Carburization of Iron Using CO-H$_2$ Gas Mixture

Ho-Sun Hwang[1], Uoo-Chang Chung[2,*], Won-Sub Chung[3], Young-Rae Cho[3],
Byong-Ho Jung[4], and G. P. Martin[5]

[1] Technical Research Laboratories, Changwon Specialty Steel Co., Ltd.
65 Sinchon-dong, Changwon 641-370, Korea
[2] Trouble Analysis and Reliability Research Center, Pusan National University
San 30 Jangjeon 2-dong, Geumjeong-gu, Busan 609-735, Korea
[3] School of Materials Science and Engineering, Pusan National University
[4] Division of Materials Science and Engineering, Pukyong University
San 100 Yongdang-dong, Nam-gu, Busan 608-739, Korea
[5] Metallurgical and Material Engineering Department, Colorado School of Mines
Golden, Colorado 80401, USA

Iron carbides formed on the surface of iron and iron oxide samples at 640 $^{\circ}$C in a gas mixture of CO-H$_2$ were characterized by scanning electron microscopy (SEM), Mössbauer spectroscopy, X-ray diffraction patterns (XRD), and by measuring mass change. The Fe$_3$C amount of the samples has been quantitatively evaluated by the weight change during carburization. While Fe$_2$O$_3$ powder was mostly completed to Fe$_3$C in the early stage, within 5 min after reduction reactions, the conversion of Fe powder sample to Fe$_3$C (iron carbide) was almost finished after 10 min. The carburization rate of a Fe sheet was very slow and intermediate products (Fe$_2$C, Fe$_5$C$_2$) were observed. This phenomenon is largely due to the difficulty of carbon diffusion into its dense surface. It was found that the carburization rate was affected by change of surface conditions and surface area by reduction, degradation, and cracks at high temperature. This study should help provide a fundamental understanding of carburization in the field of iron-making and suggest a direction for its further development.

Keywords: carburization, iron carbide, Fe and Fe$_2$O$_3$ powder, Fe sheet, gas mixture

1. INTRODUCTION

The particulate iron carbide is a very important material for the development of new steel-making technologies and will be used as a metallurgical product in the near future. Iron carbide offers numerous benefits, including a low level of tramp elements, making it useful as an alternative to high quality iron scrap, potential to serve as an auxiliary heat source, non-pyrophoric property in contrast to reduced iron, and speedy injection into the bath. Furthermore, with its use, lower nitrogen levels in steel can be realized [1-4].

The mechanism for carburization can be developed on the basis of fundamental concepts of adsorption kinetics. Conejo *et al.* [5] have previously considered adsorption as the rate-limiting step during conversion of iron to cementite. The adsorption behavior was modeled and systematized by Turk-dogan and Vinters [6]. From their results, the chemi-sorption of both CO and H$_2$ are considered to be at equilibrium. It was

supposed that carbon is formed by dissociation of rate-controlling reactions. The carburization reaction is much faster than two dissociation reactions. This is because the intrinsic rate of carburization, that is, a reaction between the absorbed carbon on the iron surface and the iron itself, is high relative to the rate at which absorbed carbon is created on the iron surface [6-8].

The general production for iron carbide has been reported in previous studies, but research on the formation of carbide and the rate of carburization is lacking [9]. Characteristics of carburization with iron sheets, iron powder, and iron oxide powder have been investigated by SEM micrographs, Möss-bauer analyses, X-ray diffraction patterns, and by measuring mass change. The results from the present research could be used as basic data for carburization.

2. EXPERIMENTAL PROCEDURES

2.1. Experimental system and materials

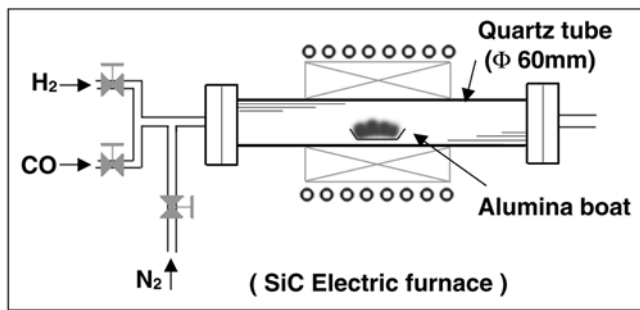The measurement of reaction rates associated with the

Fig. 1. Schematic diagram of tubular reactor system.

conversion of the samples to carbides was conducted using a horizontal tube furnace. A schematic diagram of the tubular reactor apparatus is shown in Fig. 1. The basic setup consists of two components: a SiC electric tube furnace (6 cm in diameter and 100 cm in length) and a gas flow control system. The physical properties are shown in Table 1. Hematite powder (reagent grade, Fe_2O_3), iron powder (reagent grade, Fe), and an iron sheet were chosen as solid reactant to compare reaction rates associated with the conversion to iron carbides. The iron sheet was coated with 5 organic materials. In order to remove organic coating, the samples were immersed in 2 % Nital solution for 10 sec and were electro-polished with 10 mA/cm^2 current density in solution (22g H_2SO_4 + 8g H_2O) for 15 sec.

2.2. Experimental procedure

Before charging the samples, nitrogen gas at 640 $^{\circ}$C was provided into the reactor for 10 min, and the reduction of iron oxide powder was carried out under a flow rate of hydrogen gas at 1 *l*/min for 15 min. After reduction, a CO and H_2 gas mixture for carburization of iron powder and the iron sheet was introduced into the reactor and the reaction time was 5, 10, and 20 min, respectively. Samples of iron powder and iron sheet were directly carbidized without reduction procedure. The gas mixture was composed of hydrogen (80 %) and carbon monoxide (20 %) and the total flow rate was kept at 1 *l*/min. A lower concentration of carbidizing gas (higher ratio $Y_{H2}/Y_{CO}=4$) was employed in order to reduce generation of free carbon and promote iron carbide. The conversion degree of iron carbide was calculated by measuring mass change. Phase analyses of the solid product were performed by SEM, XRD, and Mössbauer spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Carburization of samples

Fig. 2 shows the carburization rates for a reactant gas mixture with a ratio $Y_{H2}/Y_{CO}=4$ at 640 $^{\circ}$C for different sample types (Fe_2O_3; hematite powder and Fe powder of reagent grade and Fe sheet). As shown in the results, the conversion of Fe_2O_3 powder and Fe powder to Fe_3C (iron carbide) was mostly completed within 5 and 10 min respectively. However the carburization rate of the Fe sheet was very slow. The carburization rate of Fe_2O_3 powder was much faster than that of the other two samples. This result may be explained by the following four mechanisms [10]:

(1) An increase in specific surface area owing to the formation of porosity in the sponge iron by the reduction of Fe_2O_3 to Fe.

(2) The diffusion of carbons through the generation of cracks by the thermal shock.

(3) An increase in specific surface area owing to degradation of particles by thermal shock in the high temperature.

(4) Degradation to small particles owing to volume expansion by carburization of Fe to Fe_3C.

These results were established by cracks and degradation produced in the particles, as shown in the SEM micrograph of Fig. 3. The measured carburization rate of Fe_2O_3 powder was compared with an experiment conducted by Conejo *et al.* [5], wherein the experimental conditions were as follows:
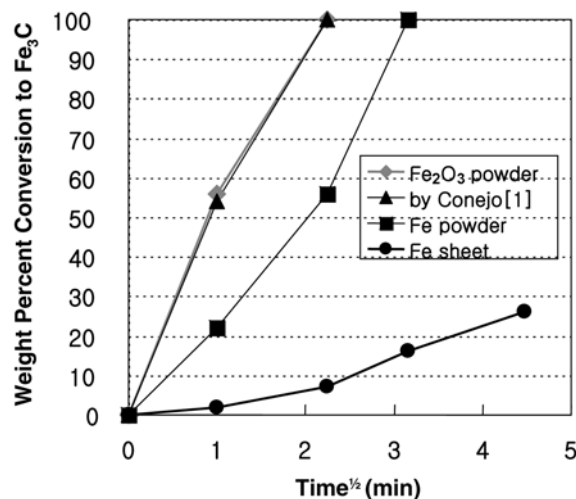

Fig. 2. Effect of Fe powder, Fe_2O_3 powder, and Fe sheet on the rates of carburization at 640 $^{\circ}$C.

Table 1. Physical properties of samples used

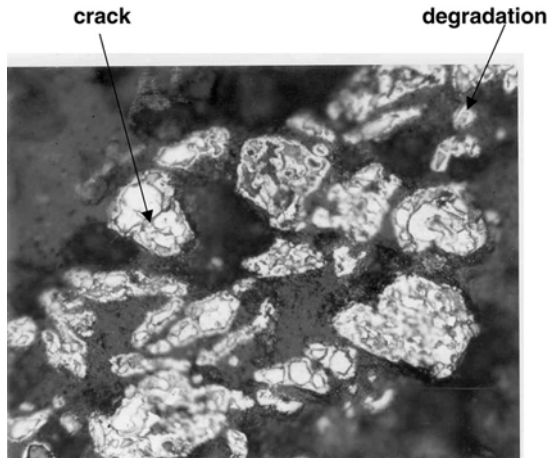| Particle types	Mean size (μm)	Thickness (μm)	Surface area (μm^2)	Weight (mg)
Fe_2O_3 powder	D=0.3		7.84×10^{10}	30.8
Fe powder	D=0.3		7.84×10^{10}	30.8
Fe sheet	(14.59 × 11.17 × 25) W × L × H	25	3.27×10^{8}	30.8

Fig. 3. SEM micrograph of Fe₂O₃ powder by cracks and degradation after reduction at 640 °C for 15 min (×1000).

Fe₂O₃, 0.2~0.4 μm, 620 °C, Y_{H2}/Y_{CO}=4. Fairly good agreement was obtained with their results. In addition, the carburization rate of the Fe sheet was much slower than those of Fe₂O₃ powder and Fe powder. This could be attributed to small specific surface area, insufficiency of degradation site, and difficulty in diffusion of carbon through the dense iron surface.

3.2. SEM observation and Mössbauer analysis

Fig. 4 shows a SEM micrograph of a carbidized Fe sheet after carburization reaction at 640 °C for 20 min under gas mixture. Carbon penetrated into the surface of sample, and iron carbide of 5~10 μm in thickness was formed from both sides of the surface as shown in Fig. 4. It is expected that the structure of iron carbide is composed of cementite (Fe₃C) and intermediate phase (Fe$_x$C$_y$). The percentage of carburization calculated from the thickness of iron carbide in the SEM
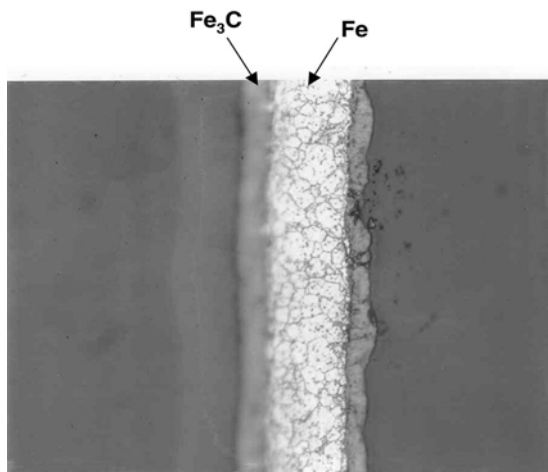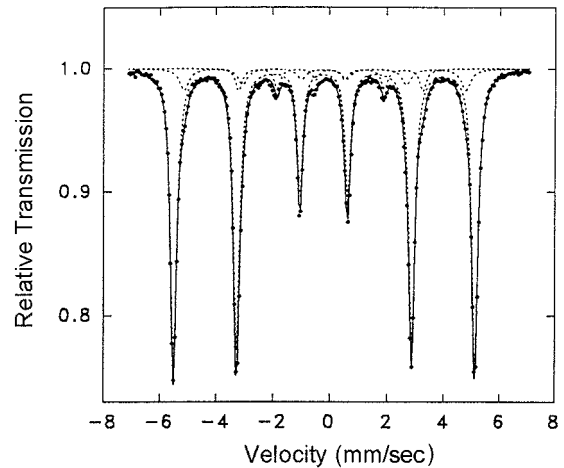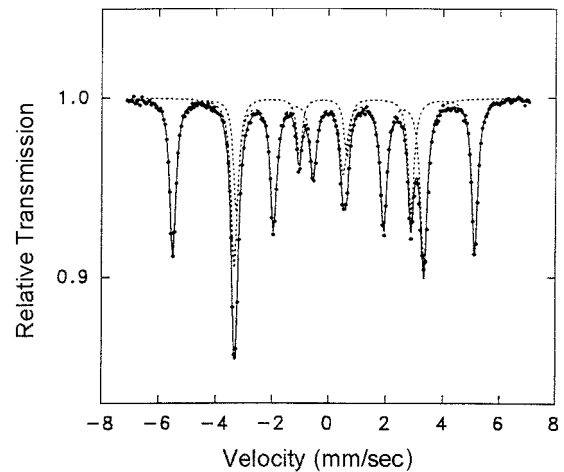

Fig. 4. SEM micrograph of Fe sheet carbidized at 640 °C for 20 min (×1000).

Fe : bcc-Fe(no C neighbors) = 84.4%
FexCy: bcc-Fe(C neighbors) = 8.8%
Fe₃C = 6.8%

Fig. 5. Mössbauer analysis of Fe sheet after carburization at 640 °C for 5 min.

Fe : bcc-Fe(no C neighbors) = 43.8%
FexCy: bcc-Fe(C neighbors) = 0%
Fe₃C = 56.2%

Fig. 6. Mössbauer analysis of Fe powder after carburization at 640 °C for 5 min.

micrograph was about 37 %. The calculated value was compared with that measured from a gravimetric system (26 %) in Fig. 2. As noted above, the discrepancy (11 %) can be explained by the fact that although iron carbide contained an intermediate phase (Fe$_x$C$_y$), the calculated value was assumed to derive from Fe₃C entirely. It was confirmed that the phases of iron carbide were composed of cementite (Fe₃C) and intermediate phase (Fe$_x$C$_y$) by Mössbauer analysis shown in Fig. 5. This agrees well with the X-ray result shown in Fig. 9. The carburization rate of the Fe sheet was very slow due to a small specific surface area, insufficiency of degrada-
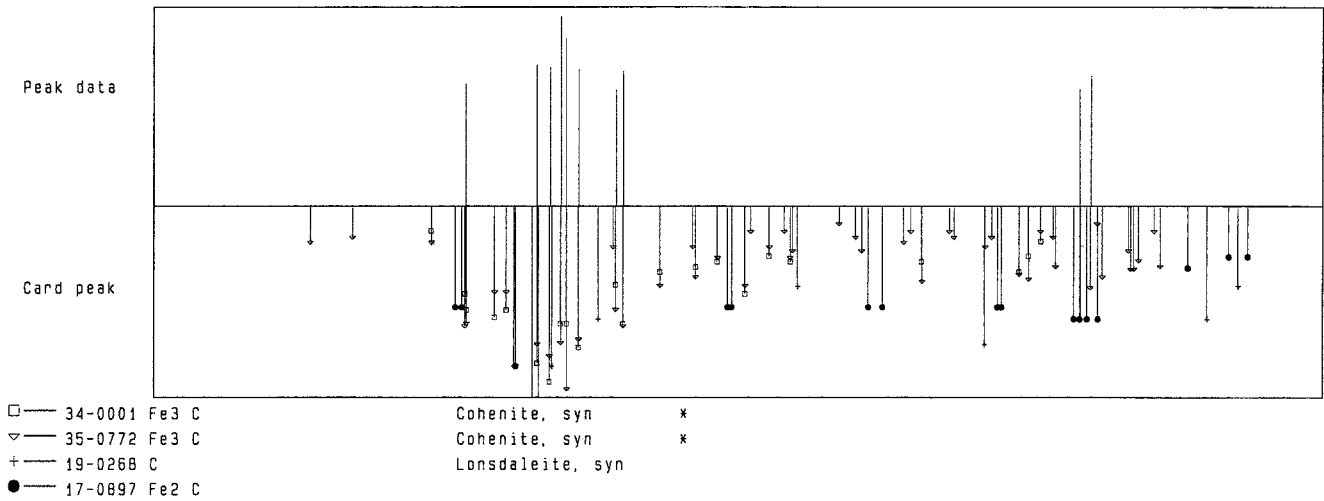
Fig. 7. X-ray diffraction patterns of Fe_2O_3 powder after carburization at 640 °C for 5 min.

tion site, and difficulty in diffusion of carbon through the dense surface. Fig. 5 shows a Mössbauer analysis of a carbidized Fe sheet after carburization at 640 °C for 5 min. The total conversion of Fe to Fe_3C in weight percent was approximately 7 %, which was equal to the measured value shown in Fig. 2.

Fig. 6 shows a Mössbauer analysis of carbidized Fe powder after carburization at 640 °C for 5 min. The total conversion of Fe to Fe_3C in weight percent was approximately 56 %. The value was compared with that measured from Fig. 2 and fairly good agreement was shown. While an intermediate phase (Fe_xC_y) was observed in the Fe sheet, it was
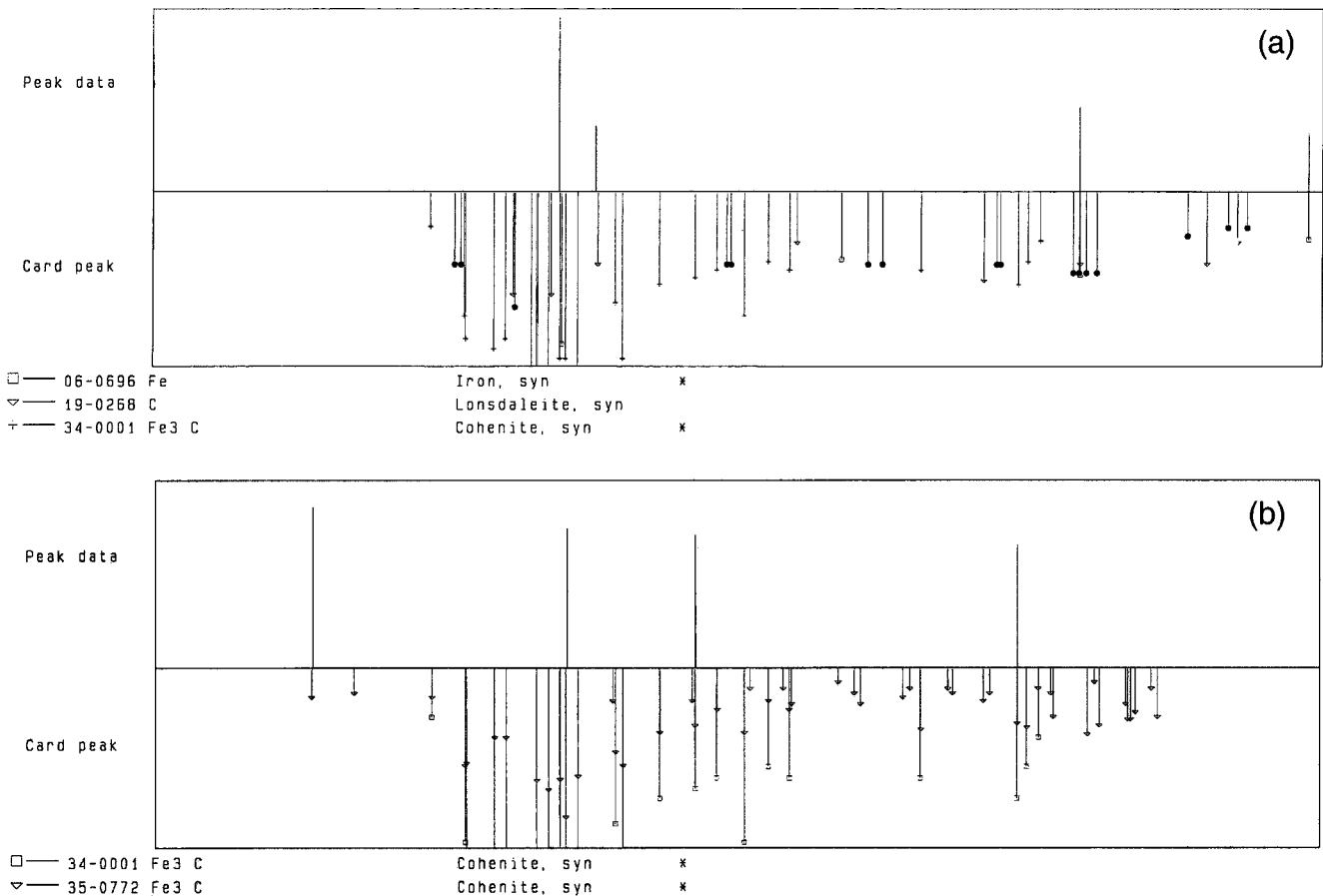

Fig. 8. X-ray diffraction patterns of Fe powder after carburization at 640 °C with time: (a) 5 min and (b) 10 min.
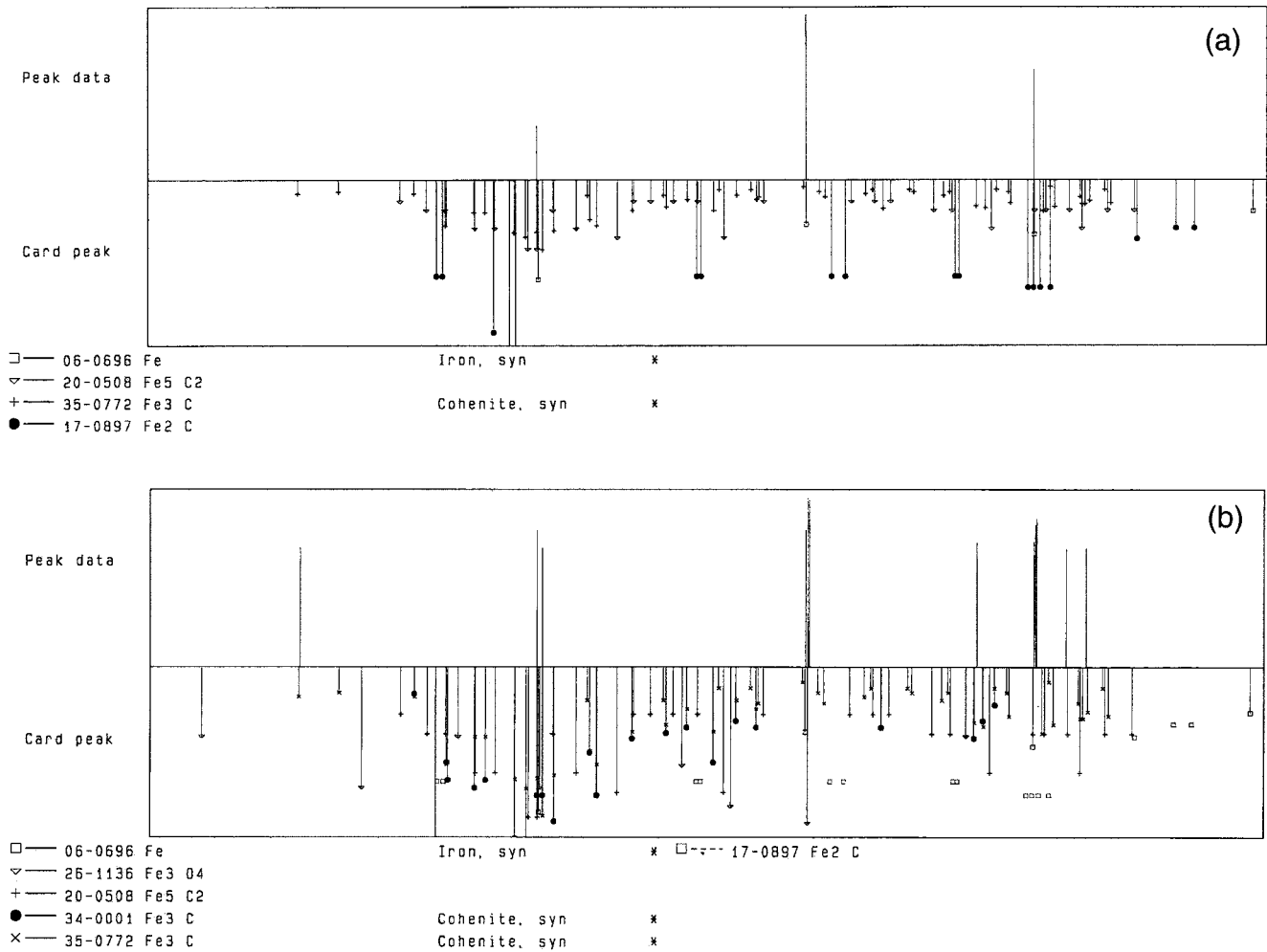
Fig. 9. X-ray diffraction patterns of Fe sheet after carburization at 640 °C with time: (a) 5 min and (b) 20 min.

not observed in the Fe powder. It is considered that the sample of Fe sheet needs time for penetration and diffusion of carbons, while Fe powders carbidized directly on the reduced surface. In addition, the carburization rate of Fe powder was much faster than that of the Fe sheet. This could be attributed to the large specific surface area of Fe powder containing fine particles.

3.3 X-ray observation

The reacted samples are examined with XRD and their diffraction patterns are shown in Figs. 7-9. The diffraction patterns were o investigated closely in order to assess the phases of iron carbide with reaction time. As shown in the results, in the case of Fe_2O_3 powder, the samples were mostly converted to Fe_3C within 5 min and partly free carbon (C), intermediate carbides (Fe_2C). It was also found that Fe powder was completely carbidized after 10 min without intermediate carbides. In the Fe sheet, Fe, Fe_2C, Fe_5C_2 and Fe_3C phases were shown after 5 min and an intermediate phase still existed after 20 min of reaction time. The conver-

sion to complete Fe_3C in Fe sheet is difficult due to its dense surface. As noted above, these results agreed with the Möss-bauer analysis shown in Figs. 5 and 6.

4. CONCLUSIONS

Iron carbide formed under a gas mixture of CO-H₂ was quantitatively analyzed by SEM, Mössbauer spectroscopy, XRD, and by measuring mass change. The following conclusions were obtained.

1. The measured carburization rate of samples was compared with the results of Mössbauer analyses and fairly good agreement was obtained. In particular, the carburization rate in Fe_2O_3 powder was the fastest, and the results corresponded closely with those of Conejo *et al.* [5].

2. The rapid carburization rate of Fe_2O_3 could be explained by the following: an increase in specific surface area due to the formation of porosity in the sponge iron through the reduction; an increase in specific surface area due to degradation of particles by thermal shock; the diffusion of carbon

due to the generation of cracks through the thermal shock; and degradation due to volume expansion through carburization of Fe to Fe_3C.

3. The carburization rate of the Fe sheet was very slow. This was attributed to its small specific surface area, a degraded particles, and difficulty in diffusion of carbon through the dense iron surface.

4. From Mössbauer and XRD observations for analysis of the phase of product carbide, it was found that Fe_2O_3 powder was converted to Fe_3C after 5 min of reaction. Fe powder was completely carbidized after 10 min without intermediate carbides. However, in the Fe sheet, an intermediate phase still existed after 20 min of reaction time due to difficulty in diffusion of carbon through its dense surface.

ACKNOWLEDGMENTS

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