Microstructure Evolution of Iron Carbide during Reaction with Steam at Elevated Temperatures

Masaaki HISA, Atsushi TSUTSUMI¹⁾ and Tomohiro AKIYAMA²⁾

Department of Chemical Engineering, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Sakai, Osaka 599-8531 Japan.

1) Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656 Japan.

2) Formerly at Department of Chemical Engineering, Osaka Prefecture University, now at Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Sapporo 060-8628 Japan. E-mail: takiyama@eng.hokudai.ac.jp

(Received on June 8, 2004; accepted in final form on July 29, 2004)

Cross-sectional microscopy and X-ray diffractometry in combination with thermogravimetry were conducted to investigate the microstructure evolution of iron-ore derived iron carbide caused by the reaction with steam at elevated temperatures. During continuous heating from 393 to 1373 K at 10 K min⁻¹, the microstructure of the iron carbide changed in the following sequence: (1) densification due to oxidation of Fe₃C, (2) coarsening by decomposition of Fe₃C and by reduction of iron oxides, and then (3) re-densification associated with oxidation of Fe. The microstructure evolution was found to correspond well to the volume change due to the phase transformations of the iron carbide. Graphite formed in the iron carbide as a result of decomposition of Fe₃C seems to have a highly crystallized lattice that contracts in its *c*-axis direction.

KEY WORDS: iron carbide; graphite; hydrogen; microstructure; oxidation; reduction; microscopy; X-ray diffractometry; thermogravimetry.

1. Introduction

Iron carbide recently draws an attention as a new iron source in the ironmaking industry.^{1,2)} In addition, iron carbide is also thought to have a potential as a hydrogen source or a hydrogen storage material.³⁾ The present authors indeed revealed the feasibility of co-production of metallic iron and hydrogen through a reaction between iron carbide and steam at temperatures around 873 K.^{3,4)} Carbon oxides were simultaneously produced by the reaction, but at lower temperatures such as 573 K hydrogen of high purity was able to be collected as a result of oxidation of iron carbide.^{3,5)}

The iron carbide used in the previous investigations was produced directly from hematite iron ore with a two-step fluidized bed method and contained a large number of cracks and pores.^{5,6)} Because the reaction of iron carbide with steam is a solid–gas reaction, its kinetics would be influenced by the microstructure of iron carbide. By using reduced iron that was also derived from hematite ore and possessed a porous microstructure, Iguchi and his colleagues carried out a systematic investigation on the carburizing process of the porous iron with mixed gases containing carbon monoxide and shed light on the influence of microstructure over the formation mechanism of iron carbide.^{7–10)} To date, however, little has been understood about the relationship between microstructure and reaction kinetics for the iron carbide–steam reaction although a previous research implied that the porosity of the hematite ore-de-

rived iron carbide can vary through the reaction with steam at temperatures lower than 1073 K.¹¹⁾

In the present investigation, which was meant as the first step to understand the correlation between microstructural features and reaction kinetics for the iron carbide–steam reaction, cross-sectional microscopy was employed to examine the microstructure evolution of the ore-derived iron carbide brought by the reaction with steam in a temperature range between 393 K and 1373 K. Phase transformations that occurred in the iron carbide through the reaction were also analyzed by X-ray diffractometry (XRD) in combination with thermogravimetry (TG) and were associated with the microstructure variation of the iron carbide.

2. Experimental Procedures

The iron carbide used in the present study was prepared directly from hematite iron ore by a two-step fluidized bed method.⁴⁾ Chemical analysis revealed that the iron carbide contained around 90 mass% of Fe₃C, as well as metallic iron and iron oxides (mainly Fe₃O₄ and Fe₂O₃) as impurities. The apparent porosity of the iron carbide was determined to be 14% by a penetration immersion method using xylene. Powder of the iron carbide was sieved with a 300 μm stainless steel sieve, about 150 mg of the sieved powder was put in a cylindrical alumina sample pan, φ6.5 mm×4 mm in size. The specimen was then set inside a furnace tube of a simultaneous thermal analyzer and subjected to TG analysis. After dried at 393 K for 3.6 ks, it was

heated continuously from 393 to 1373 K at a constant rate of 10 K min^{-1} . All of the operations were conducted under a flow of argon containing 4.6 ppm of moisture, the flow rate of which was set at $50 \text{ cm}^3 \text{ min}^{-1}$.

For microstructure investigation, three specimens were collected by terminating the TG measurement at preset temperatures (773, 973 and 1373 K), followed by natural cooling to 298 K in the furnace (furnace cooling). They were molded in polyester resin and polished mechanically with a standard polishing technique. The microstructure of the polished specimens was examined under an optical microscope.

The specimens were also examined by XRD for phase identification. An X-ray powder diffractometer equipped with a rotational copper anode and a graphite monochromator was employed. The tube voltage and current were set at 50 kV and 300 mA, respectively.

3. Results and Discussion

3.1. Structural Evolution during Continuous Heating

Figure 1 shows a TG curve for the hematite ore-derive iron carbide. As reported in previous papers,^{3,4)} the reaction between iron carbide and steam contains three stages depending on temperature. Those stages were characterized by a three-step weight change: monotonic increase (Stage I), drastic decrease (Stage II) and re-increase (Stage III). Three specimens representing each stage were collected at the points marked with a, b and c in Fig. 1, *i.e.* 773, 973 and 1373 K, and subjected to phase identification by XRD and microstructure investigation by cross-sectional microscopy.

XRD spectra of the iron carbide treated under various temperatures are displayed in Fig. 2. The spectrum shown in Fig. 2(b) reveals that Fe_3C was still a dominant phase in the specimen at Stage I, but reflections of Fe_3O_4 and Fe_2O_3 increased their intensity due to oxidation of Fe_3C ,⁵⁾ *i.e.*

In Stage II, as shown in Fig. 2(c), reflections of Fe_3C weakened significantly and, on the other hand, reflections from Fe became predominant. The majority of Fe formed in this stage was thought to arise from the decomposition of Fe_3C through the co-production reaction described by the following equation^{3,4)}:

The rest of Fe was to be derived from iron oxides and graphite that formed in Stage I,⁵⁾ *e.g.*

The XRD spectrum for Stage III, which is shown in Fig. 2(d), reveals that reflections from FeO, Fe_3O_4 and Fe_2O_3 tended to be strengthened. It was confirmed, therefore, that Fe formed in the previous stage was gradually oxidized in this stage.

Fig. 1. TG curve for the iron carbide heated at 3.1% steam atmosphere from 393 to 1373 K at a constant rate of 10 K min^{-1} . Specimens for microstructure examination and phase identification were collected at the points marked with a, b and c in the figure.

Fig. 2. XRD spectra of the iron carbide: (a) as received; heated up to (b) 773 K, (c) 973 K and (d) 1373 K at a constant rate of 10 K min^{-1} , followed by furnace-cooling to 298 K. Reflections are labeled according to the Powder Diffraction File (PDF) provided by the International Center for Diffraction Data.

On the other hand, diffraction peaks from Fe yet kept high intensity even in Stage III. In addition, the reflections of graphite were intensified significantly. The presence of these strong reflections implies that the direct decomposi-

Fig. 3. Optical micrographs showing the microstructure of the iron carbide: (a) as received; heated up to (b) 773 K, (c) 973 K and (d) 1373 K at a constant rate of 10 K min^{-1} , followed by furnace cooling to 298 K.

tion of Fe_3C , which resulted in the simultaneous formation of Fe and C as

was probably enhanced at temperatures above 973 K. The temperature was found to correspond well with the decomposition temperature for $\theta\text{-Fe}_3\text{C}$ reported by Iguchi *et al.*¹²⁾ According to the Fe–C (graphite) binary phase diagram,¹³⁾ the solid solubility of C in Fe varies widely with temperature above 1011 K. Therefore, Fe presented in the specimen at Stage III was likely to contain relatively high concentration of C at 1373 K, and during cooling to an ambient temperature, C atoms dissolved in the Fe phase would also have precipitated out to form a graphite structure.

The microstructure evolution that the iron carbide showed at elevated temperatures was quite interesting. As shown in **Fig. 3(a)**, particles of the iron carbide used in the

Table 1. Summary of phase transformations and corresponding microstructure variations observed in the iron carbide during continuous heating up to 1373 K.

	Phase transformations	Microstructure variations
Stage I (773 K)	Oxidation of Fe_3C	Densification
Stage II (973 K)	Decomposition of Fe_3C Reduction of FeO_x	Coarsening
Stage III (1173 K)	Oxidation of Fe	Densification Coarsening

Table 2. Type of phase transformation and associated volume change for the iron carbide–steam reaction.

Eq. No.	Type of phase transformation	Volume change
(1a)	$\text{Fe}_3\text{C} \rightarrow \text{Fe}_3\text{O}_4$	+90 %
(1b)	$2\text{Fe}_3\text{O}_4 \rightarrow 3\text{Fe}_2\text{O}_3$ (maghemite)	+11 %
(1b)	$2\text{Fe}_3\text{O}_4 \rightarrow 3\text{Fe}_2\text{O}_3$ (hematite)	+2 %
(2)	$\text{Fe}_3\text{C} \rightarrow 3\text{Fe}$	–9 %
(3b)	$\text{Fe}_3\text{O}_4 \rightarrow 3\text{Fe}$	–110 %
(4a)	$3\text{Fe} \rightarrow 3\text{FeO}$	+70 %
(4b)	$3\text{FeO} \rightarrow \text{Fe}_3\text{O}_4$	+24 %
(5)	$\text{Fe}_3\text{C} \rightarrow 3\text{Fe}$	–9 %

present investigation natively contained fine cracks and micropores, the size of which was in the order of 10^{-6} m or less. When heated up to 773 K (Stage I), those cracks and pores were partially filled with a grayish phase, which was identified as iron oxides,⁵⁾ resulting in densification of the microstructure (**Fig. 3(b)**). In Stage II, as presented in **Fig. 3(c)**, the oxide phase observed in the prior stage disappeared because of reduction by reducing gases that were generated through a graphite–steam reaction.¹¹⁾ In addition, the reduced microstructure seemed to be somewhat coarsened and rounded, compared with the microstructure of the as-received specimen shown in **Fig. 3(a)**. The structure coarsening was found to proceed to a further extent in Stage III, and the resultant microstructure exhibited granular morphology, as shown in **Fig. 3(d)**. At the same time, the microstructure was partially densified due to the formation of iron oxides that were derived from Fe formed in the previous stage. It was also found that internal cracks and pores in the microstructure acted as preferential nucleation sites for the oxidation, so that they were gradually filled with iron oxides (appearing gray in **Fig. 3(d)**) during prolonged heating.

Table 1 summarizes the phase transformations and corresponding microstructure variations of the iron carbide brought by continuous heating to 1373 K. The table implies that the structure evolution of the iron carbide may be correlated with volume change arising from the phase transformations. In order to evaluate this assumption, the volume change ΔV was calculated by the following equation and

the results are presented in **Table 2**.

$$\Delta V = \frac{n_P M_P / d_P - n_R M_R / d_R}{n_R M_R / d_R} \times 100 \dots\dots\dots (6)$$

where n , M and d are respectively the molar amount, the molar weight and the density of the iron-related substances (*i.e.* metallic iron, iron carbide and iron oxides) involved in the phase transformations, and the suffixes of R and P represent the reactant and the product of each transformation. The calculation revealed that the reactions leading to the formation of iron oxides accompany large volume expansion, whereas both the reduction of iron oxides and the decomposition of Fe_3C result in volume contraction. The structure densification occurring in Stages I and III should thus be attributable to the volume expansion due to oxidation. On the other hand, the mechanism of the structure coarsening observed in Stages II and III was not fully clarified in the present investigation. Nevertheless, the following might be proposed as a possible explanation for the coarsening process. The volume contraction associated with the reactions (2), (3b) and (5) shrinks the microstructure that is densified by oxidation in Stage I, so that the Fe phase formed through those reactions is expected to have a porous microstructure somewhat similar to that shown in Fig. 3(a). Because the temperature in Stages II and III is comparable to or higher than $0.5T_m^{\text{Fe}}$ (T_m^{Fe} is the absolute melting temperature of Fe, *i.e.* 1 809 K), atomic diffusion of Fe should greatly be enhanced in those stages and, consequently, the microstructure of Fe containing a large amount of internal pores would tend to grow and become rounded easily by surface diffusion in order to decrease its surface energy.

The phase transformation from α -Fe to γ -Fe (and vice versa), which occurs at 1 011 K,¹²⁾ also results in about 3 % of volume expansion (or contraction). Although the amount of volume change is small, the phase transformation of this kind might also influence the microstructure evolution of the iron carbide.

The present study suggests that the porous nature of the iron carbide produced by the two-step fluidized bed process seems to be associated with volume change due to phase transformation. In the first step of the process iron ore containing Fe_2O_3 is partially reduced by H_2 to form FeO; *i.e.* $\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{FeO} + \text{H}_2\text{O}$. This reaction accompanies a volume reduction of about 22 %, and the volume reduction would contribute to increase the porosity in FeO, which should become a precursor for a porous Fe_3C in the second step.

3.2. Nature of Graphite Formed in the Heat Treated Iron Carbide

The XRD spectrum presented in **Fig. 4** reveals the nature of graphite formed in the iron carbide that was heated up to 1 373 K. Interestingly, the 0002 reflection (appearing around $2\theta = 26^\circ$) of the graphite shows a narrow profile and shifts towards the high angle side of the spectrum, compared to the corresponding reflection of reagent graphite (purity 99.7 % and particle size ca. 5 μm). In addition, the former reflection was found to split into two peaks, which corresponded to the K- L_3 and K- L_2 lines of Cu radiation. These distinctive features for the diffraction peak strongly suggest

Fig. 4. XRD spectra showing the 0002 reflection of graphite: (a) graphite formed in the iron carbide that was heated up to 1 373 K at a constant rate of 10 K min⁻¹ and then furnace-cooled to 298 K; (b) commercially available graphite reagent.

that the graphite in the iron carbide possesses a crystal lattice with a considerably high degree of crystallinity and that the lattice contracts in the direction parallel to its c -axis. This situation is identical to that observed for graphite formed through the iron carbide–steam reaction described by the Eq. (1).⁵⁾ Therefore, such structural nature might be common over any types of graphite derived from iron carbide.

4. Conclusion

As the first step to clarify the influence of microstructure on reaction kinetics for the iron carbide–steam reaction, the present investigation focused on the microstructure evolution of the hematite ore-derived iron carbide brought by the reaction with steam. Cross-sectional microscopy and XRD analysis were employed for microstructure characterization and phase identification of the iron carbide that was TG-analyzed at temperatures between 393 and 1 373 K. The microstructure evolution that the iron carbide exhibited in the temperature range is summarized as follow.

- (1) Densification by oxidation of Fe_3C (Stage I)
- (2) Coarsening by decomposition of Fe_3C and by reduction of Fe_3O_4 and Fe_2O_3 that are formed in Stage I (Stage II)
- (3) Re-densification by oxidation of Fe formed in Stage II (Stage III)

The iron carbide–steam reaction includes various types of phase transformation, each of which accompanies volume change: expansion by oxidation, and contraction due to decomposition and reduction. The microstructure variation summarized above seems to be attributed to the volume change associated with the series of phase transformation. The present investigation also revealed that self-decomposition of the Fe_3C phase in the hematite ore-derived iron carbide resulted in the formation of graphite at temperatures above 973 K. XRD analysis suggested that the graphite is likely to possess a crystal lattice which is highly crystallized and contracts in the direction parallel to its c -axis.

Acknowledgement

The authors wish to thank Dr. Munetake Satoh, formerly a Professor of Osaka Prefecture University, for his assistance in specimen preparation for microscopy. New Energy and Industrial Technology Development Organization of Japan is greatly appreciated for the provision of a grant aid "The project of Fundamental Technology Development for Energy Conservation" that supported a part of the present investigation.

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