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Cementite dispersed in carbons from ferrocene, vinylferrocene, divinylbenzene systems

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Cementite-dispersed carbon was synthesized by pressure pyrolysis of divinylbenzene-vinylferrocene and divinylbenzene-ferrocene below 600° C. The magnetization of divinylbenzene-ferrocene polymer was higher than that of divinylbenzene-vinylferrocene copolymer at temperatures from 300 to 400° C. The saturation magnetization of cementite-dispersed carbon formed above 500° C was dependent only on the iron concentration in the carbon matrix. The coercive force of cementite-dispersed carbon synthesized from divinylbenzene-vinylferrocene copolymer was about 900 Oe as a maximum value, whereas divinylbenzene-ferrocene polymer gave cementite-dispersed carbon with lower coercive force of 200 Oe. The size of cementite particles dispersed in the carbon from divinylbenzene-vinylferrocene copolymer was less than 50 nm diameter, while divinylbenzene-ferrocene (DVB-Fc) polymer gave a carbon containing larger particles up to 130 nm. The feasible initial aggregation of paramagnetic species in DVB-Fc polymer gave large particles of cementite with multiple magnetic domain. Fixation of ferrocene by the carbon–carbon bond to the parent polymer matrix was found to be effective for fine dispersion of cementite particles in the resultant carbon.

1. Introduction

Carbons with finely dispersed magnetic metallic particles have various applications, such as magnetic materials and catalysts. Metal-dispersed carbons of various morphologies can be synthesized by pressure pyrolysis of organometallic polymers in high carbon yields. Marsh *et al.* [1] reported the mesophase structure obtained from the pressure carbonization of a mixture of ferrocene and anthracene. Hirano *et al.* [2] synthesized carbon spherulites by the pressure pyrolysis of vinylferrocene copolymerized with divinylbenzene for the fine dispersion of metal particles. Hirano *et al.* [3] also demonstrated the synthesis of iron-dispersed carbons with various morphologies by pressure pyrolysis of organoiron copolymers.

The morphology of metal-dispersed carbon is affected by the concentration of metals in a starting polymer as well as pyrolysis conditions [3]. The crystallinity and particle size of the dispersoid in the carbon matrix can be controlled by the selection of carbon–carbon and carbon–metal bond of the parent organometallic polymers [4].

The present paper describes the effect of fixation of the ferrocene molecule to a polymer matrix via the carbon–carbon bond on the dispersion of cementite particles in the resultant carbon. Divinylbenzene-vinylferrocene makes a carbon–carbon bond between the ferrocene unit and polydivinylbenzene, whereas no such bond is formed in divinylbenzene-ferrocene polymer. The pyrolysis process was studied by the change of the magnetization of the pyrolysed compounds. The properties of the cementite particles dispersed in the carbon matrix were characterized by the saturation magnetization, the coercive force and the size distribution of particles.

2. Experimental procedure

Divinylbenzene (a mixture of 55% *m*- and *p*-divinylbenzene and 45% ethylbenzene) and ferrocene are commercially available. Vinylferrocene was prepared according to the method described by Arimoto and Haven [5].

Pressure pyrolyses were carried out using a hydrothermal apparatus of the cold-seal type. Organoiron compounds were dissolved in divinylbenzene (DVB). Then the solution was sealed under nitrogen in a thin-walled gold capsule 3.0 or 5.0 mm diameter and 50 mm long [6].

The ferrocene (Fc) or vinylferrocene (VF) solution of divinylbenzene was polymerized at 300° C for 2 h under 100 MPa and then heat-treated at temperatures from 350 to 600° C for 3 h under 125 MPa. The temperature was raised at 10° C min^{-1} at a constant pressure of 125 MPa. The pressure was kept isobaric by releasing water as a pressure-transporting medium during heating. 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 sample was quenched after an experimental run.

The magnetization of the iron-containing product in a gold capsule was measured using a magnetic balance at room temperature. The relative magnetization was calculated using gold and ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, dependent upon the magnitude of magnetization. The pyrolysis

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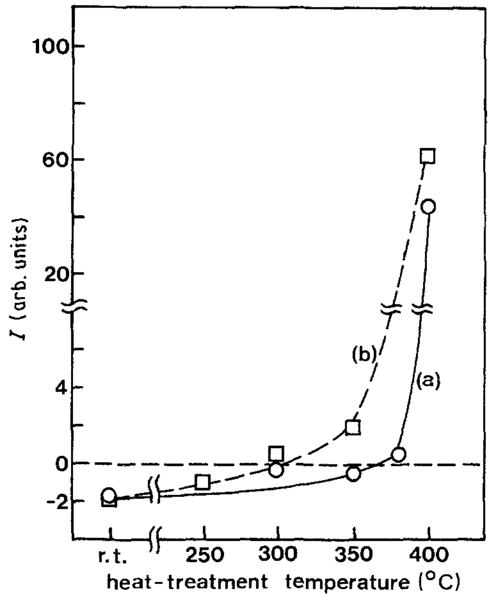

Figure 1 Magnetization of organoiron polymers containing 3.0 wt % iron treated at temperatures from 250 to 400° C for 2 h under 100 MPa. (a) Divinylbenzene-vinylferrocene, (b) divinylbenzene-ferrocene.

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 vibrating sample magnetometer (VSM) at room temperature. The particle diameter of cementite in a carbon matrix was measured by transmission electron microscopy (TEM).

3. Results and discussion

3.1. Changes of magnetization during pyrolysis process

3.1.1. Magnetization of product formed below 400° C

DVB solutions with 3.0 wt % iron as organoiron compound were pyrolysed under pressure at several heat treatment temperatures (HTT). The magnetization of the pyrolysed polymer was measured with a magnetic balance at room temperature. Variations of magnetization with HTT are shown in Fig. 1.

Since vinylferrocene, ferrocene and divinylbenzene are diamagnetic, the solutions of DVB-VF and DVB-Fc are diamagnetic at room temperature. DVB-VF and DVB-Fc polymers changed from being diamagnetic to paramagnetic at 350 and 300° C, respectively. The magnetization of DVB-Fc polymer was higher than that of DVB-VF copolymer at HTT between 300 and 350° C, and was about one and a half times that of DVB-VF copolymer after heat treatment at 400° C. A rapid increase of magnetization temperatures between 350 and 400° C in both organoiron polymers corresponded to the formation temperature of tar-like components from hard polydivinylbenzene polymers.

The degradation of organoiron polymer begins with the scission of the carbon–iron bond of ferrocene to give paramagnetic species. The generation and concurrent aggregation of the paramagnetic species in the pyrolysed polymer increase the magnetization with increase of pyrolysis temperature. Therefore, the carbon–carbon bond between the ferrocene molecule and the polymer matrix in DVB-VF copolymer hinders the aggregation of the paramagnetic species more effectively than that in DVB-Fc polymer which has no such carbon–carbon bond.

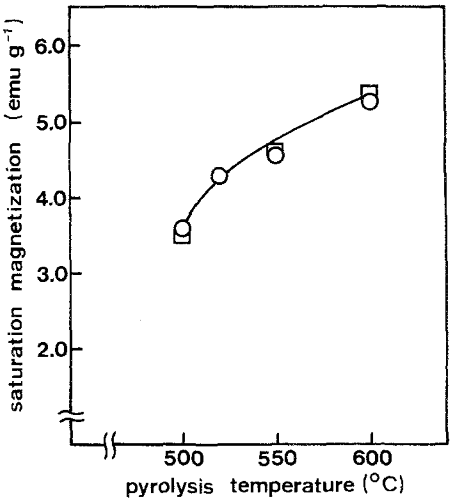

Figure 2 Saturation magnetization of the pyrolysed product formed from organoiron polymers containing 3.0 wt % iron by pyrolysis at temperatures from 500 to 600° C for 3 h under 125 MPa. (○) Divinylbenzene-vinylferrocene, (□) divinylbenzene-ferrocene.

3.1.2. Saturation magnetization of product formed above 500° C

DVB-VF and DVB-Fc polymers containing 3.0 wt % iron were pyrolysed at temperatures between 500 and 600° C under 125 MPa pressure. The saturation magnetizations (σ_s) at various pyrolysis temperatures are shown in Fig. 2. The σ_s of products formed from both kinds of organoiron polymers were comparable and increased with increase of pyrolysis temperature.

When both organoiron polymers were pyrolysed at 500 and 550° C, the weight percentages of THF-insoluble component in the resultant products were 68% and 95%, respectively. No difference of the percentage of THF-insoluble solid was observed between the products synthesized from the two starting polymers of DVB-VF and DVB-Fc. Since the carbonization of both organoiron polymers proceeds significantly above 500° C, ferromagnetic cementite contributes mainly to the σ_s of the resultant carbon. Therefore, the comparable value of σ_s of the cementite-dispersed carbon formed from DVB-VF and DVB-Fc polymers is attributable to the similar extent of carbonization of organoiron polymers above 500° C. The σ_s of cementite-dispersed carbon synthesized above 550° C increases due to the increase of crystallinity of cementite particles in the carbon.

3.2. Magnetic properties and size distribution of cementite particles in carbon

3.2.1. Saturation magnetization

The saturation magnetization (σ_s) of cementite-dispersed carbons formed by pyrolysis of DVB-FV

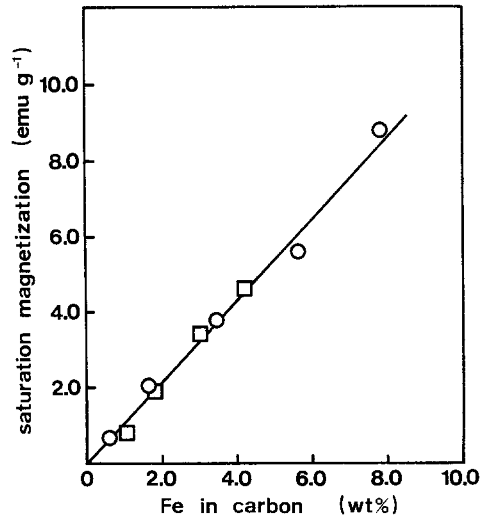

Figure 3 Saturation magnetization of cementite-dispersed carbons formed from organoiron polymers by pyrolysis at 550° C for 3 h under 125 MPa. (○) Divinylbenzene-vinylferrocene, (□) divinylbenzene-ferrocene.

and DVB-Fc polymers at 550° C and 125 MPa is correlated to the concentration of iron as shown in Fig. 3.

Fe_3C-dispersed carbons revealed the σ_s of about 70% of the theoretically calculated value on the basis of pure Fe_3C itself. σ_s increased linearly as the concentration of iron in carbon increased. When the concentration of iron in the carbon matrix had the same value, σ_s of Fe_3C-dispersed carbon from DVB-VF coploymer was comparable with that from DVB-Fc polymer. These facts indicate that cementite particles of comparable crystallinity are dispersed uniformly in the resultant carbon synthesized from both organoiron polymers.

3.2.2. Coercive force and particle size distribution

Fig. 4 illustrates the features of coercive force (*Hc*) of Fe_3C-dispersed carbon synthesized from DVB-VF and DVB-Fc polymers at 550° C for 3 h under 125 MPa. The *Hc* of Fe_3C-dispersed carbon from DVB-VF copolymer depended upon the concentration of iron, and showed a maximum value of about 900 Oe. On the other hand, DVB-Fc polymer gave the Fe_3C-dispersed carbon with an *Hc* of about 200 Oe.

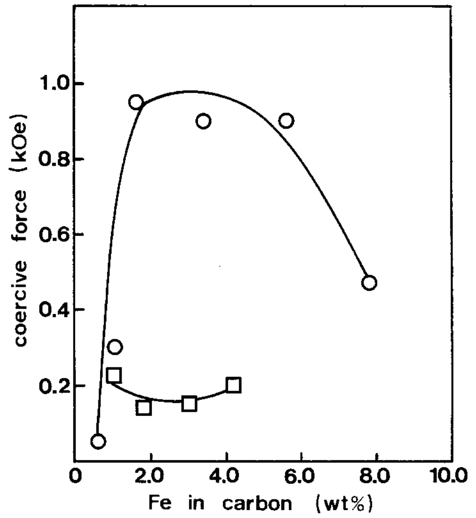

Figure 4 Coercive force of cementite-dispersed carbons synthesized from organoiron polymers by pyrolysis at 550° C for 3 h under 125 MPa. (○) Divinylbenzene-vinylferrocene, (□) divinylbenzene-ferrocene.

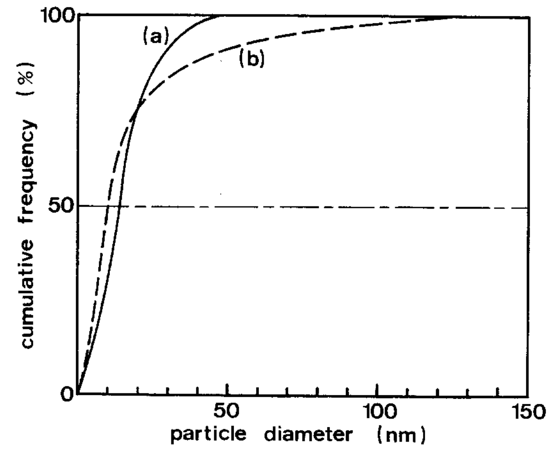

Figure 5 Size distribution of cementite particles dispersed in carbon formed from organoiron polymers including 3.0 wt % iron by pyrolysis at 550° C for 3 h under 125 MPa. (a) Divinylbenzene-vinylferrocene, (b) divinylbenzene-ferrocene.

Fig. 5 summarizes particle diameter distributions of cementite formed from DVB-VF and DVB-Fc polymers containing 3.0 wt % iron by pyrolysis at 550° C and 125 MPa. The median diameter of the cementite particles dispersed in the carbon from DVB-VF copolymer was about 10 nm which was similar to that from DVB-Fc polymer. However, the carbon matrix from DVB-Fc polymer included particles of cementite both less than 50 nm and those up to 130 nm, while the diameter of the cementite particles from DVB-VF copolymer was smaller than 50 nm. The difference of aggregation of paramagnetic species below 400° C results in the different size of cementite dispersed in the carbon formed at 550° C and 125 MPa.

The smaller coercive force of the specimen from DVB-Fc polymer than that from DVB-VF copolymer is attributed to the larger size of cementite particles of the former with multiple magnetic domain. The decrease of *Hc* of the specimen from DVB-VF copolymer at a concentration of iron more than 6.0 wt % is also explained by the aggregated cementite particles with multiple magnetic domain. Large particles of about 100 nm diameter were observed in the specimen with a high iron content of 7.8 wt %. The fine particles of cementite could be dispersed in the carbon matrix without aggregation up to about 6.0 wt % iron, when DVB-VF copolymer was used as the parent organic compound.

4. Conclusion

The magnetization process of two kinds of organoiron polymers and the magnetic properties of the resultant cementite-dispersed carbon were correlated to the nature of the carbon–carbon bond in ferrocene and divinylbenzene polymer as starting organic compounds.

The saturation magnetization of cementite-dispersed carbon was dependent upon the concentration of iron in the carbon and showed no differences between the products from DVB-VF and DVB-Fc polymers. However, the size of cementite particles and the coercive force of cementite-dispersed carbon reflected the initial aggregation of paramagnetic species below 400° C, which could be suppressed by the carbon–carbon bond between ferrocene and polydivinylbenzene. DVB-VF copolymer was found to be a better parent organoiron polymer than DVB-Fc polymer for the fine and uniform dispersion of cementite in the carbon.

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