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Iron dispersed carbon composites formed from iron–polyvinylalcohol complexes

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Iron–polyvinylalcohol (Fe–PVA) complexes have been pyrolysed at the temperatures up to 1000 K, and the iron–carbon composites formed have been characterized. The yield of carbon was much higher for the complexes than for PVA alone. The degree of carbon graphitization and the chemical form of iron species were dependent on the pyrolysis temperature. About 30 wt% fine particles of Fe_3O_4 or α-Fe were dispersed in the matrix of amorphous carbon at 800 or 900 K, respectively. At 1000 K, α-Fe was partly transformed to Fe_3C, and the agglomeration of α-Fe was not so significant. At this temperature the carbon was graphitized, which resulted in a lowering of the surface area of the composite. It is suggested that the graphitization proceeds through the mechanism involving the formation and subsequent decomposition of Fe_3C. Thus, the use of Fe–PVA complexes achieves a high yield of carbon and a high dispersion of a large amount of iron species throughout the carbon matrix.

1. Introduction

Metal- or metal oxide-dispersed carbons have been the subject of increasing interest as advanced composites such as chemical sensors, electronic and magnetic materials, and novel catalysts. Polymers and condensed aromatics containing organometallic compounds such as metallocenes are frequently used as the precursors for these composites [1–3]. Polymer–metal complexes may be more preferable starting materials for the synthesis of composites which can contain large amounts of metal or metal oxide finely dispersed throughout the carbon matrix [4], because such complexes can provide essentially atomic dispersion of metal cations prior to pyrolysis [5, 6].

In the present study, therefore, an iron–polyvinylalcohol (PVA) complex was used as a precursor for the iron–carbon composite. PVA is a simple water-soluble synthetic polymer, and the Fe–PVA can readily be prepared in the aqueous system [7], similar to other PVA complexes such as Cu–PVA [5, 8, 9]. Consequently, carbon composites with large amounts of fine iron particles can be produced by the pyrolysis of Fe–PVA complexes with different iron contents. The effect of iron content and pyrolysis conditions on the carbon yield, the chemical form and the dispersion state of iron, and the properties of the composites were all elucidated.

2. Experimental procedure

2.1. Materials

Hydrolysed (100%) PVA with average molecular weight 14000 (Aldrich Chemical Co.) was used without further purification. $Fe(NO_3)_3$, NH_3 and acetone were commercial reagents of guaranteed grade, and they were used as-received.

2.2. Preparation of Fe–PVA complex

The preparation was carried out according to the method for preparing PVA–metal complexes [7, 8]; NH_3 was added dropwise into the mixture of PVA (0.45 M) and Fe^{3+} (0.50 M) aqueous solutions until the pH reached 10, and then the yellowish-brown Fe–PVA complex was separated from the alkaline solution by acetone extraction. Although KOH is usually used as an alkaline additive [7, 8], NH_3 was used instead of KOH in the present work in order to avoid the influence of potassium on the pyrolysis behaviour of Fe–PVA complex. Prior to pyrolysis the separated complex was dried *in vacuo* at room temperature until no further change in weight was observed.

2.3. Preheating and carbonization

Because the Fe–PVA complex as well as PVA alone was swollen during heating, the sample mounted on to a quartz boat in a flow reactor was first preheated to 573 K at 10 K min^{-1} in a helium stream of 200 cm^3 (STP) min^{-1} and soaked for 90 min. The resulting sample is referred to as the 573 K composite throughout this paper. This composite was ground and then carbonized in a thermobalance under flowing helium, and the weight loss during carbonization was monitored. The carbonization conditions were as follows: heating rate 10–200 K min^{-1}, temperature

800–1000 K, soaking time 30 min. The yield of carbon for the iron–carbon composite formed at each temperature is expressed as the weight per cent of original polymer on an iron-free basis.

2.4. Characterization

The carbon and hydrogen elements were analysed by the conventional combustion method, and the iron content was determined by ashing the composite. Mössbauer spectra were measured at room temperature by a constant acceleration spectrometer with a 20 mCi ^{57}Co in a rhodium matrix source, pure α-Fe foil being used for velocity calibration. X-ray diffraction (XRD) measurements were made using manganese-filtered FeK_α radiation. The average crystallite size of the iron species was determined by the Debye–Scherrer method. The interplanar spacing, d_{002}, and average crystallite height, L_c, of graphitized carbon were also determined from the XRD data calibrated with a silicon standard. Fourier transform–infrared (FT–IR) spectra were measured using a diffuse reflectance method. The surface area was determined by CO_2 adsorption at room temperature.

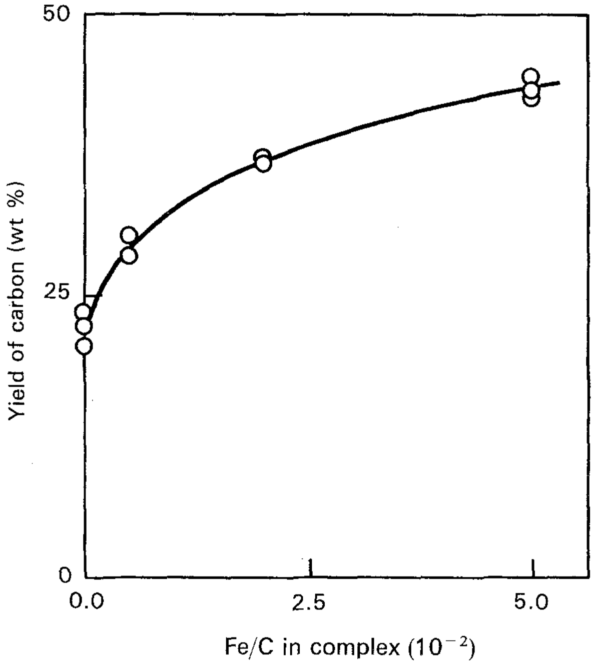

Figure 1 Yield of carbon after preheating Fe–PVA complexes with different atomic ratios of Fe/C.

3. Results and discussion

3.1. Preheating at 573 K

A large amount of water due to the dehydration of PVA was evolved during preheating in every case. Brown tarry materials were also condensed on to the downstream part of the reactor. The amount of tar condensed was apparently lower for the Fe–PVA complex than for PVA alone. Almost all the samples were swollen during preheating. The degree of swelling was the largest for PVA alone, and it decreased considerably as the iron content was increased.

Fig. 1 illustrates the yield of carbon after preheating as a function of the atomic ratio of Fe/C in the starting Fe–PVA complex. The yield for PVA alone was as low as < 25 %, which means that more than 75 % PVA was decomposed during preheating up to 573 K. A higher yield was observed with the complex, and the yield increased with increasing iron content in the complex; the yield at the Fe/C ratio of 0.05 was approximately twice that for PVA alone.

It is known that the pyrolysis of PVA up to around 600 K involves dehydration accompanied by chain scission [10–12]. Water and some volatile products are formed in this temperature region, and the residual solid is composed predominantly of macromolecules having polyene structure. If the intra-chain dehydration alone proceeds, the theoretical amount of water evolved corresponds to 41 wt % original polymer. However, the observed weight loss, > 55 %, was much larger than the theoretical value, showing the occurrence of a great degree of chain scission. The iron in the Fe–PVA complex may promote the secondary cracking of volatile matters formed by chain scission, because transition metals, such as iron and nickel, are active towards the cracking of such products [13, 14]. This would be supported by lower amounts of tar evolved for Fe–PVA complexes. Volatile products would be decomposed on the surface of the iron to form coke and carbon, which leads to higher yields of carbon for Fe–PVA complexes (Fig. 1).

The extremely reduced degree of swelling observed in the presence of iron suggests the development of cross-linking structure. Some inter-chain dehydration leading to ether cross-linking bonding may take place more predominantly than the intrachain dehydration during preheating. The presence of the cross-linking structure, which is more resistant to degradation than the simple polyene structure, may increase the yield of carbon.

3.2. Properties of 573 K composites

When Fe–PVA complexes with the Fe/C ratios of 0.5 $\times 10^{-2}$, 2×10^{-2}, and 5×10^{-2} were preheated at 573 K, composites with 4, 12, and 17 wt % Fe were prepared, respectively. Table I shows the elemental analysis. Carbon contents were less than 80 wt % in all the samples, and large amounts of oxygen, 14–17 wt %, remained; a slightly larger oxygen content was observed for the composite with a higher iron content. The H/C ratio seemed independent of the iron content. The FT–IR spectra revealed the existence of OH and C–O groups, which shows that the monomer unit of PVA remained, and scission of some C–C bonds results in the formation of the carbonyl ends [10, 12].

The XRD measurements showed that no diffraction lines attributable to graphitized carbon and iron species were detectable for any of the composites, indicating that the carbon phase in the composite is amorphous and the iron species are very finely dispersed. In order to elucidate the chemical form of the iron species, the Mössbauer spectrum for the composite with 17 wt % Fe was measured. Mössbauer parameters are summarized in Table II. A doublet with

TABLE I Elemental analysis of 573 K composites

Fe (wt %)	Element (wt %)[a]			H/C[b]	Fe/C[b]
	C	H	$O_{diff.}$		
0	78.5	7.7	13.8	1.2	0
4	77.9	7.5	14.6	1.2	0.011
12	77.7	7.4	14.9	1.1	0.037
17	76.4	6.9	16.7	1.1	0.063

[a] On an iron-free basis.
[b] Atomic ratio.

TABLE II Mössbauer parameters[a]

Sample	IS (mm s^{-1})	QS (mm s^{-1})	H (kOe)
573 K composite[b]	0.36	0.72	0
α-FeOOH[c]	0.50	0.41	365
Fine FeOOH[d]	0.41	0.89–0.92	0

[a] IS, isomer shift relative to α-Fe at room temperature; QS, quadrupole splitting; H, hyperfine field.
[b] 17 wt % Fe.
[c] Commercial bulk compound (99.999 % pure).
[d] [15], fine particles of FeOOH on brown coal.

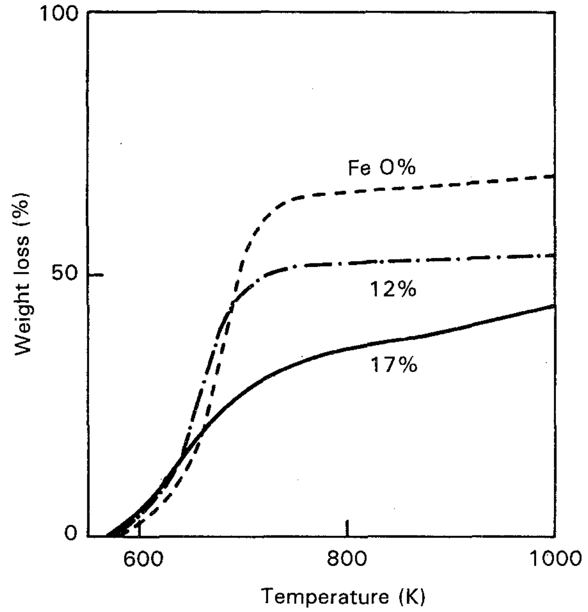

Figure 2 Weight loss during carbonizing of 573 K composites at a heating rate of 10 K min^{-1}.

isomer shift (IS) of 0.36 mm s^{-1} and quadrupole splitting (QS) of 0.72 mm s^{-1} was observed for the composite. This spectrum was quite different from the spectra for bulk compounds of α-FeOOH and Fe_3O_4 showing the sextet signals. As is seen in Table II, the present Mössbauer parameters are close to those [15] for fine FeOOH particles which have a doublet spectrum. This suggests that iron species in the 573 K composite may be stable as FeOOH. The particle size of FeOOH must be very small, because no magnetic hyperfine splitting was observed (Table II). Accordingly, it is suggested that the composite synthesized at 573 K is composed of the amorphous carbon precursor with a large amount of ultra-fine particles of FeOOH.

3.3. Carbonization at 800–1000 K

The weight loss during the heating of 573 K composites at 10 K min^{-1} up to 1000 K is illustrated in Fig. 2, where the loss is expressed as weight per cent on an iron-free basis. The decomposition of the carbon precursor derived from PVA alone took place rapidly at 600–750 K, but further decomposition beyond 750 K proceeded very slowly. In this case the weight loss up to 1000 K reached 65 %. The presence of iron suppressed the decomposition at 600–750 K considerably, a smaller weight loss being observed at a higher iron content. The decomposition of the composites with iron contents up to 12 wt % was almost complete at 800 K, while the weight for the composite with 17 wt % Fe was lost gradually at 800–1000 K. The macromolecules consisting mainly of polyene structure with aldehyde and methyl ketone ends are further degraded to yield carbon finally in the decomposition of PVA alone at temperatures above 600 K [12]. The iron may promote the secondary cracking of volatile matters evolved during degradation, which causes carbon deposition. Consequently, the presence of iron would apparently suppress the decomposition, as is seen in Fig. 2.

Fig. 3 shows the yield of carbon at 1000 K as a function of the iron content in the 573 K composite. Up to 4–5 wt % Fe had no effect on the yield. When the iron content was increased to > 10 wt %, however, the yield increased considerably with the content, and reached 55 wt % at 17 wt % Fe. Thus, it is found that the iron content is a key factor controlling the yield of carbon. Table III shows the effect of the heating rate on the yield of carbon after the carbonization at 1000 K. The smaller the heating rate, the higher was the yield, indicating that a smaller heating rate is favourable for the carbonization of the composite.

3.4. Properties of iron–carbon composites formed at 800–1000 K

Fig. 4 shows the XRD profiles when the 573 K composite with 17 wt % Fe was further heated to 800–1000 K. Because the weight loss took place during heating (Fig. 2), the iron was enriched, the iron content being 27, 30 and 31 wt % at 800, 900 and 1000 K, respectively. Very weak and broad XRD lines were detectable for the 800 K composite, and they were identified as Fe_3O_4. It should be noted that the diffraction intensities are extremely low in spite of a large iron content of 27 wt %, suggesting a low degree of the crystallization of Fe_3O_4, i.e. very small size of Fe_3O_4 particles. Because the iron in the 573 K composite possibly exists in the form of fine FeOOH particles (Table II), the transformation from FeOOH to Fe_3O_4 takes place during heating from 573 K to 800 K. However, there may be some possibility that part of the iron remains as FeOOH, because highly dispersed FeOOH is present on the surface of carbon even at temperatures of around 800 K [16].

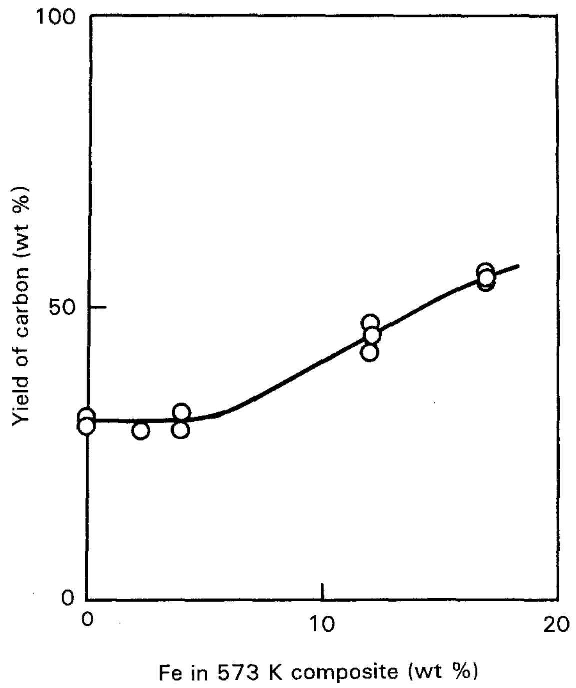

Figure 3 Yield of carbon after the carbonization of 573 K composites up to 1000 K.

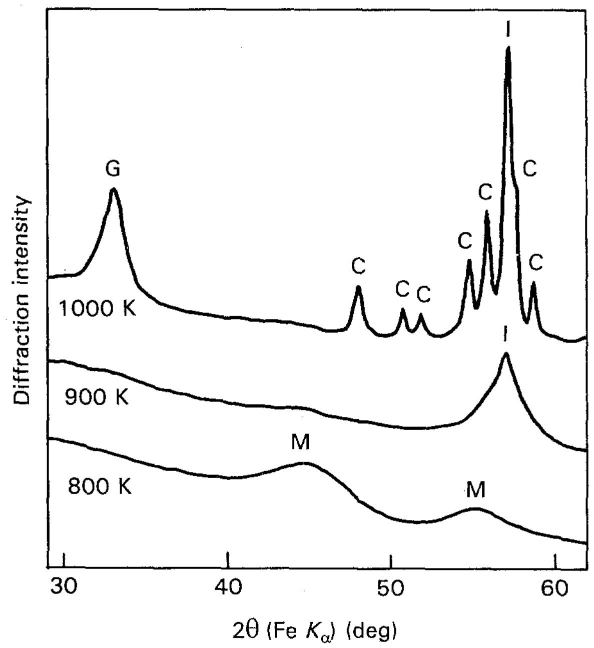

Figure 4 XRD profiles after the carbonization of 573 K composite with 17 wt % Fe at 800–1000 K. C, Fe_3C; G, graphitic carbon; I, α-Fe; M, Fe_3O_4.

TABLE III Effect of heating rate on the yield of carbon at 1000 K

Fe in 573 K composite (wt %)	Heating rate (K min^{-1})	Yield of carbon[a] (wt %)
12	10	45
	50	39
	200	35
17	10	55
	50	50
	200	48

[a] On an iron-free basis.

TABLE IV Elemental analysis of iron–carbon composites formed at 1000 K

Fe (wt %)	Element (wt %)[a]			H/C[b]	Fe/C[b]
	C	H	$O_{diff.}$		
13	97.4	0.6	2.0	0.07	0.033
24	96.7	0.6	2.7	0.07	0.072
31	93.6	0.7	5.7	0.08	0.10

[a] On an iron-free basis.
[b] Atomic ratio.

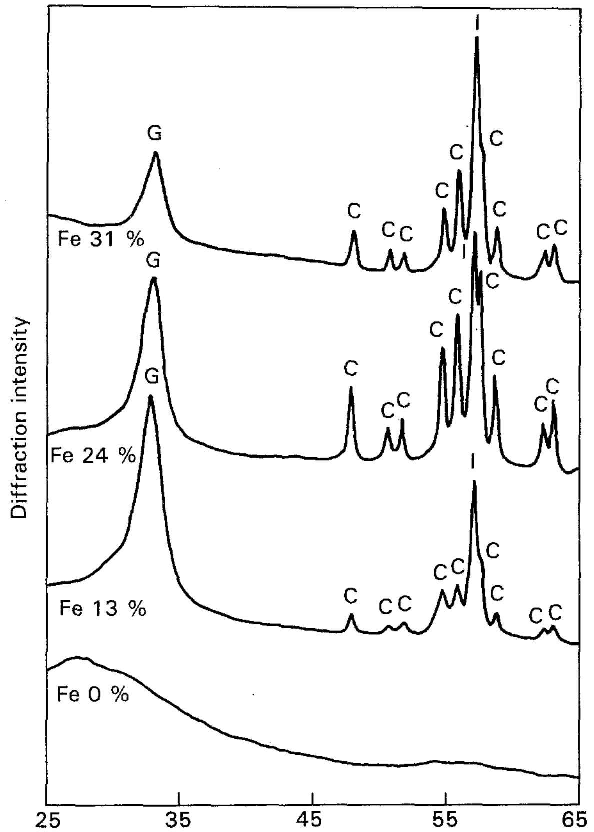

Figure 5 XRD profiles for 1000 K composites with different iron contents. C, Fe_3C; G, graphitic carbon; I, α-Fe.

When the carbonization temperature was raised from 800 K to 900 K, the XRD signals of Fe_3O_4 disappeared and instead the broad diffraction lines due to α-Fe newly appeared (Fig. 4). Because hydrogen, carbon monoxide and hydrocarbons are evolved during pyrolysing PVA in this temperature region [17], Fe_3O_4 was reduced to metallic iron by these gases and/or carbon itself. As is seen in Fig. 4, the XRD peaks of Fe_3C (cementite) as well as α-Fe were observed for the composite synthesized at 1000 K. The formation of Fe_3C shows the reaction of metallic iron with carbon. Furthermore, the diffraction lines due to C(002) were also detectable. In other words, the graphitization of carbon proceeded readily even at a low temperature of 1000 K.

XRD profiles for the samples carbonized at 1000 K are shown in Fig. 5, where the iron content is varied.

TABLE V Properties of iron–carbon composites synthesized at different temperatures

Temp. (K)	Fe (wt %)	Carbon phase[a]			Iron phase[a]	
		Structure	d_{002} (nm)[b]	L_c(nm) [b]	Species	Size (nm)[c]
800	27	Amorphous	–	–	Fe_3O_4	<5
900	30	Amorphous	–	–	α-Fe	7
1000	0	Amorphous	–	–	–	–
1000	13	Graphitic	0.342	6.1	α-Fe, (Fe_3C)	27
1000	24	Graphitic	0.341	6.3	α-Fe, (Fe_3C)	29
1000	31	Graphitic	0.341	7.1	α-Fe, (Fe_3C)	37

[a] Determined by XRD measurements.
[b] d_{002}, interplanar spacing, L_c, average crystallite size.
[c] Average size of α-Fe crystallites.

No XRD lines due to C(0 0 2) could be detected for the carbon derived from PVA alone. On the contrary, the XRD signals of C(0 0 2) as well as α-Fe and Fe_3C were observed for all the iron–carbon composites. Table IV shows the elemental analysis of 1000 K composites with different iron contents from 13–31 wt %. The carbon content on an iron-free basis seemed independent of the iron content, and it was as high as 94–97 wt %. As a result, one atom of iron per ten atoms of carbon is found to be introduced at the highest iron content (31 wt %).

Table V summarizes the properties of the composites synthesized at 800–1000 K. The 800 K composite consisted of amorphous carbon with highly dispersed Fe_3O_4 particles. At 900 K the carbon remained amorphous, but the iron was reduced to ultrafine particles of metallic iron with the average size of 7 nm. Thus, a large amount of metallic iron, 30 wt %, was found to be highly dispersed throughout the carbon matrix. The CO_2 surface area of the 900 K composite was as large as 240 $m^2 g^{-1}$ composite. The carbon phase in all the 1000 K composites with 13–31 wt % Fe was graphitized. The interplanar spacing, d_{002}, about 0.34 nm, was almost the same among the composites. The crystallite size, L_c, seemed to increase slightly with increasing the iron content. These XRD parameters of the carbon suggest that the graphitized carbon has the turbostratic structure, that is, not the three-dimensionally ordered graphitic carbon [18]. As is seen in Table IV, the composition of graphitized carbon was independent of the iron content; 94–97 wt % C was contained and the atomic ratio of H/C was 0.07–0.08. With iron species in the 1000 K composite α-Fe and Fe_3C were detected by XRD and α-Fe was predominant in every case (Fig. 5). The average size of metallic iron increased slightly with increasing iron content, but it was as small as around 30 nm. The surface area of the composite with 31 wt % Fe was 60 $m^2 g^{-1}$ composite, which was much lower than that (240 $m^2 g^{-1}$) for the 900 K composite because of the graphitization of carbon.

The studies on the application of these composites are in progress. It was found in the preliminary experiments that these composites, especially with the large surface area, have high abilities to activate and adsorb hydrogen, and further show high activities to remove the nitrogen from nitrogen-containing heteroaromatics. Accordingly, these composites may be promising as novel catalysts for improving energy and environmental problems.

When the 1000 K composite containing 31 wt% Fe was further carbonized at a high temperature of > 1500 K, the graphitization took place to a larger extent [19]. The values of d_{002} and L_c at 1900 K were 0.336 and > 100 nm, respectively. At this temperature the XRD lines of Fe_3C disappeared, and α-Fe was the only iron species. These observations suggest that the iron-catalysed graphitization of carbon derived from PVA proceeds through the following mechanism; Fe_3C is formed by the reaction of amorphous carbon with ultra-fine iron particles, and subsequently Fe_3C is decomposed to α-Fe and graphitic carbon. Even if PVA alone was heated at a temperature as high as 2300 K, no graphitization took place.

4. Conclusions

Iron–polyvinylalcohol (Fe–PVA) complexes were preheated in an inert atmosphere at 573 K and then carbonized at 800–1000 K. The following conclusions were drawn.

1. Composites of the amorphous carbon precursor (< 80 wt % C) with very small particles of iron species, possibly FeOOH, are formed during preheating at 573 K. The yield of carbon precursor increases with increasing iron content in the starting complex.
2. When the composite formed at 573 K is carbonized, both the degree of carbon graphitization and the chemical form of iron species depend on the carbonization temperature. The presence of iron apparently suppresses the decomposition of PVA, and thus a higher yield of carbon is attained at a larger iron content.
3. A large amount (about 30 wt %) of Fe_3O_4 or α-Fe particles is very finely dispersed throughout the matrix of amorphous carbon in the composite produced at 800 or 900 K, respectively. The composite at 1000 K consists of the graphitized carbon with fine particles of α-Fe.

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