into solid iron.[9] However, it was recognized that this carburization can take place appreciably even under the saturated chemisorption of sulfur over iron. Because carbon atom radii are fairly less than sulfur anion radii, carbon atoms could pierce the sulfur ad-layer to migrate into bulk iron. Moreover, the iron surface brocked by sulfur should suppress carbon precipitation. Therefore, it is naturally considered that carbon atoms entering bulk iron could be converted easily to carbides without carbon precipitation on solids with their high stability. The authors reported earlier that traces of gaseous sulfur promotes some iron morphologies like porous or fibrous forms.[10,11] It is supposed that these iron structures having much micropores will provide the relatively larger overall conversion rates. Thus, the stability of iron carbides without carbon deposition can be explained as a result of inactivation of the fresh iron surface by sulfur adsorption.

Hutchings et al.[12] had reacted iron ores in a fluidized bed with H_2–CH_4 gas mixtures at 900 ~ 1 100 K and found out partly iron carbides besides free carbon and metallic iron. This is probably because their tests were done under unknown lower sulfur pressures than this work. Nakagawa et al.[13] have also recognized fairly iron carbides in the reactor without sulfur. But their carbides became unstable with further reaction periods. Motlagh[14] had developed a reaction plant named SIC process for producing carbides with a high carbon content of 40 mass% C. This product likely contains much free carbon because the form Fe_3C amounts to 6.7 mass% C.

Utilizing a fluidized bed reactor, further reaction tests will be necessary to manufacture economically a large amount of stable high grade iron carbides.

5. Conclusions

In order to synthesize iron carbides, particles of hematite ores were reacted with H_2–CO gas mixtures having low sulfur pressures at 823 ~ 1 223 K. The following results were obtained.

(1) Within these various conditions nearly one hour reaction could convert their particles completely into iron carbides as mostly cementite Fe_3C, partly $Fe_{2.5}C$ and Fe_2C with the excellent phase stability. It was found that traces of gaseous sulfur prefers iron carbides rather than free carbon or metallic iron.

(2) For producing iron carbides, it was concluded that the conditions of $a_S = 1.0 \sim 2.0$ at $823 \le T < 923$ K, $a_S = 0.7 \sim 2.0$ at 923 K, and $a_S = 0.05 \sim 1.0$ at $923 < T \le 1\,223$ K are more favorable and the conditions of $a_S = 0.10 \sim 1.0$ at $973 \le T \le 1\,123$ K are most favorable.

(3) Their conversion yields were insensitive to the H_2/CO mole ratio and ore types. Total sulfur contents in carbides obtained under lower sulfur pressures were as low as usual reduced irons.

(4) Sulfur species adsorbed on iron surface is supposed to have a couple of actions. One is that it inhibits precipitation of carbon. The other is that it stabilizes iron carbides through carburizing substantially into iron bulk even under the highly sulfur adsorption.

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