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MÖSSBAUER MEASUREMENTS OF IRON ATOMS DISPERSED IN AMORPHOUS GLASSLIKE CARBONS

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Various iron species have been prepared by pyrolyzing acetylferrocene-furfural resins at 400°C in vacuum, and analysed by means of Mössbauer spectroscopy. The Mössbauer spectra show that the iron species in an amorphous glasslike carbon matrix are free iron atoms, Fe^+ ions, iron clusters, superparamagnetic irons and ferromagnetic irons.

As a basis for measuring physical properties of metals in an infinitesimal state, recently there has been an increased number of researches in methods of preparation of ultrafine particles and isolated atoms of metals. In carrying out an investigation of superparamagnetic systems, Mulay et al. developed novel synthetic methods for controlling the particle size (below 20 Å in diameter) of magnetic species dispersed in vitreous silicates$^{1)\sim3)}$ and a zeolite matrix,$^{4)}$ and measured the magnetic susceptibility and Mössbauer spectra of these systems. Barrett et al.$^{5)\sim9)}$ prepared isolated atoms of iron (^{57}Fe) and tin (^{119}Sn) near the liquid helium temperature in frozen rare-gas matrices of argon, krypton, xenon and nitrogen, and carried out Mössbauer investigations. However, isolated atoms were only present near the liquid helium temperature but coagulated to cluster above 20.5°K.

Table 1. Iron concentration in the heat-treated resins

Notation of samples	Fe (wt%) (Heat-treated at 400°C)
2-Resin	13.20
10-Resin	7.96
30-Resin	2.54
100-Resin	1.00

In the present investigation, ultrafine particles of iron atoms and free iron atoms stable at relatively high temperatures were prepared in an amorphous glasslike carbon matrix by pyrolyzing an acetylferrocene-furfural resin. The above procedure followed the concept that ferrocene molecules decomposed by heattreatment release the iron atom.$^{10)}$ Mulay et al.$^{11)}$ reported the possibility of dispersing ultrafine particles of iron in amorphous glasslike carbons which were prepared by pyrolyzing furfuryl alcohol and

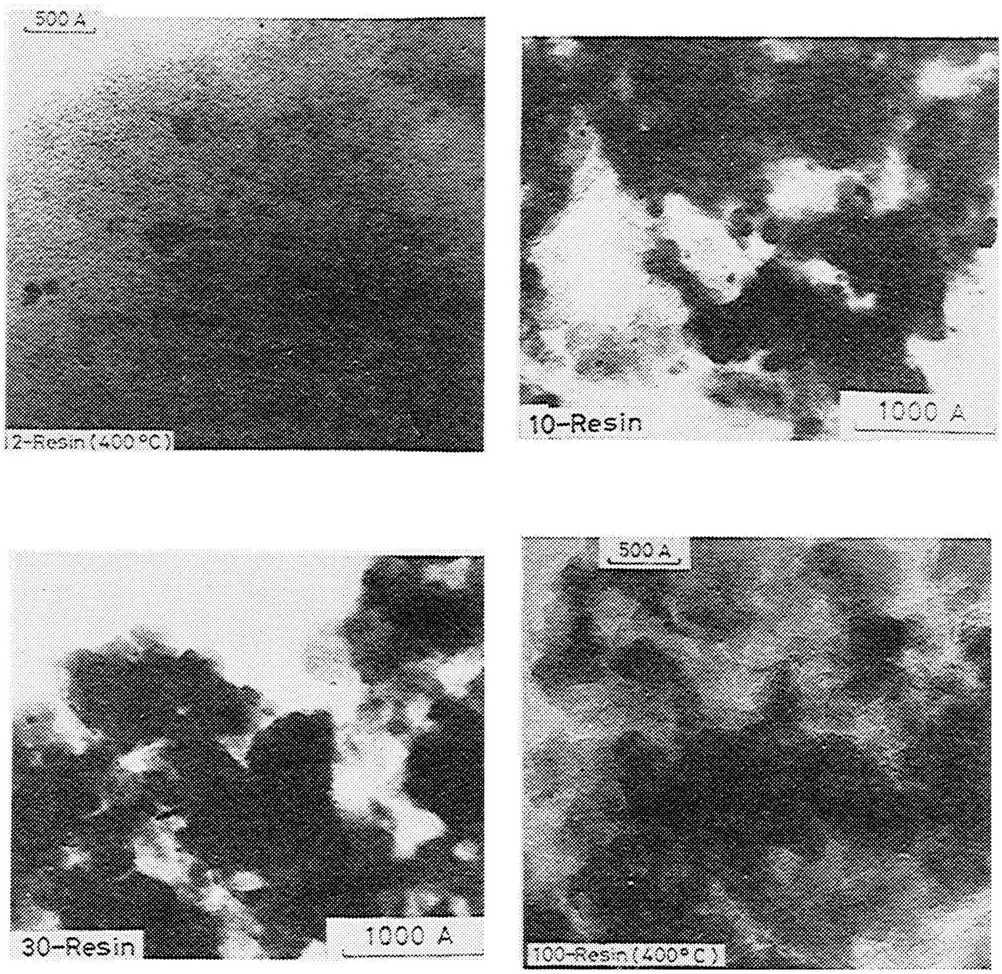

Fig. 1. Electron microscope photographs of the heat-treated resins.

1,1'-dicarboxyferrocene or vinylferrocene resins in inert atmosphere. In their experiments, however, no detailed description was given for free iron atoms.

In a previous paper,[12)] electron microscopic observations, magnetic susceptibility measurements and ESR spectroscopy revealed that iron atoms released from ferrocene skeltons were very likely to be in an atomic form in the amorphous glasslike carbon matrix. The previous Mössbauer measurements on the resins did not show any resolved absorption lines, because of the scarcity of ^{57}Fe in natural iron. Therefore, it was very difficult to confirm the presence of free iron atoms.

In the present experiments, resins were synthesized using ^{57}Fe instead of natural iron to obtain stronger Mössbauer spectra. The Mössbauer spectra were analysed and interpleted using results of ESR spectra[12)] and electron microscopic observations. This paper describes the results of Mössbauer spectroscopy and discusses the observed states of iron atoms in the amorphous glasslike carbon matrix.

Acetylferrocene-furfural resins were synthesized from acetylferrocene, furfural and acetone. A detailed description of the method of preparation has already been given in the previous paper.[12)] It should be noted that, in the present work, acetylferrocene was prepared from Fe_2O_3 (90.42% enriched in ^{57}Fe) via several reactions.[12)~15)]

This resin was heattreated in vacuum at 400°C[12] and then mixed with silicon grease in a grove box filled with argon gas. The Mössbauer spectra were taken on an automechanical constant acceleration spectrometer using a ^{57}Co-in-Cu source. All of the isomer shifts were reported with respect to the centroid of iron metal at 300°K.

Electron microphotographs of the heat-treated resins are shown in Fig. 1. The iron content and ESR spectra for the heat-treated resins are indicated in Table 1 and Fig. 2 respectively, which have already been reported elesewhere.[12] The Mössbauer spectra of the heat-treated resins are shown in Fig. 3. The IR spectra represented that the structure of a resin (5-Resin) was markedly changed by the heat-treatment between 300° and 400°C.[12] The pyrophoric phenomena were observed in the heat-treated 10-Resin (400°C) as the result of the oxidation of activated irons which may be unstable ions or ultrafine particles. As shown in Fig. I-a, 2-Resin showed a uniform distribution of iron particles which had diameters of 10∿30 Å, with the presence of larger particles (30∿150 Å) which were randomly located. In 10-Resin (Fig. I-b), particles of various sizes (10∿250 Å) were present. In the case of 100-Resin, particles could no longer be distinguished in the amorphous glasslike carbon matrix. In this case the size of iron particles seemed to be less than 10 Å.

Bleaney and Heyes[16] showed the resonance line (g = 4.344 ± 0.002) by spectroscopy of a single crystal of NaF after gamma irradiation, and ascribed this line (g = 4.344 ± 0.002) to Fe$^+$ ions contained as an iron impurity in the sample. In MgO, moreover, Fe$^+$ ions were found to have a g-value of 4.15 ± 0.01.[17] The Fe$^+$ ions are in the field of cubic symmetry in these cases, while they seem to be in the field of spherical symmetry in the amorphous glasslike carbon matrix in the present experiments. For the calculation of g-values in some systems, similar results can be obtained in both fields of cubic and spherical symmetry. Thus, the ESR absorption lines (Fig. 2) near g = 4.28 observed for 30- and 100-Resins are considered to result from Fe$^+$ ions. Other lines in Fig. 2 were analysed in the previous paper[12] as follwos: The broad line near g = 2.1 comes from ferromagnetic resonance absorption. The resonance line near g = 2.002 is due to the free electrons in carbonaceous material.[18] However, no information about the superparamagnetic species was obtained from the ESR measurements in the previous experiments.

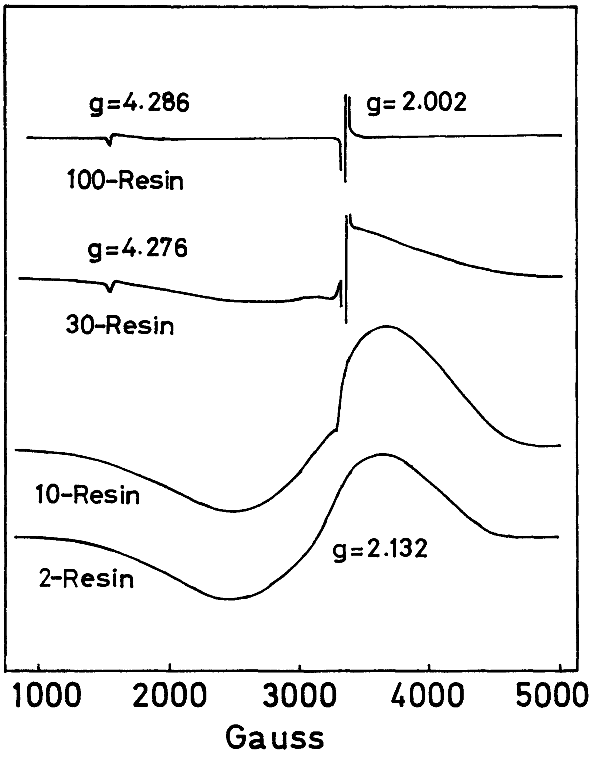

Fig. 2. ESR spectra of the heat-treated resins.

In the Mössbauer spectrum of 2-Resin, as shown in Fig. 3, eight absorption lines are observed. Four weak broad lines indicated by "M" are explained by the magnetic hyperfine splitting of the ferromagnetic irons.[19] Künding and Bömmel[20] examined the Mössbauer spectra of α-Fe$_2$O$_3$ as a function of the average particle size, and observed quadrupole splitting of the superparamagnetic α-Fe_2O_3 particles of less than 100 Å in diameter. Therefore, a pair of two narrow lines ("Q" in Fig. 3) is taken to be the quadrupole doublet of the superparamagnetic irons with an isomer shift of +0.21 ± 0.03 mm/sec and the separation of 1.44 ± 0.03 mm/sec. As the iron content is decreased, the line with an isomer shift of -0.08 ± 0.05 mm/sec "C" in Fig. 3 becomes remarkable, and "Q" decreases. This line "C" is considered to correspond to the line of iron clusters reported by Mann and Broida.[21] A small line "I" is observed near an isomer shift of 1.7 mm/sec (Fig. 3). This value is higher than that of the Fe^{2+} ion; 1.40 ± 0.05 mm/sec for FeF_2 and 1.40 ± 0.05 mm/sec for $FeSO_4.7H_2O$.[22] The correlation between the isomer shift and the 4S electron density proposed by Walker et al.[22] indicates that "I" results from Fe^+ ions. Moreover, the experimental value of 1.7 mm/sec is in approximate agreement with 1.77 ± 0.08 mm/sec for Fe^+ ions as reported by Barrett et al.[9] The Mössbauer spectra of 10-Resin are similar to those of 2-Resin as shown in Fig. 3. For 30-Resin, "M" and "Q" lines are not observed, while "C" and "I" lines still persist. The line with an isomer shift of -0.46 ± 0.04 mm/sec "A" corresponds to one of the "Q" lines. However, the line is considered to be different from the two narrow "Q" lines, because the other line "Q" (+0.94 ± 0.03 mm/sec) is very small in 30-Resin. The isomer shift of "A" is similar to that (-0.75 ± 0.03 mm/sec) of isolated atoms reported by Barrett et al.[6∼8] For 100-Resin, the Mössbauer absorption spectra are quite similar to those of 30-Resin though slightly different in line intensity. In 100-Resin, the "Q" lines are no longer detectable. As shown in Fig. I-d, an electron microscopic photograph represents no iron particles in 100-Resin. This implies that "A", "C", and "I" lines result from free

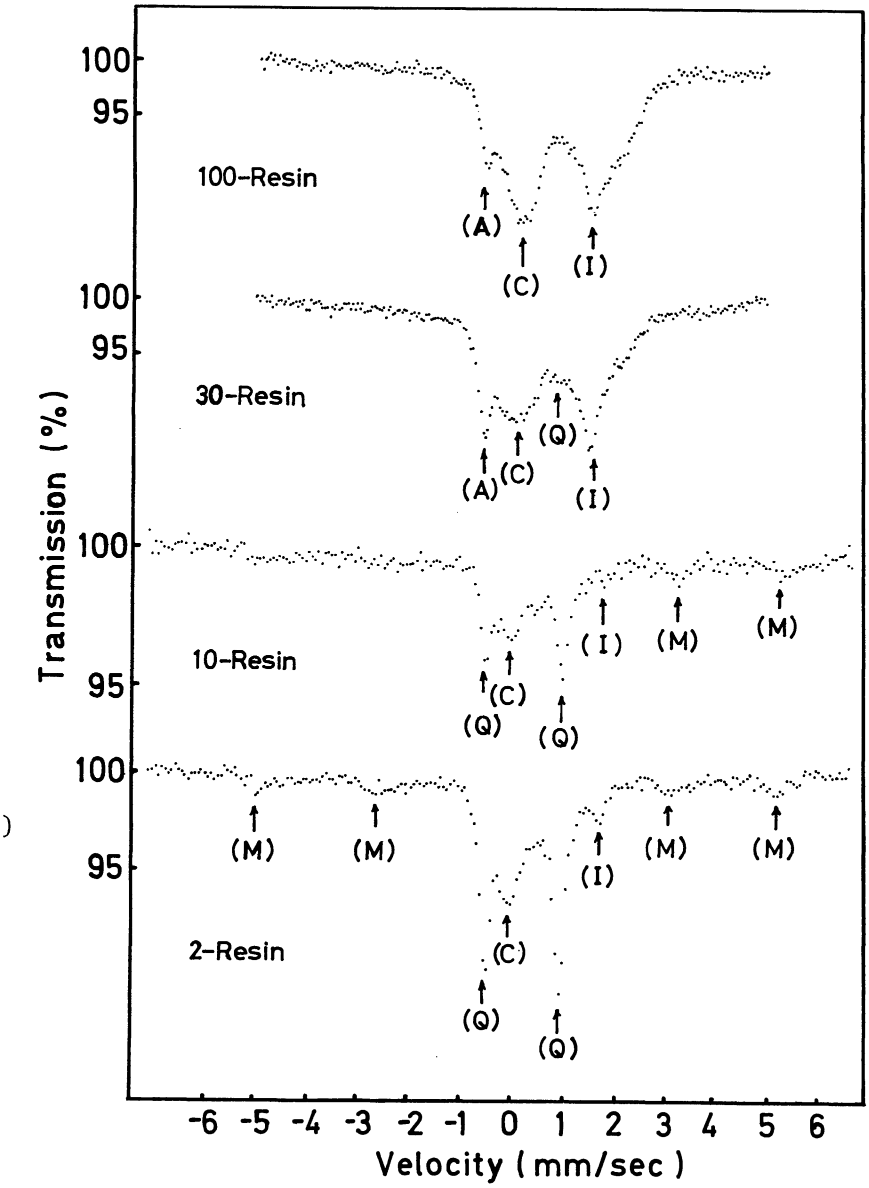

Fig. 3. Mössbauer absorption spectra of the heat-treated resins (4.2°K).

irons, iron clusters, and Fe^+ ions respectively, and not from iron particles.

The fact that Fe^+ ions and free iron atoms are stable even in the resins heat-treated at 400°C can be explained as follows: Some of iron atoms released from ferrocene skeltons by the heattreatment coagulate to clusters at this temperature. Other iron atoms cannot easily coagulate because of the complicated structure of the amorphous glasslike carbon matrix, and consequently they are considered to be transformed into Fe^+ ions by an interaction with the carbon matrix. Barrett et al.9) also considered that Fe^+ ions interact with a rare gas matrix. Similarly free iron atoms seem to interact with the amorphous glasslike carbon matrix to be stable. From the above considerations it indicates that the following resonance occurs among Fe^+ ions, free iron atoms and the amorphous glasslike carbon matrix:

$$\mathrm{Fe} + \mathrm{C} \rightleftharpoons \mathrm{Fe}^+ + \mathrm{C}^- .$$

Moreover, the resonance may also occur between iron clusters and the amorphous glasslike carbon matrix.

In this study, as described above, free iron atoms, Fe^+ ions, iron clusters, and superparamagnetic irons were successfully obtained in an amorphous glasslike carbon matrix by the pyrolysis of acetylferrocene-furfural resins.

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