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Synthesis of cementite-dispersed carbons by pressure pyrolysis of organoiron copolymers

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Cementite-dispersed carbons were synthesized by pressure pyrolysis of divinylbenzene–vinylferrocene and styrene–vinylferrocene copolymer at temperatures below 600° C and the pressure of 125 MPa. The pyrolysis process of both copolymers was analysed by infrared spectra and magnetization of the pyrolysed substances. The absorption band of iron–carbon bond of divinylbenzene–vinylferrocene copolymer decreased on increasing its pyrolysis temperature from 300 to 450° C and finally disappeared at 500° C. The carbonization of divinylbenzene–vinylferrocene proceeded more rapidly than styrene–vinylferrocene at temperatures between 450 and 500° C. Styrene–vinylferrocene was heat-treated at 250° C for 2 h under 100 MPa affording a paramagnetic product, whereas the paramagnetic character of divinylbenzene–vinylferrocene was revealed after heat-treatment at 380° C. The saturation magnetization of cementite-dispersed carbon synthesized from both kinds of copolymers was comparable when the pressure pyrolysis was carried out at temperatures between 520 to 600° C at 125 MPa. The saturation magnetization of cementite-dispersed carbon formed at 550° C under 125 MPa was correlated linearly with the iron content in carbon. Three-dimensional cross-linked divinylbenzene–vinylferrocene copolymer gave the highly dispersed cementite particles less than 50 nm with the coercive force of 950 Oe. On the other hand, the larger particle size of cementite up to 120 nm and the lower coercive force about 400 Oe were obtained in carbon matrix prepared by the pressure pyrolysis of styrene–vinylferrocene copolymer.

1. Introduction

The properties of carbon–carbon bond in the carbon materials originate from the bond nature of carbon atoms in their starting organic compounds. The organic compounds and their pyrolysis conditions should be controlled in order to prepare carbon materials with the desired functions.

The pressure pyrolysis of organic compounds is one of the versatile methods for the synthesis of carbon because of its high carbon yield and the control of the morphology of formed carbons, though carbon materials have been synthesized by various methods. Several workers have reported syntheses of carbons by pressure pyrolysis of a variety of organic compounds [1–6]. The structural difference of starting organic compounds is known to have an effect on the process of pyrolysis and the nature of product carbons.

Organometallic compounds are suitable sources for the dispersion of the second elements in the resultant carbon matrix. Marsh *et al.* [3] reported the synthesis of anisotropic carbon spherulites by carbonization of a mixture of anthracene and ferrocene under pressure. Hirano *et al.* [5] synthesized the carbon spherulites by pressure pyrolysis of divinylbenzene containing vinylferrocene. The ferrocene unit is introduced to polydivinylbenzene matrix via carbon–carbon bond of vinyl groups for the purpose of fine dispersion of metal particles in the resultant carbon matrix. Hirano *et al.* [7] also reported the synthesis of iron-dispersed carbons with various morphologies by pressure pyrolysis of divinylbenzene containing vinylferrocene up to 25 mol %. The morphology of carbon was found to be dependent upon both the pyrolysis conditions and the metal concentration of starting copolymer.

The stability of carbon–carbon bond and carbon–metal bond as well as the pyrolysis conditions of copolymer influence the properties of metal-dispersed carbon with controlled morphology. The present report deals with the effect of carbon–carbon bond of starting polymer on the properties of dispersed cementite in the carbon matrix. Polydivinylbenzene has the cross-linked carbon–carbon bonds via benzene ring, whereas such a cross-linkage does not form in polystyrene. Two different kinds of organoiron copolymers prepared from divinylbenzene or styrene were pyrolysed under pressure. The pyrolysis processes were investigated by means of their infrared (IR) spectra and magnetization of pyrolysed substances. In addition, the properties of cementite particles dispersed in the resultant carbon were elucidated by transmission electron microscopy (TEM) and using a vibrating sample magnetometer (VSM).

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2. Experimental procedures

Commercially available divinlylbenzene (a mixture of 55% *m*- and *p*-divinybenzene and 45% ethylbenzene) and styrene were used for the preparation of starting polymers. Vinylferrocene was prepared according to Arimoto and Haven [8].

All pressure work was carried out in a hydrothermal apparatus of the cold-seal type. The vinylferrocene (VF) was dissolved in divinylbenzene (DVB) or styrene (St). Then the solution was sealed in nitrogen atmosphere into a thin-walled gold capsule of 3.0 or 5.0 mm in diameter and 50 mm in length.

The various vinylferrocene solutions of divinylbenzene or styrene were polymerized at 300° C for 2 h under 100 MPa pressure and then heat-treated at various temperatures from 350 to 600° C for 3 h under 125 MPa pressure. The pressure was measured with a calibrated Heise gauge and the temperature was controlled with a calibrated sheathed thermocouple set inside the pressure vessel. The temperature was raised at a heating rate of 10° C min^{-1} and quenched after an experimental run.

The magnetization of iron-containing products in a gold capsule was measured using a magnetic balance at room temperature. The relative magnetization was calculated using gold and ferrous ammonium sulphate $FeSO_4(NH_4)_2SO_46H_2O$, respectively, depending upon the magnitude of magnetization. IR spectra of pyrolysed substances were measured as liquid films or KBr disks. The pyrolysis product was extracted with tetrahydrofuran (THF) at room temperature and then the THF insoluble solid was collected by centrifuging.

The yield of carbon was as high as about 80%. The cementite-dispersed carbon was identified by X-ray diffraction analysis. Both the saturation magnetization and the coercive force of cementite-dispersed carbons were evaluated with a VSM. The particle diameter of cementite in a carbon matrix was measured by TEM.

3. Results and discussion

3.1. Pyrolysis process of organoiron copolymers

The spectroscopic changes of polydivinylbenzene itself during pyrolysis under pressure were reported in a previous work [6]. The pyrolysis process of iron-containing copolymer was also analysed by IR spectra.

The IR spectra of original DVB–15.5 mol % VF copolymer and the pyrolysed products are shown in Fig. 1. Ferrocene with one unsubstituted cyclopentadienyl ring gives two sharp bands near 1100 and 1000 cm^{-1} [9]. The ring-metal stretching of ferrocene is manifested by the band at 478 cm^{-1} [10]. The DVB–VF copolymer obtained at 300° C shows the absorption bands at 1100, 1000 and 480 cm^{-1}, which are assigned to the ferrocene unit of the copolymer.

As the pyrolysis temperature is raised from 300 to 450° C, the decrease was observed in the intensity of absorption bands due to cyclopentadienyl rings coordinated to iron. The breakdown of both main carbon–carbon chains and carbon–metal bonds constitutes the initial stage of pyrolysis of copolymers. However, the intensities of the bands of 1100, 1000 and 480 cm^{-1} decrease drastically in comparison with the decreases of carbon–hydrogen and carbon–carbon absorption bands of polydivinylbenzene matrix. The absorption bands due to ferrocene unit last up to the pyrolysis temperature of 450° C. Since no absorption band due to iron–carbon bonds remains at 500° C, the scission of the iron–carbon bond was found to terminate practically at 500° C.

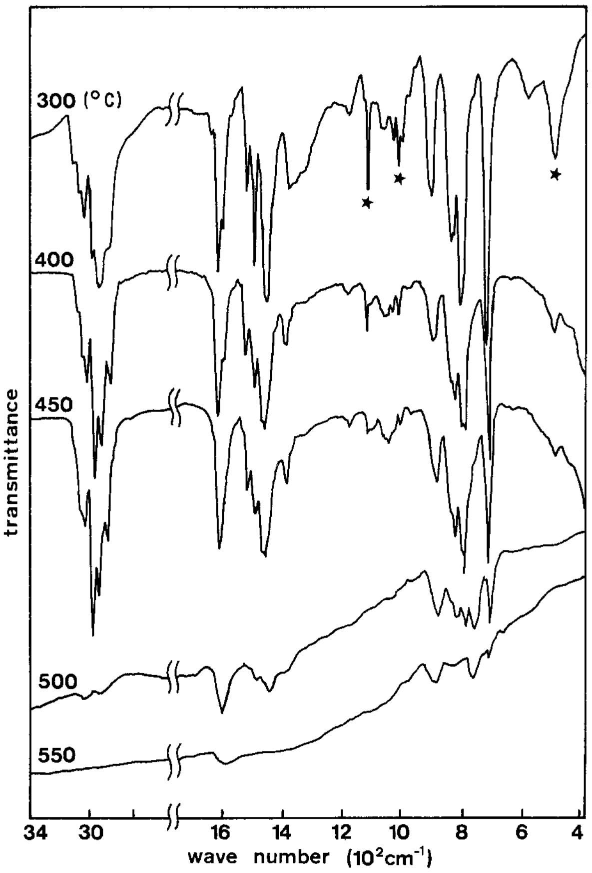

Figure 1 IR spectra of original divinylbenzene–15.5 mol % vinylferrocene copolymer prepared at 300° C and 100 MPa for 2 h, and its pyrolysed product treated at various temperatures for 3 h under 125 MPa.

The pyrolysis of polydivinylbenzene matrix also proceeds rapidly at 500° C. The aborption bands of aromatic and aliphatic C–H stretching at about 3050 and 2950 cm^{-1} disappeared eventually after carbonization at 500° C. The IR spectrum of pyrolysed product at 550° C shows that the pyrolysis of copolymer almost ends up under these conditions.

The St–VF copolymer containing 3.0 wt % iron changed to viscous organic liquid at 350° C, while the solid matrix of polystyrene was converted to a homogeneous organic liquid at 390° C. The DVB–VF copolymer including the same content of iron decomposed to oligomers at 400° C which is lower by 40° C than the decomposition temperature of polydivinylbenzene itself [6].

As the pyrolysis of copolymer proceeds considerably, the pyrolysed part with high carbon content separates out from the fluid phase composed of the oligomers of low molecular weight. DVB–VF and St–VF copolymers containing 3.0 wt % iron were pyrolsed at various temperatures from 400 to 550° C and then the pyrolysis product was extracted with tetrahydrofuran (THF).

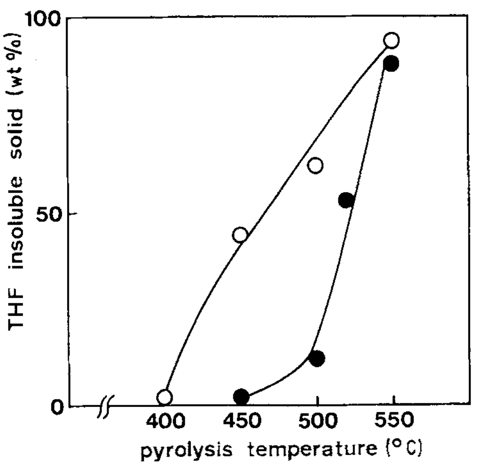

Figure 2 Temperature dependence of amount of carbonized product prepared from organoiron copolymer by pyrolysis at 125 MPa for 3 h. (○) Divinylbenzene-vinylferrocene (3.0 wt % Fe) (●) styrene-vinylferrocene (3.0 wt % Fe).

THF dissolves the organic compounds of low molecular weight and leaves the THF insoluble highly carbonized products.

The weight percentages of THF insoluble product obtained from DVB–VF or St–VF copolymers are shown in Fig. 2. The amount of THF insoluble part from DVB–VF increases gradually as the pyrolysis temperature increases from 450 to 550° C. The 95 wt % of pyrolysed product from DVB–VF was insoluble in THF after heat-treatment at 550° C for 3 h under 125 MPa pressure.

The THF insoluble product appears at 400° C in the case of DVB–VF copolymer, the VF–St copolymer leaves the THF insoluble solid at 450° C by the pyrolysis. The DVB–VF copolymer shows the weak absorption at about 3000 cm^{-1} ascribed to C–H stretching after pyrolysis at 500° C as shown in Fig. 1. On the other hand, the C–H absorptions relating to the aromatic and aliphatic bonds with medium strength are observed in the St–VF copolymer treated even at 500° C. The result of the IR spectrum illustrates the fact that a considerably larger amount of organic C–H bonds remains in the pyrolysed St–VF copolymer than that of the DVB–VF copolymer at 500° C. However, the St–VF copolymer undergoes the carbonization in a narrower temperature range above 500° C, compared with the pyrolysis of the DVB–VF copolymer. The THF insoluble part of the pyrolysed product of St–VF at 550° C reached 88% of carbonized solid.

The reconstruction of formed oligomers during the pyrolysis of copolymer begins to afford the carbonized product at the temperature from 400 to 450° C as shown in Fig. 2. The initial state of the pyrolysed products with 3.0 wt % iron was important to understand the pyrolysis process and the dispersion of the iron in the formed carbon matrix. The microstructures of carbons formed at 450° C for 3 h under 125 MPa were observed under TEM. The representative microstructure is shown in Fig. 3. The black particles dispersed in the matrix were confirmed to be cementite by electron diffraction. Iron carbide particles less than 40 nm were dispersed in the carbon matrix formed from the DVB–VF copolymer. However, the carbon formed from the St–VF copolymer contained large particles of cementite of about 150 nm. The structural differences of copolymer effect on the initial stage of carbonization to afford the different size of iron carbide formed at 450° C.

3.2. Magnetization of pyrolysed organorion copolymers

The degradation of copolymer was characterized by its increase of magnetization. The magnetization of copolymers containing 3.0 wt % iron treated at various temperatures for 3 h under 125 MPa are summarized in Fig. 4.

Since vinylferrocene, divinylbenzene and styrene are diamagnetic, the solution of vinylferrocene in divinylbenzene or styrene itself is diamagnetic before copolymerization. The St–VF copolymer becomes paramagnetic at 250° C, whereas the DVB–VF copolymer is diamagnetic up to 350° C during polymerization. The magnetization of copolymer treated at 300° C exhibits the sharp contrast between copolymers of DVB–VF and St–VF. The St–VF copolymer increases its magnetization as the pyrolysis temperature increases from 250 to 400° C. The magnetization of St–VF copolymer is about twice that of DVB–VF after heat treatment at 400° C.

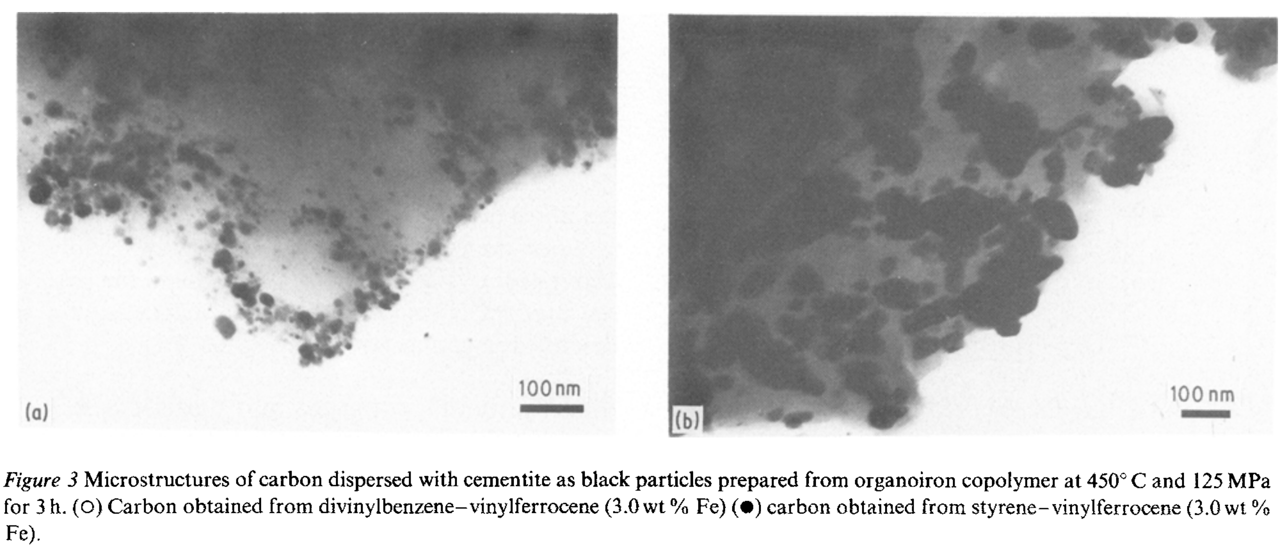

Figure 3 Microstructures of carbon dispersed with cementite as black particles prepared from organoiron copolymer at 450° C and 125 MPa for 3 h. (○) Carbon obtained from divinylbenzene–vinylferrocene (3.0 wt % Fe) (●) carbon obtained from styrene–vinylferrocene (3.0 wt % Fe).

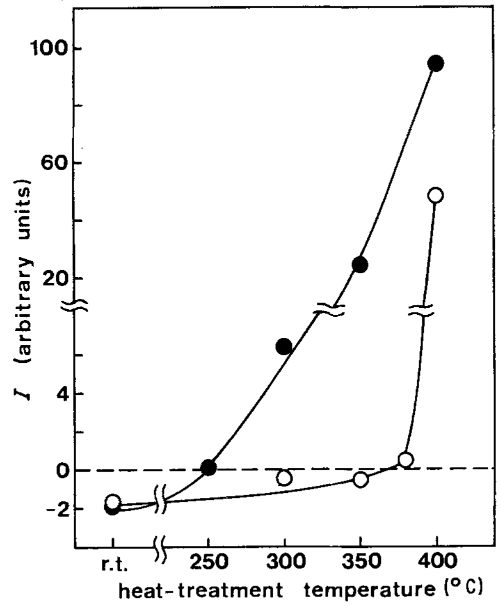

Figure 4 Magnetization of pyrolysed organoiron copolymer including 3.0 wt % iron treated at various temperatures for 3 h under 125 MPa. (○) Divinylbenzene–vinylferrocene (●) styrene–vinylferrocene.

The magnetization of DVB–VF copolymer suddenly increases by several orders of magnitude when the pyrolysis temperature rises from 380 to 400° C. The abrupt increase of magnetization is attributable mainly to the change of DVB solid copolymer to tarry oligomers. However, the microstructure of DVB–VF copolymer has already changed in the solid polymer at 380° C as shown in its increase of mangnetization. On the other hand, the generation of paramagnetic species and their aggregation developed significantly in the solid St–VF copolymer at 300° C, although the appearance of copolymer changes to viscous organic liquid at 350° C.

Fig. 5 shows the relation between the saturation magnetization and the pyrolysis temperature of copolymer above 500° C. The saturation magnetization of Fe_3C-dispersed carbon increases as the pyrolysis temperature of copolymer increases. The Fe_3C-dispersed carbon from the DVB–VF copolymer has the comparable value of saturation magnetization with that from St–VF when the pyrolysis was conducted above 520° C.

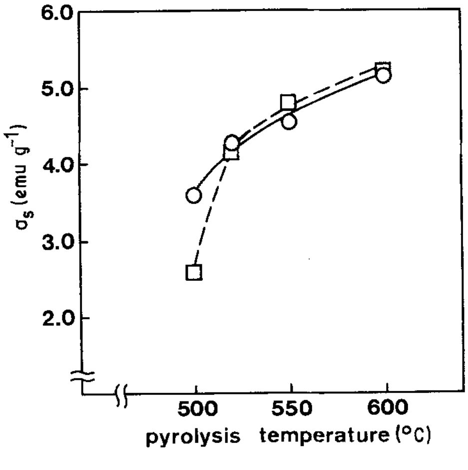

Figure 5 Saturation magnetization of cementite-dispersed carbons prepared from organoiron copolymer containing 3.0 wt % iron by pyrolysis at various temperatures for 3 h under 125 MPa. (○) divinylbenzene–vinylferrocene (□) styrene–vinylferrocene.

The magnetization of Fe_3C-dispersed carbons from the DVB–VF copolymer is larger than that from the St–VF copolymer at the pyrolysis temperature of 500° C, although the magnetization at the pyrolysis lower than 400° C was reversed. This is due to the fact that the carbonization of DVB-copolymer proceeds more rapidly than St-copolymer at the temperature from 450 to 500° C as shown in Fig. 2. Therefore, the amount of ferromagnetic cementite formed in the pyrolysis of the DVB–VF copolymer was higher than the St–VF copolymer at 500° C. The X-ray diffraction analysis after the pyrolysis at 600° C for 3 h under 125 MPa revealed that the iron compound in the formed carbon was cementite only and the cementite did not decompose to metallic iron under these conditions. Therefore, the increase of crystallinity of cementite is considered to contribute to the increase of the saturation magnetization of the carbon product obtained above 550° C.

The differences between the magnetization of carbons from the DVB–VF copolymer and the St–VF copolymer shows that the aggregation of paramagnetic species is easier in the matrix of St–VF than in that of DVB–VF.

The degradation of organoiron copolymer starts with the scission of the iron–carbon bond to form a paramagnetic species. The aggregation of paramagnetic products in the DVB–VF copolymer takes place readily when the copolymer undergoes the thermal decomposition. The thermal decomposition of the DVB–VF copolymer at 400° C results in the formation of the oligomer having the lower molecular weight. The molecular weight of oligomer obtained from the polydivinylbenzene is larger than that derived from polystyrene. Thus, the microstructure of the oligomer depends strongly on the structural features of original organoiron copolymers. The structural unit of oligomers from the DVB–VF copolymer is composed mainly of the matrix enriched of three dimensional cross-linkage via benzene ring. When the organoiron copolymer decomposes to oligomers, such a cross-linked structure is considered to prevent the aggregation of the formed ferromagnetic cementite.

On the other hand, the generation of paramagnetic species proceeds concurrently with their local aggregation in the St–VF copolymer in the early stage of pyrolysis. The absence of three dimensional structures facilitates the aggregation of the paramagnetic product in the St–VF copolymer even at lower temperatures below 350° C.

When the organoiron copolymers were pyrolysed above 450° C, the amount of cementite in the pyrolysed product is responsible for the magnetization as described in connection with Fig. 5.

3.3. Magnetic properties and particle size distribution of cementite-dispersed carbons

The cementite-dispersed carbons were synthesized by the pressure pyrolysis of various organorion

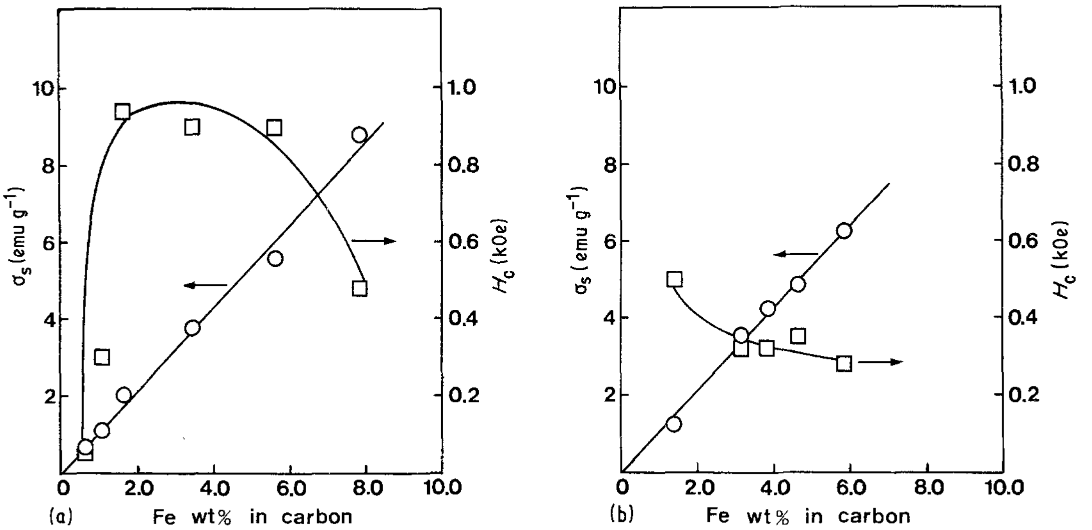

Figure 6 Saturation magnetization and coercive force of cementite-dispersed carbons prepared from organoiron copolymer by pyrolysis at 550° C and 125 MPa for 3 h. (○) saturation magnetization, (□) coercive force. (a) Divinylbenzene–vinylferrocene (b) styrene–vinylferrocene.

copolymers at 550° C for 3 h under 125 MPa. Both the saturation magnetization and the coercive force of Fe_3C-dispersed carbon from DVB–VF and St–VF copolymers are summarized in Figs. 6a and b, respectively.

The saturation magnetization (σ_s) of Fe_3C-dispersed carbon increases linearly as the iron content in the carbon matrix increases. When the iron content in the carbon matrix has the same value, the σ_s of Fe_3C-dispersed carbon from the DVB–VF copolymer is almost comparable with the value that from the St–VF copolymer. The coercive force of Fe_3C-dispersed carbon from the DVB–5.1 mol % VF copolymer has the maximum value of about 950 Oe. On the other hand, the coercive force of cementite-dispersed carbon from the St–VF copolymer is about 400 Oe when the carbon contains the same concentration of iron as in the DVB–VF copolymer.

Fig. 7 shows the distributions of particle diameter of cementite in the carbon synthesized from organoiron copolymer containing 3.0 wt % iron at 550° C for 3 h under 125 MPa pressure. The particle size of cementite in the carbon obtained from the DVB–VF copolymer is smaller than 50 nm as shown in Fig. 7. The carbon matrix from the St–VF copolymer includes the particle of cementite in large amount of the size less than 50 nm, but with wide distribution up to 120 nm. The median diameter of cementite in the carbon obtained by the pyrolysis of the St–VF copolymer is about twice that from the DVB–VF copolymer. The lower coercive force of Fe_3C-dispersed carbon from the St–VF copolymer is attributable to the aggregation of dispersed cementite in the carbon matrix which leads to the cementite particles with multiple domains (Fig. 7). The larger diameter of cementite particles in the carbon formed from the St–VF copolymer than that from the DVB–VF copolymer is in agreement with the results of microstructure of carbon formed at 450° C (Fig. 3).

The coercive force of Fe_3C-dispersed carbon from the DVB–VF copolymer also depends upon the particle size distributions of cementite related with the concentration of iron in the starting copolymer. The large content of iron in the starting DVB–VF copolymer causes the local aggregation of cementite particle, which results in the lower coercive force. For example, the DVB–24.0 mol % VF copolymer gave the cementite-dispersed carbon with the lower coercive force of about 480 Oe, compared with the maximum coercive force of 950 Oe from the DVB–5.1 mol % VF copolymer. The wide distribution of cementite particles from 100 to 150 nm were also observed by TEM in the carbon from the copolymer with higher iron content.

On the other hand, cementite particles with the coercive force of 50 Oe had dispersed in the carbon matrix when DVB–2.0 mol % VF copolymer was carbonized under the same conditions. The most abundant diameter range of cementite particles is that less than 10 nm with the frequency of 85%.

The fine particles of cementite disperse in the carbon matrix without the aggregation up to about 6.0 wt % of iron. The value of coercive force decreases when the iron content in carbon exceeds this value.

4. Conclusions

In this work, carbons with highly dispersed cementite

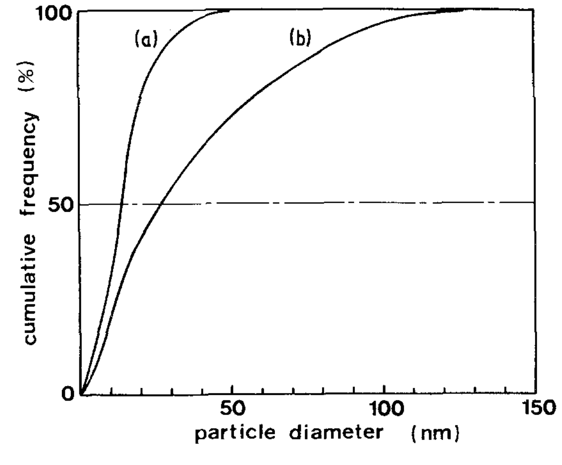

Figure 7 Size cumulative curves of cementite particles dispersed in carbon formed from organoiron copolymer including 3.0wt % iron by pyroysis at 550° C and 125 MPa for 3 h. (a) Divinylbenzene–vinylferrocene (b) styrene–vinylferrocene.

could be synthesized. The distribution and the size of dispersed cementite particles could be found to be controllable by the proper selection of the polymer matrix and the pyrolysis conditions.

The generation of paramagnetic species due to the scission of iron–carbon bond and their aggregation contribute to the increase of magnetization of organoiron copolymer at the initial pyrolysis process below 400° C. The cross-linkage structure of divinylbenzene–vinylferrocene impedes the aggregation and shows the abrupt increase of magnetization at the higher temperature than that of styrene–vinylferrocene. As the carbonization proceeds above 450° C, the magnetization of carbonized product depends upon the amount of produced ferromagnetic cementite. Since both organoiron copolymers undergo carbonization to similar extent above 550° C, the cementite-dispersed carbon formed at 550° C has the comparable value of saturation magnetization. However, the coercive force of cementite-dispersed carbon synthesized from divinylbenzene–vinylferrocene copolymer is higher than that from the sytrene–vinylferrocene copolymer, because the latter contains the larger size of cementite particles with multiple magnetic domains. The particle size of cementite formed at 550° C originates from the extent of aggregation of paramagnetic species at the early stage of pyrolysis of copolymers below 400° C.

Differences of the carbon–carbon bonds of starting copolymers reflect the character and the dispersion state of cementite in the resultant carbon materials. The characteristic three dimensional cross-linkage of divinlylbenzene was found to be a better structure than styrene for the purpose of fine dispersion of metal particles in the carbon.

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