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Identification and properties of ultra-fine iron particles dispersed in a glass-like carbon matrix

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Various kinds of iron particles and an iron species were synthesized from acetylferrocene-furfural resins in a glass-like carbon matrix by heat-treatment. These irons were investigated in terms of magnetic susceptibility, saturation magnetization, esr, and the Mössbauer effect. Body-centred cubic (b c c) iron, expanded b c c iron, hexagonal close-packed iron, and cluster iron were present as ultra-fine iron particles. The presence of Fe^+ was well established as an iron species. The formation of iron particles and Fe^+ is discussed on the basis of the pyrolysis of ferrocene skeletons in the resin.

1. Introduction

A variety of operating techniques is available for the synthesis of fine particles of materials, e.g. the process of vapour condensation of metals [1], the freeze-drying process [2], and the dispersion of iron and nickel in silicate glasses and zeolites [3–5]. The particle size prepared by these methods can be controlled in varying degrees. However, these particles have no ability to continue growing once they have been synthesized.

The ultra-fine iron particles dispersed in a glass-like carbon matrix have been reported by the present authors [6–8]. The dispersed iron particles are synthesized from acetylferrocene-furfural resins by heat-treatment. The particle size varies with iron content, and increases continuously with increasing temperature. The purpose of this work is to present a detailed account of the kinds and properties of ultra-fine iron particles and an iron species dispersed in the glass-like carbon matrix. The magnetic susceptibility, saturation magnetization, esr, and the Mössbauer effect were used to study the nature of the iron particles and the iron species. The iron was readily oxidized upon exposure to air; the oxidation was also clarified by Mössbauer spectra.

2. Experimental procedure

2.1. Preparation of resins

The processes for the synthesis of acetylferrocene-furfural resins under consideration have been presented elsewhere [6, 8]. The resins containing a small amount of iron were not adequate for the Mössbauer spectrum measurement, since the amount of ^{57}Fe is small in natural abundance. Therefore, the ferrocene enriched with ^{57}Fe was synthesized from Fe_2O_3 (90.42% enriched with ^{57}Fe). The heat-treatment of resins was the same as that reported in a previous work [8]. The sampling of heat-treated resins was carried out in an argon-substituted glovebox.

2.2. Measurement of properties

The magnetic susceptibility was recorded by the Faraday method at temperatures 77 to 293 K. The saturation magnetization was determined at 293 K with the aid of the Cioffi recording fluxmeter [9]. The esr spectra were recorded at 293 K on a Hitachi model 771-0061 spectrometer, and the Mössbauer spectra were measured with an auto-mechanical acceleration spectrometer using a ^{57}Co-in-Cu source at 4.2 and 110 K. All of the isomer shifts were obtained with respect to the

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centroid of the iron metal at 293 K. Electron microscope observation was carried out using a JEM-100B electron microscope at a direct magnification of x 150 000.

3. Results and discussion

As acetylferrocene-furfural resins are pyrolysed in vacuum at 400° C, iron atoms are liberated from ferrocene skeletons and coagulated to form iron particles. The size and crystal structure of iron particles have been investigated by means of electron microscopy and X-ray diffraction analysis. The analytical data on iron particles are summarized in Table I [7, 8]. The electron micrographs of iron particles are shown in Fig. 1 to 3. The particles of 10 to 25 Å diameter were formed in 2-Resin heat-treated at 400° C [2-Resin (400° C)], as shown in Fig. 1. No particles were observed in 100-Resin (400° C), as shown in Fig. 2. As the heating temperature of 100-Resin was raised to 600° C, the particles became a detectable size of 10 to 50 Å diameter as shown in Fig. 3. All of the particles grow to a diameter of more than 30 Å when 2- to 100-Resins were heat-treated at 800° C. The crystal structure of the large particle is a standard body-centred cubic (b c c) iron [8]. The ultra-fine particles of ferromagnetic materials show a magnetic behaviour different from that of the same materials in a coarse crystalline form. When the particles are less than 100 Å diameter, the magnetization is found to be a function of HT^{-1} only. This magnetic behaviour is known as superparamagnetism [10]. The magnetization of 40- and 100-Resins (400° C) was a function of T^{-1} from 77 to 293 K. The effective magnetic moment of 40- and 100-Resins (400° C) was 6.6 μ_B at 293 K. The iron in these resins (400° C)

TABLE I Analytical data on iron particles dispersed in a glass-like carbon matrix

Sample	Fe (wt %)	Diameter (Å)	Crystal structure
2-Resin	13.2	10–25	ε-Fe, α-Fe*
		30–150	–
5-Resin	10.6	10–25	ε-Fe, α-Fe*
		30–200	–
10-Resin	7.96	10–25	ε-Fe, α-Fe*
		30–150	–
30-Resin	2.54	10–100	–
40-Resin	2.06	< 10	–
100-Resin	1.00	< 10	–

*The lattice is expanded as compared with a standard α-Fe.

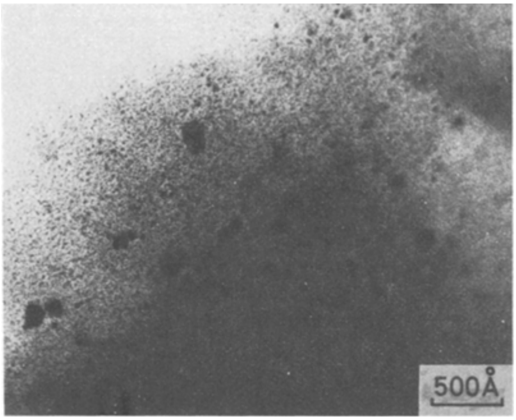

Figure 1 Transmission electron micrograph of 2-Resin heat-treated at 400° C.

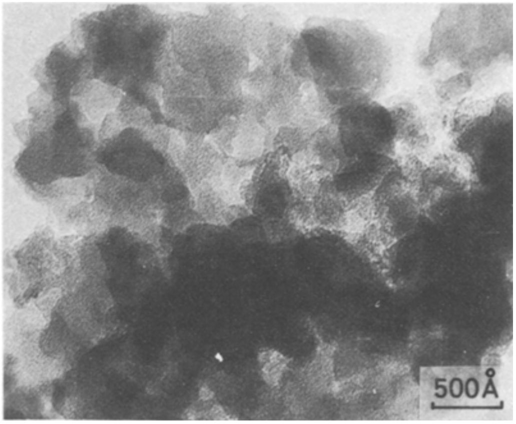

Figure 2 Transmission electron micrograph of 100-Resin heat-treated at 400° C.

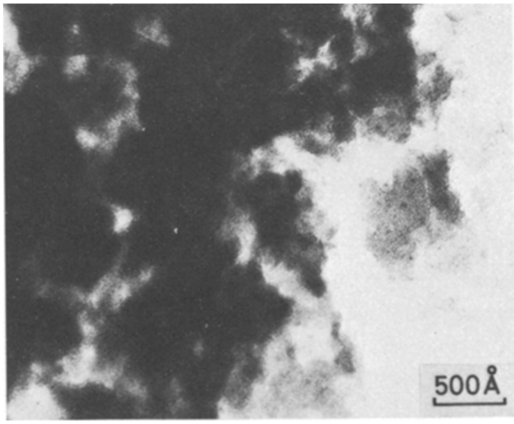

Figure 3 Transmission electron micrograph of 100-Resin heat-treated at 600° C.

was superparamagnetic, paramagnetic, or both. On the other hand, 2- to 30-Resins (400° C) were ferromagnetic. The saturation magnetization of 20-Resin (400° C) was 89.2 emu g^{-1} and less than that of iron metal (221.9 emu g^{-1} [11]). In 2-Resin (400° C), there existed large iron particles, 30 to 150 Å diameter, as shown in Fig. 1. The value of saturation magnetization could not be well explained from the limited number involved. It is necessary to take into account the contribution of the particles of 10 and 25 Å diameter. These particles consitst of two kinds of iorn crystals, as shown in Table I. One is a hexagonal close-packed (h c p) iron. The other is the b c c iron of which the lattice is expanded as compared with the standard b c c iron. There are two different interpretations of the magnetic property of h c p iron, namely, paramagnetism [12] and antiferromagnetism [13, 14]. Both of the magnetisms do not contribute to the saturation magnetization. The saturation magnetization arose from the expanded b c c iron. It has been concluded that the expanded b c c iron is superparamagnetic, since its size is less than 25 Å diameter.

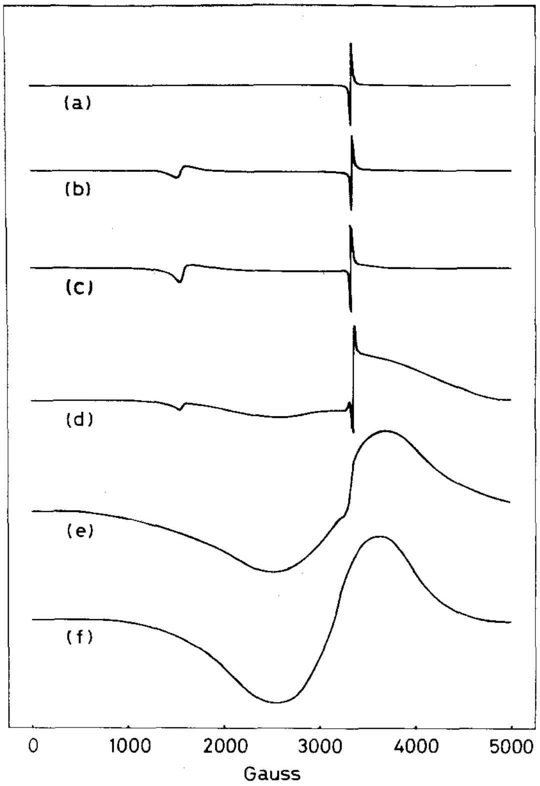

Figure 4 Esr spectra of resins heat-treated at 400° C. (a) Furan resin; (b) 100-Resin; (c) 40-Resin; (d) 30-Resin; (e) 10-Resin; (f) 2-Resin.

Fig. 4 illustrates the esr spectra of 2-, 10-, 30-, 40-, 100-Resin, and Furan resin heat-treated at 400° C. The spectrum of Furan resin free from iron showed a sharp resonance line at $g = 2.002$ that corresponded to the resonance line expected for charcoal, coal, and similar carbonaceous substance formed at low temperature [15]. The broad resonance line was observed at $g = 2.13$ in the spectrum of 2-Resin (400° C). Such a broad resonance line does not come from paramagnetic materials and ferromagnetic single crystals. The resonance linewidth of ferromagnetic polycrystals is several to tens of times broader than that of the single crystal [16, 17]. Even if the ultra-fine iron particles in the heat-treated resin are present as a single crystal, the crystal axis may not be oriented in one direction in the glass-like carbon matrix. The magnetic property of the whole glass-like carbon would be very similar to that of the ferromagnetic polycrystal. In this case, the ferromagnetic line seemed to be due to an iron metal (α-Fe). The resonance line due to the carbonaceous substance was not detected in 2- to 10-Resins (400° C) because of the high intensity of the ferromagnetic resonance line. The broad line vanished in the spectra of 40- to 100-Resins (400° C). In the electron micrographs of heat-treated resin (400° C), the iron particle was detected in 2- to 30-Resins (400° C) but not in 40- and 100-Resins (400° C), as shown in Table I and Fig. 2. This finding was consistent with the disappearance of the ferromagnetic resonance line. The esr spectrum of 100-Resin (600° C) is presented in Fig. 5. In Fig. 5, an upper partial spectrum was recorded by the high sensitivity measurement compared to a lower full spectrum. The broad line manifested itself in the lower full spectrum, as shown in Fig. 5. The shape of this

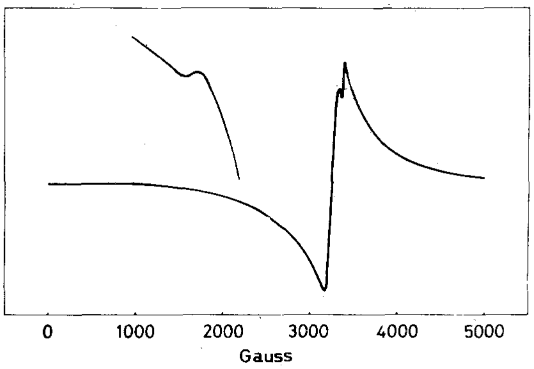

Figure 5 Esr spectrum of 100-Resin heat-treated at 600° C.

resonance line differed from that in 2- to 10-Resins (400° C). The distinction would be due to the different size of ferromagnetic iron particles. The resonance line, which was detected in the lowest magnetic field, was found in the spectra of 30- to 100-Resins (400° C), its g-value being 4.28. The g-value of transition metal ions varies with a ligand field. The experimental values of ligand field stabilization have been given for transition metal ions of the first series. The ions of electronic configuration other than $3d^5$ and $3d^{10}$ are more stable in octahedral than tetrahedral environments. The stabilization energy of $3d^5$ and $3d^{10}$ ions is the same in the two different environments [8]. In the case of amorphous material, those ions become stabilized in the aforementioned environments having a higher stabilization energy. For example, the chromium (III) ion ($3d^3$) in binary sodium borate glasses is most stable in the octahedral environment as compared to any other configuration [19]. It is reasonable to note that the same is valid for iron ions in the glass-like carbon matrix. The g-value of Fe^0, Fe^{2+}, and Fe^{3+} did not correspond to the value of 4.28. Fe^+ ions have an electronic configuration of $3d^7$, and are more stable in the octahedral symmetry than in the tetrahedral symmetry. The g-value of Fe^+ is 4.344 ± 0.002 in the octahedral enviroment [20]. These facts suggested that Fe^+ was contained in the resin heat-treated at 400° C. The resonance line of Fe^+ still remained in 100-Resin (600° C), as shown in the upper partial spectrum of Fig. 5.

The Mössbauer spectra of 2-, 10-, 30- and 100-Resins (400° C) are shown in Fig. 6. Eight absorption lines appeared in the spectrum of 2-Resin (400° C). The outer four lines, of which the isomer shifts were about $+5.3$, $+3.3$, -2.6 and $-5.0\,\mathrm{mm\,sec^{-1}}$, were ascribed to the magnetic hyperfine splitting of ferromagnetic iron metal [21]. This splitting was due to the large iron particle (30 to 150 Å). The presence of two sharp lines observed near zero velocity was the result of doublet splitting. There are two ideas to explain the doublet splitting: one is that the sharp doublet arises from a quadrupole interaction; the other is that two broad lines result from the overlapping of six lines due to the magnetic hyperfine splitting. In this case, the doublet splitting probably came from the quadrupole interaction, since the linewidth of the doublet was small. The centre of gravity of the doublet was $+0.21\,\mathrm{mm\,sec^{-1}}$, its quadrupole splitting being $1.44\,\mathrm{mm\,sec^{-1}}$. This quadrupole splitting was due to the h c p iron particle having an electric field gradient. The doublet splitting was present in 10-, 30-, and 100-Resins (400° C). The symmetry of the doublet decreased in the spectra of 30- and 100-Resins (400° C).

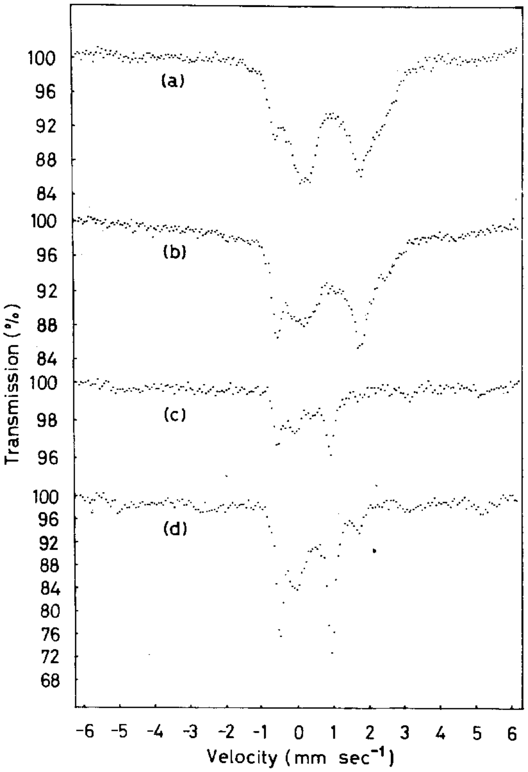

Figure 6 Mössbauer spectra (4.2 K) of resins heat-treated at 400° C. (a) 100-Resin; (b) 30-Resin; (c) 10-Resin; (d) 2-Resin.

Two kinds of single absorption lines (-0.08 and $+1.75\,\mathrm{mm\,sec^{-1}}$) were observed in the spectrum of 2-Resin (400° C). The absorption line of the isomer shift $+1.70\,\mathrm{mm\,sec^{-1}}$ corresponded to that of Fe^+ [22, 23]. The absorption line due to Fe^+ was present in the spectra of 10-, 30-, and 100-Resins (400° C), with isomer shifts of $+1.75$, $+1.76$ and $+1.85\,\mathrm{mm\,sec^{-1}}$, respectively. The single line near zero velocity was observed in the spectra of all resins (400° C); isomer shifts were -0.03, $+0.16$ and $+0.20\,\mathrm{mm\,sec^{-1}}$ for 10-, 30-, and 100-Resins (400° C), respectively. These isomer shifts suggested the existence of metallic iron [22]. The expanded b c c iron was one of the metallic irons present in the heat-treated resin (400° C). A cluster is known as a metallic state in microscopic size [24]; the absorption line due to the cluster of iron manifests itself in the vicinity

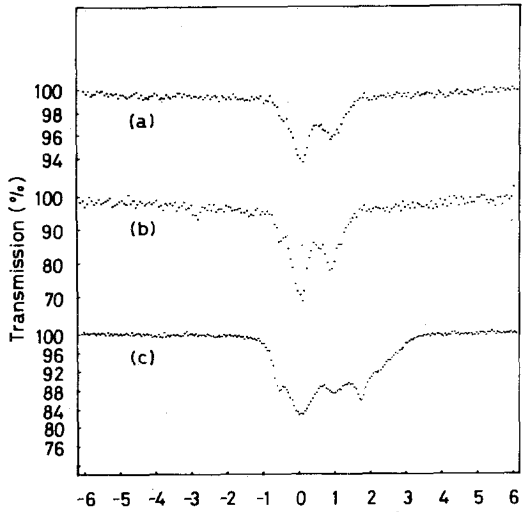

Figure 7 Mössbauer spectra (110 K) of heat-treated (400° C) and partially oxidized resins. (a) 40-Resin; (b) and (c) 30-Resin.

of zero velocity in the solid rare gas [25]. There was a possibility of the existence of a cluster in the heat-treated resin, since the iron particles of 100-Resin (400° C) were less than 10 Å diameter as shown in Fig. 2.

The Mössbauer spectra of partially oxidized 30- and 40-Resins (400° C) are shown in Fig. 7. The absorption line due to Fe$^+$ became weak in intensity in spectrum (c) and disappeared in spectra (a) and (b). The oxidation of Fe$^+$ proceeded progressively in oxidized resins (a) and (b) compared to oxidized resin (c). A new absorption line appeared in the vicinity of $+1.0\,\mathrm{mm\,sec^{-1}}$ in these spectra. Moreover, the line intensity near zero velocity increased to a considerable extent.

These findings indicated the appearance of two absorption lines due to the quadrupole interaction. The isomer shift and the quadrupole splitting in spectrum (b) were $+0.49$ and $0.88\,\mathrm{mm\,sec^{-1}}$, respectively. The Fe$^+$ would be oxidized to Fe^{2+} or Fe^{3+}. The Mössbauer spectra of Fe^{2+} and Fe^{3+} in a glass show different features with respect to the isomer shift and the quadrupole splitting. Fe^{2+} gives an isomer shift of $+1.15\,\mathrm{mm\,sec^{-1}}$ and a quadrupole splitting of $2.16\,\mathrm{mm\,sec^{-1}}$, while Fe^{3+} shows an isomer shift of $+0.50\,\mathrm{mm\,sec^{-1}}$ and a quadrupole splitting of $0.88\,\mathrm{mm\,sec^{-1}}$ [26]. The oxidation of Fe$^+$ proceeded to give Fe^{3+} in the 30- and 40-Resins (400° C). The h c p iron was partially oxidized as a result of the decreased intensity of the absorption line.

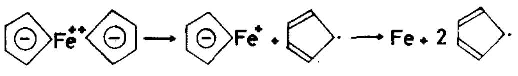

Figure 8 Cleavage of a ferrocene skeleton.

In the present study, the formation of iron particles and Fe$^+$ is interpreted as follows. Ferrocene skeletons decompose to a cyclopentadienyl iron (I) and a cyclopentadienyl radical, as shown in Fig. 8. The cyclopentadienyl iron (I) is stabilized in the glass-like carbon; therefore, Fe$^+$ can be detected by esr and Mössbauer spectroscopy. Iron atoms are liberated by the decomposition of cyclopentadienyl iron (I). The iron atoms are coagulated in the increasing order of cluster, h c p iron, expanded b c c iron, and standard b c c iron. The cluster is less than 10 Å. The h c p iron has a size of 10 to 25 Å and is paramagnetic. The expanded b c c iron is superparamagnetic with a diameter of 10 to 25 Å. Particles larger than 30 Å are revealed as the ferromagnetic standard b c c iron. Fe$^+$ is found to be more sensitive to the oxidation than iron particles.

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